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**Effect of homogeneous Fenton combined with electron transfer on  
the fate of inorganic chlorinated species in synthetic and  
reclaimed municipal wastewater**

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**ABSTRACT**

This study newly investigates in detail the fate of inorganic chlorinated species and potential interference with other inorganic compounds such as phosphate, inorganic carbon and nitrogenous species during the electro-Fenton treatment of synthetic and reclaimed wastewater. A mathematical model was proposed to validate reaction pathways and rate constants of chlorinated species. The comparison of modeling results with experimental data of both synthetic and real solutions was quite good, with root mean square error (RMSE) values less than 0.084. Upon further testing, the results also showed that adding carbonate, phosphate and inorganic nitrogen species did not affect the chlorate and volatile chlorinated species accumulation subsequent to the decay of chloride ions during electro-Fenton. The established pathway in both synthetic and real chlorinated matrices could help to understand and predict the concentration profiles of chlorinated species in wastewater when implementing such electrocatalysis as a complementary treatment. This work also highlights the need to take into account the management of chlorinated intermediates when implementing this technology at larger scale.

**Keywords:** electro-oxidation/reduction; electro-Fenton; kinetic modeling; chlorinated inorganic species; reclaimed wastewater

## 19           1. Introduction

20 Water is in high demand due to rising global population, rapid urbanization, increased agriculture, and  
21 economic growth while, concurrently, water quality is degrading [1]. As a result of these circumstances,  
22 providing people access to clean water becomes more and more challenging every day. Wastewater  
23 treatment plants (WWTP) are being increasingly contaminated with micropollutants that are released  
24 into the waterbodies [2]. This increase, in combination with industrial discharge and agricultural runoff,  
25 result in approximately 80% of wastewater returning to the environment without treatment [1].

26 Categorized into several groups, micropollutants include pharmaceuticals consumed and discharged by  
27 humans, metals from industry, or pesticides used in agriculture [2]. Freshwater in Europe is being  
28 contaminated by more than 100,000 registered chemicals. The increasing commonality and production  
29 of chemicals coupled with an increase in population and demand for clean drinking water pose new  
30 challenges for wastewater treatment facilities [3]. The major biological treatment processes currently  
31 being employed at most municipal WWTP are unable to fully degrade many of the organic compounds  
32 in the effluent stream [2]. The presence of organic micropollutants in drinking water and surface water  
33 is causing great concern for the health of humans and aquatic organisms. Even in low concentrations,  
34 organic micropollutants may have negative hormonal, carcinogenic and reproductive impacts in human  
35 health and otherwise harm the environment [4].

36 There are opportunities to decrease this quantity of micropollutants and increase the water quality  
37 through actions such as the reuse of treated wastewater by implementing complementary advanced  
38 physico-chemical treatment technologies [3]. In this study, the water treatment method of electrolysis is  
39 investigated using electro-Fenton conditions, an advanced oxidation process for biorecalcitrant organic  
40 pollutants removal in wastewater. The electrochemical advanced oxidation processes (EAOPs) have  
41 gain increasing interests for their ability to continuously produce hydroxyl radicals ( $\cdot\text{OH}$ ) using low  
42 concentration of chemicals or even no reagents by implementing electrocatalysis [5,6].  $\cdot\text{OH}$  can react  
43 very quickly with biorecalcitrant organic compounds, especially with double C=C bonds, which made  
44 them very useful for such water application [7]. EAOPs allow reaching very high degradation and  
45 mineralization yields in synthetic or real effluents, as compared to the chemical AOPs [8,9]. Electro-  
46 Fenton (EF) has been widely studied due to some advantages compared to chemical Fenton. It allows

47 regenerating ferric ion ( $\text{Fe}^{3+}$ ) into  $\text{Fe}^{2+}$  (Eq. 1) and electrogenerating  $\text{H}_2\text{O}_2$  *in situ* (Eq. 2) through  
48 reduction reactions at the cathode.



51

52 The combination of  $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$  then permits the production of  $\cdot\text{OH}$  through the Fenton reaction (Eq.  
53 3).



55

56 Numerous investigations have been performed on the degradation/mineralization kinetics study of single  
57 pollutant or with cocktail of pollutants in synthetic solution [10–14] while some investigations have  
58 been performed in real effluents [15–18]. However, one of the disadvantages of the oxidation processes  
59 is the potential to generate harmful by-products, even more harmful than the original pollutants [19,20].  
60 Some efforts have been made to identify and quantify the organic by-products formed during the  
61 electrolysis and assess the ecotoxicity. The fate of the inorganic matrix and its influence on kinetics has  
62 been barely studied, especially in homogeneous Fenton process combined with direct electro-  
63 oxidation/reduction. The concentration profiles of inorganic nitrogen species has been studied in  
64 advanced electro-oxidation conditions [21–26] and more recently in electro-Fenton process combined  
65 with a modeling study [27]. The evolution of concentration of inorganic chlorinated species has been  
66 mainly studied in electro-oxidation process, especially for electro-disinfection purpose [28–36]. Boron-  
67 doped diamond (BDD) is well-known to be a non-active anode that has a strong oxidation power,  
68 allowing not only the generation of  $\cdot\text{OH}$ , but also the direct oxidation of chloride ions until perchlorate  
69 [5].

70 The concentration profiles of inorganic chlorinated species in homogeneous Fenton combined with  
71 electron transfer using an active anode has never been investigated in detail. For the first time, the  
72 reaction mechanisms and kinetic pathways of various chlorinated inorganic compounds including  
73 volatile species were investigated and supported by a kinetic model study. The influence of phosphate  
74 and carbonate has been also investigated and the comparison with reclaimed municipal wastewater  
75 effluent was then examined. Through deeper understanding of the potential by-products that can be

76 created, this study brings new insights on the redox cycle of inorganic chlorinated species in synthetic  
77 and real effluent along with emphasizes on the possible unwanted remaining inorganic species after  
78 electrolysis.

79

## 80 **2. Experimental**

### 81 2.1. Chemicals

82 Sodium hypochlorite (NaOCl), chlorite (NaClO<sub>2</sub>), chlorate (NaClO<sub>3</sub>) and perchlorate (NaClO<sub>4</sub>) were  
83 supplied by Sigma-Aldrich (Saint-Quentin-Fallavier, France). Sodium carbonate (NaHCO<sub>3</sub>), sodium  
84 hydrogen phosphate (Na<sub>2</sub>HPO<sub>4</sub>) and sodium chloride (NaCl) were provided by VWR International  
85 (Fontenay-sous-Bois, France). Heptahydrated ferrous sulfate (FeSO<sub>4</sub>·7H<sub>2</sub>O) and sulfuric acid (H<sub>2</sub>SO<sub>4</sub>)  
86 were purchased from Thermo-Fisher Scientific (Karlsruhe, Germany). All the chemicals were of  
87 analytical grade and were used as is.

88

### 89 2.2. Effluent characteristics

90 The fate of inorganic chlorinated species taking into account Cl<sup>-</sup>, ClOH/ClO<sup>-</sup>, ClO<sub>2</sub><sup>-</sup>, ClO<sub>3</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup> and  
91 chlorinated volatile species (Cl<sub>volatile</sub>) was determined first in synthetic wastewater to better understand  
92 each mechanism independently. A concentration of 150 mg L<sup>-1</sup> for Cl<sup>-</sup> was implemented, which is a  
93 representative concentration in reclaimed wastewater [27], while a concentration of 20 mg L<sup>-1</sup> was used  
94 for ClOH/ClO<sup>-</sup>, ClO<sub>2</sub><sup>-</sup>, ClO<sub>3</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup>. The concentration of Cl<sub>volatile</sub> was estimated by mass balance,  
95 considering that Cl<sup>-</sup>, ClOH/ClO<sup>-</sup>, ClO<sub>2</sub><sup>-</sup>, ClO<sub>3</sub><sup>-</sup> and ClO<sub>4</sub><sup>-</sup> were the main stable dissolved inorganic  
96 chlorinated species present in the treated solution. The influence of phosphate (PO<sub>4</sub><sup>3-</sup>) (20 mg L<sup>-1</sup>) and  
97 carbonate (CO<sub>3</sub><sup>2-</sup>) (20 mg L<sup>-1</sup>) has been also assessed in synthetic solution, as they can be found in  
98 reclaimed wastewater in a range of concentrations that can vary according to the treatment implemented  
99 before the exit of the plant. In all experiments, the synthetic solutions were prepared with ultrapure water  
100 from a Purelab<sup>®</sup> water purification system (Veolia Water, Antony, France) with a resistivity higher than  
101 18 MΩ cm at room temperature. The concentration profiles of the inorganic chlorinated species were  
102 then monitored in reclaimed wastewater sampled at the outlet of a municipal wastewater treatment plant  
103 (Reims, France). The main physico-chemical characteristics of the reclaimed wastewater has been

104 described in a previous study [27]. In order to avoid the presence of any potential residual particulate  
105 pollution, the reclaimed wastewater has been filtered (0.45  $\mu\text{m}$ ) first before use.

106

### 107 2.3. Electrolytic treatments

108 Electrolysis experiments were conducted in a 180 mL-undivided cylindrical glass reactor connected to  
109 a HAMEG 7042-5 (Beauvais, France) power supply and operated in batch mode at  $25 \pm 1$  °C [27]. The  
110 current density was set at  $2.5 \text{ mA cm}^{-2}$ , since it is the average optimal value depicted in previous works  
111 in similar electro-Fenton conditions [27,37,38]. Both cathode and anode used for the experiments were  
112 made out of carbon felt pieces (Mersen; Gennevilliers, France) having a geometric surface area of 50  
113  $\text{cm}^2$ . They were pre-conditioned in order to remove any impurity from the surface through a one-hour  
114 sonication in a acetone/ultrapure water mixture [39]. Subsequently, they were rinsed with ultrapure  
115 water and stored at 60°C for 24 h. The pieces have been renewed for each experiment in order to have a  
116 better repeatability and to avoid any contamination by adsorption phenomena that could interfere the  
117 subsequent experiment using the same felt. The electrodes were placed in parallel by keeping the inter-  
118 electrode distance to 1.5 cm [27]. An active anode, i.e. low  $\text{O}_2$  evolution overvoltage (1.6 V vs SHE),  
119 has been selected in order to avoid the production of  $\cdot\text{OH}$  at its surface as previously shown in literature  
120 [27,40,41]. It ensured that the only source of  $\cdot\text{OH}$  could come from the Fenton reaction while only direct  
121 electron transfer could occur at cathode and anode [27]. The pH of solution was adjusted to a value of 3  
122 with  $\text{H}_2\text{SO}_4$ , which has been found to be optimal for the Fenton process [42], and ferrous iron  
123 ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) was maintained at the optimal concentration (0.1 mM) referenced in literature [27,42–  
124 44]. A source of  $\text{O}_2$  from air for  $\text{H}_2\text{O}_2$  electrogeneration was supplied continuously throughout the  
125 electrolysis. The solutions were continuously stirred at 500 rpm with a magnetic stirrer (Corning PC-  
126 410D) for homogeneous mixing. The addition of supporting electrolyte was not required since the  
127 average conductivity of synthetic and reclaimed wastewater was around  $1 \text{ mS cm}^{-1}$  which was high  
128 enough. It also minimized the possible interference of the additional electrolyte with the mechanism of  
129 oxidation and reduction of the studied species during the electrolytic treatments.

130

131

132

133 2.4. Analytical procedures

134 To measure the total organic carbon (TOC), total inorganic carbon (TIC) and total nitrogenous species  
135 (TN) a Shimadzu (Marne-La-Vallée, France) V<sub>CSH</sub> analyzer combined with a TNM-1 analyzer was used.  
136 The ion chromatography was conducted on a Dionex/Thermo-Fisher ICS 3000 (Noisy-Le-Grand,  
137 France) and measured nitrite (NO<sub>2</sub><sup>-</sup>), nitrate (NO<sub>3</sub><sup>-</sup>), chloride (Cl<sup>-</sup>), chlorite (ClO<sub>2</sub><sup>-</sup>), chlorate (ClO<sub>3</sub><sup>-</sup>),  
138 perchlorate (ClO<sub>4</sub><sup>-</sup>), phosphate (PO<sub>4</sub><sup>3-</sup>) and sulfate (SO<sub>4</sub><sup>2-</sup>) ions using an AS-19 anion-exchange column  
139 in the conditions described previously [27].  
140 Hypochlorous acid and ammonium ions have been quantified by colorimetric method using diethyl-p-  
141 phenylene diamine (DPD) (program 80) and salicylate (program 801) procedures, respectively, from  
142 Hach kit tests using DR-2400 Hach equipment (Lognes, France).

143

144 2.5. Kinetic modeling

145 MATLAB<sup>®</sup> modeling software was used to create a kinetic model of the concentration profiles of  
146 inorganic chlorinated species. The model used ordinary differential equations (ODE15s) to solve the  
147 system. The FMINSEARCH tool of MATLAB<sup>®</sup> was used to calibrate the model. To assess the fitting  
148 of the model in comparison with experimental data, the root mean square error (RMSE), model  
149 efficiency (ME) and the index of agreement (IoA) were calculated according to the following equations  
150 (Eqs. 4-6) [27,44]:

151 
$$\text{RMSE} = \sqrt{\frac{\sum_{i=1}^K (y_i - y'_i)^2}{K}} \quad (4)$$

152 
$$\text{ME} = 1 - \frac{\sum_{i=1}^K (y_i - y'_i)^2}{\sum_{i=1}^K (y_i - y_M)^2} \quad (5)$$

153 
$$\text{IoA} = 1 - \frac{\sum_{i=1}^K (y_i - y'_i)^2}{\sum_{i=1}^K (|y'_i - y_M| + |y_i - y_M|)^2} \quad (6)$$

154

155 where  $K$  is the number of observed values,  $y_i$  is the single numerically simulated value,  $y'_i$  is the  
156 corresponding experimentally observed value,  $y_M$  is the average of the numerically simulated values.

157

158

159



160 **3. Results and discussion**

161 Before discussing about the fate of the inorganic chlorinated species, it is important to check whether  
162 the sulfate ions added for pH adjustment was involved in the redox reactions or not. A previous study  
163 has shown that in the applied conditions the sulfate ions did not have any impact on the reactions [27].  
164 Therefore, it is assumed that only chlorinated species are involved in the results presented in this section.

165

166 3.1. Redox cycle of inorganic chlorinated species in synthetic solution

167 3.1.1. Profiles of single inorganic chlorinated species

168 Experiments with single inorganic chlorinated species ( $\text{Cl}^-$ ,  $\text{ClOH}$ ,  $\text{ClO}_2^-$ ,  $\text{ClO}_3^-$ ,  $\text{ClO}_4^-$ ) have been  
169 performed in synthetic solutions and in acidic media (pH 3). At this pH, hypochlorous acid is the  
170 dominant species as compared to hypochlorite ion ( $\text{ClO}^-$ ), since the acid dissociation constant (pKa) of  
171  $\text{ClOH}/\text{ClO}^-$  couple is 7.5 [45]. Therefore, only  $\text{ClOH}$  was considered in this study. The profiles of  $\text{Cl}^-$ ,  
172  $\text{ClOH}$ ,  $\text{ClO}_2^-$ ,  $\text{ClO}_3^-$ ,  $\text{ClO}_4^-$  and  $\text{Cl}_{\text{volatile}}$  species as function of the specific charge (Q) are displayed in  
173 Fig. 1.  $\text{Cl}_{\text{volatile}}$  could be ascribed to  $\text{Cl}_2$ ,  $\text{ClO}_2$  and  $\text{Cl}_2\text{O}$  that were the main volatile inorganic chlorinated  
174 species identified in electro-oxidation process with BDD according to a previous study [46]. Moreover,  
175 the bubbling applied during the process should facilitate the volatilization of  $\text{Cl}_{\text{volatile}}$ .

176 All the equations, i.e. direct and indirect oxidation/reduction reactions involved in the redox cycle of  
177 inorganic chlorinated species, have been represented in Table 1.

178

179

180 **Table 1.** direct and indirect oxidation/reduction reactions involved in the redox cycle of inorganic

181 chlorinated species.

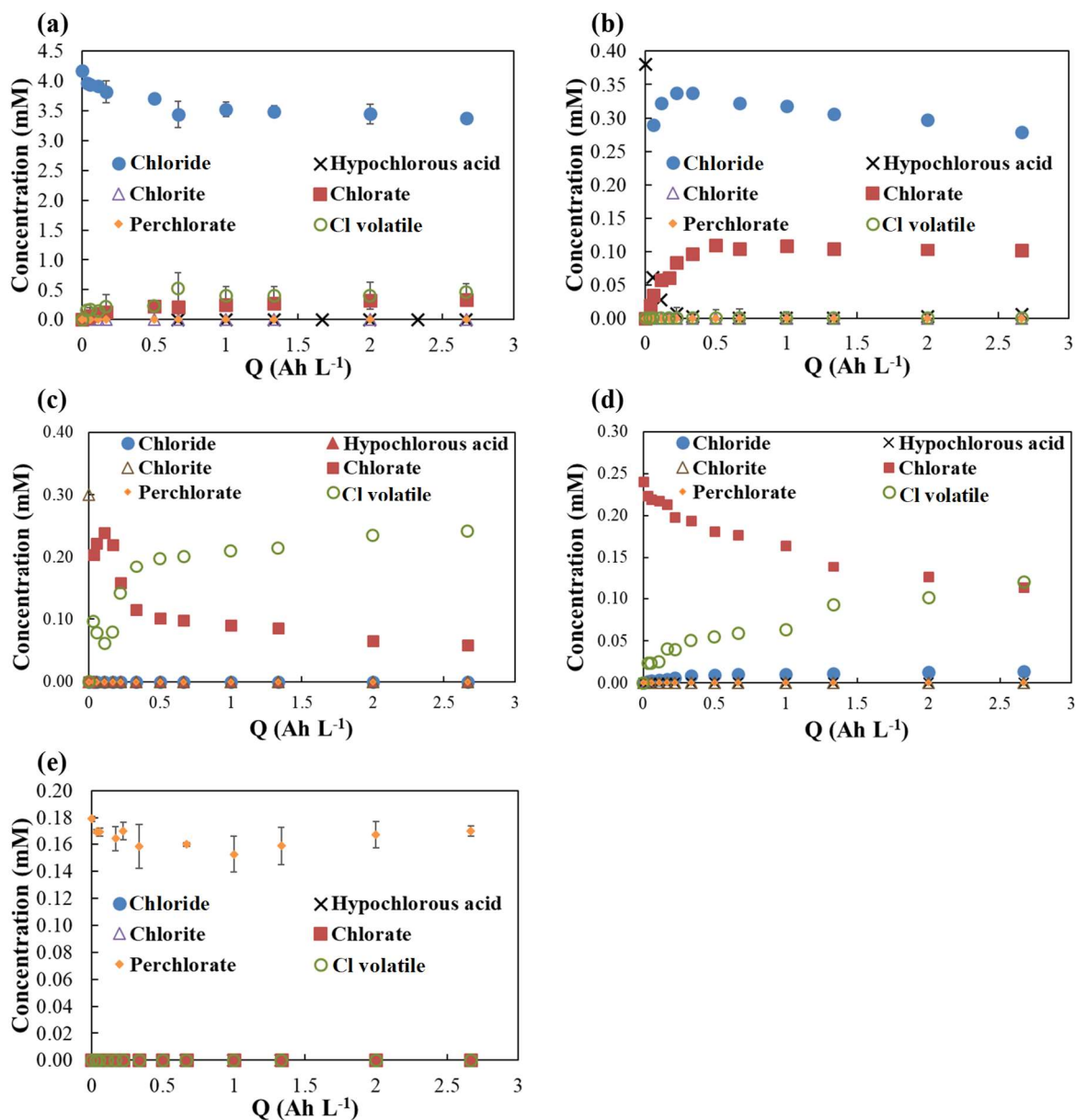
Reactions	Ref.
(7) $\text{Cl}^- + 3\text{H}_2\text{O} \rightarrow \text{ClO}_3^- + 6\text{H}^+ + 6\text{e}^-$	[47]
(7') $\text{ClO}_3^- + 6\text{H}^+ + 6\text{e}^- \rightarrow \text{Cl}^- + 3\text{H}_2\text{O}$	[47]
(8) a $2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$	[45]
b $\text{Cl}^- + 2\text{H}_2\text{O} \rightarrow \text{ClO}_2 + 4\text{H}^+ + 5\text{e}^-$	[28]
c $2\text{Cl}^- + \text{H}_2\text{O} \rightarrow \text{Cl}_2\text{O} + 2\text{H}^+ + 4\text{e}^-$	[46]
(8') a $\text{Cl}_2 + 2\text{e}^- \rightarrow 2\text{Cl}^-$	[45]
b $\text{ClO}_2 + 4\text{H}^+ + 5\text{e}^- \rightarrow \text{Cl}^- + 2\text{H}_2\text{O}$	[28]
c $\text{Cl}_2\text{O} + 2\text{H}^+ + 4\text{e}^- \rightarrow 2\text{Cl}^- + \text{H}_2\text{O}$	[46]
(9) $\text{Cl}^- + \cdot\text{OH} \rightarrow \text{ClOH}^-$	[46]
(9') $\text{ClOH}^- \rightarrow \text{Cl}^- + \cdot\text{OH}$	[46]
(10) $\text{ClO}_3^- + 5\text{Cl}^- + 6\text{H}^+ \rightarrow 3\text{H}_2\text{O} + 3\text{Cl}_2$	[48]
(10') $3\text{Cl}_2 + 3\text{H}_2\text{O} \rightarrow \text{ClO}_3^- + 5\text{Cl}^- + 6\text{H}^+$	[48]
(11) $\text{ClO}_3^- + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{ClO}_2^- + 2\text{H}_2\text{O}$	[26]
(11') a $\text{ClO}_2^- + 2\text{H}_2\text{O} \rightarrow \text{ClO}_3^- + 2\text{H}^+ + 2\text{e}^-$	[26]
b $\text{ClO}_2^- + \cdot\text{OH} \rightarrow \cdot\text{ClO}_2 + \text{HO}^-$	[26]
c $\cdot\text{ClO}_2 + \cdot\text{OH} \rightarrow \text{ClO}_3^- + \text{H}^+$	[26]
(12) $2\text{ClO}_3^- + 4\text{Cl}^- + 3/2\text{O}_2 + 12\text{H}^+ + 6\text{e}^- \rightarrow 6\text{ClOH} + 3\text{H}_2\text{O}$	[26]
(12') a $6\text{ClOH} + 3\text{H}_2\text{O} \rightarrow 2\text{ClO}_3^- + 4\text{Cl}^- + 3/2\text{O}_2 + 12\text{H}^+ + 6\text{e}^-$	[26]
b $\text{ClOH} + 2\text{ClO}_2 + \text{H}_2\text{O} \rightarrow 2\text{ClO}_3^- + \text{HCl} + 2\text{H}^+$	[49]
(13) $\text{ClO}_2^- + 3\text{H}^+ + 2\text{e}^- \rightarrow \text{ClOH} + \text{H}_2\text{O}$	[26]
(13') a $\text{ClOH} + \text{H}_2\text{O} \rightarrow \text{ClO}_2^- + 3\text{H}^+ + 2\text{e}^-$	[26]
b $\text{ClOH} + \cdot\text{OH} \rightarrow \cdot\text{ClO} + \text{H}_2\text{O}$	[26]
c $\cdot\text{ClO} + \cdot\text{OH} \rightarrow \text{ClO}_2^- + \text{H}^+$	[26]
(14) $\text{ClO}_2^- \rightarrow \text{ClO}_2 + \text{e}^-$	[28]
(14') $\text{ClO}_2 + \text{e}^- \rightarrow \text{ClO}_2^-$	[28]

182

183 During the electrolysis of chloride ion, only chlorate (Eq. 7) and  $\text{Cl}_{\text{volatile}}$  (Eqs. 8a-8b) accumulated in  
 184 solution (Fig. 1a).

185 The oxidation power involved in this process was not high enough to produce perchlorate, which is the  
 186 inorganic chlorinated compound having the highest oxidation state. This is an interesting feature since  
 187 this compound is known to be hazardous and has been classified as disinfection by-products [33]. This  
 188 can be an advantage compared to non-active anode system, such as BDD-based electrolysis, that  
 189 preferentially produce perchlorate [29,36]. The absence of generation of perchlorate is confirmed  
 190 through the other experiments performed with ClOH (Fig. 1b),  $\text{ClO}_2^-$  (Fig. 1c) and  $\text{ClO}_3^-$  (Fig. 1d). The  
 191 electrolysis of  $\text{ClO}_4^-$  itself (Fig. 1d) did not lead to any oxidation or reduction as its concentration remain  
 192 constant all along the electrolysis, which further emphasized the stability of this compound. Perchlorate

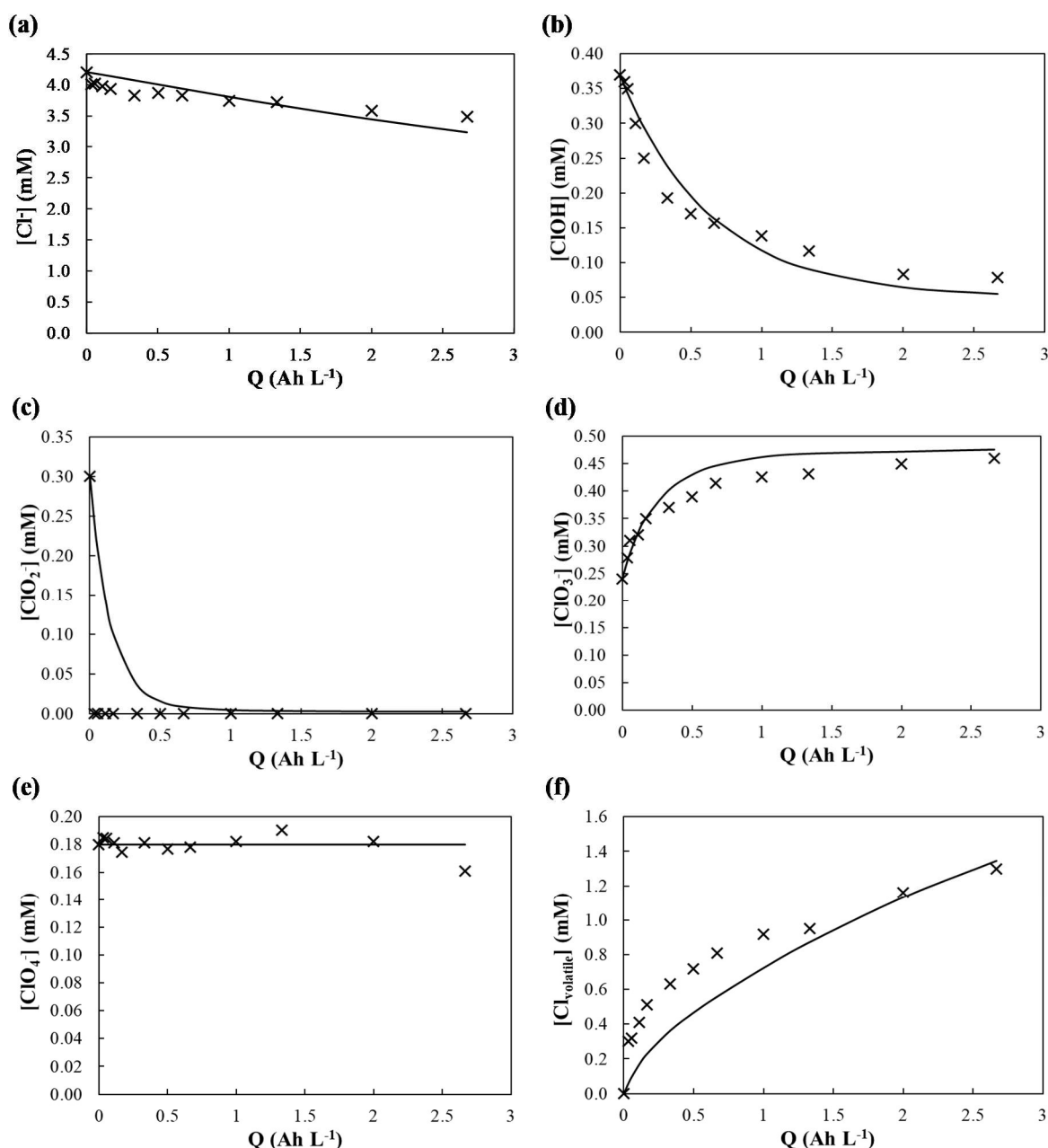
193 is known to be a stable species that is the inorganic chlorinated end-product in strong oxidation  
194 conditions involved in anodic oxidation process [29,50]. During the electrolysis of ClOH, its reduction  
195 into chloride (Eq. 9') was rather quick and the decay of ClOH was complete at a specific charge of 0.5  
196 Ah L<sup>-1</sup>. However, ClOH did not convert quantitatively into Cl<sup>-</sup> because the later was oxidized to chlorate  
197 at the anode (Eq. 7). ClOH could be also directly oxidized into chlorate (Eq. 12'a) (Fig. 1b).  
198 Contrastingly, chlorite was quickly oxidized into chlorate (Eq. 11'a-11'c) along with the chlorinated  
199 volatile production (Eq. 14) (Fig. 1c). Cl<sub>volatile</sub> seems to be predominantly produced from chlorate  
200 according to their respective opposite concentration evolution. This is in agreement with previous results  
201 that highlighted the fast formation of ClO<sub>2(g)</sub> from ClO<sub>2</sub><sup>-</sup> (Eq. 14) [28]. The fast decay of chlorite could  
202 explain why it was not accumulated in the experiments with Cl<sup>-</sup> and ClOH (Eqs. 13'a-13'c) unlike  
203 perchlorate that has been found to accumulate in every experiment, except with perchlorate. It is  
204 important to note that in acidic condition (pH 3), HClO<sub>2</sub> is also present in solution (10%) while ClO<sub>2</sub><sup>-</sup>  
205 remain predominant (90%), according to their pKa (HClO<sub>2</sub>/ClO<sub>2</sub><sup>-</sup>) of 2.0. It could slightly decrease the  
206 ClO<sub>2</sub><sup>-</sup> reactivity as compared to experiments performed at neutral pH or in alkaline condition such as  
207 anodic oxidation process.  
208 During the electrolysis of chlorate, Cl<sub>volatile</sub> was the main intermediate, while chloride was produced at  
209 lower extent. A reduction reaction (Eq. 7') could occur in acidic media as suggested by previous authors  
210 [47].  
211



212  
 213 **Fig. 1.** Profiles of  $\text{Cl}^-$ ,  $\text{ClOH}$ ,  $\text{ClO}_2^-$ ,  $\text{ClO}_3^-$ ,  $\text{ClO}_4^-$  and  $\text{Cl}_{\text{volatile}}$  in synthetic solutions containing initially  
 214 (a)  $\text{Cl}^-$ , (b)  $\text{ClOH}$ , (c)  $\text{ClO}_2^-$ , (d)  $\text{ClO}_3^-$  and (e)  $\text{ClO}_4^-$  as a function of the applied charge during electro-  
 215 Fenton treatment. Initial conditions: pH 3,  $[\text{Fe}^{2+}] = 0.1 \text{ mM}$ ;  $[\text{Cl}^-] = 4.2 \text{ mM}$  (a),  $[\text{ClOH}] = 0.37 \text{ mM}$   
 216 (b),  $[\text{ClO}_2^-] = 0.30 \text{ mM}$  (c),  $[\text{ClO}_3^-] = 0.24 \text{ mM}$  (d),  $[\text{ClO}_4^-] = 0.18 \text{ mM}$  (e).

217  
 218  
 219 3.1.2. Profiles and reaction pathway of inorganic chlorinated species mixture  
 220 The kinetics evolution of the chlorinated inorganic species has been then determined in an acidic mixture  
 221 (Fig. 2). The results were in accordance with the profiles depicted in single compound study (section  
 222 3.1.1). The chlorate and  $\text{Cl}_{\text{volatile}}$  tended to accumulate while the concentrations of chloride, chlorite and

223 hypochlorous acid were decreasing and the concentration of perchlorate remained constant. Still, a  
 224 difference with ClOH profile was noticed, since its decay was not complete after 2.7 Ah L<sup>-1</sup> (Fig. 2b).  
 225 With the initial presence of ClO<sub>2</sub><sup>-</sup>, the presence of ClO<sub>2</sub> generated from Eq. 14 could also contribute to  
 226 the oxidation of ClOH (Eq. 12'b). In the meantime, ClOH could be produced from Cl<sup>-</sup> oxidation (Eq.  
 227 9), ClO<sub>2</sub><sup>-</sup> reduction (Eq. 13) and ClO<sub>3</sub><sup>-</sup> reduction (Eq. 12), which compensated the rate of ClOH decay.  
 228

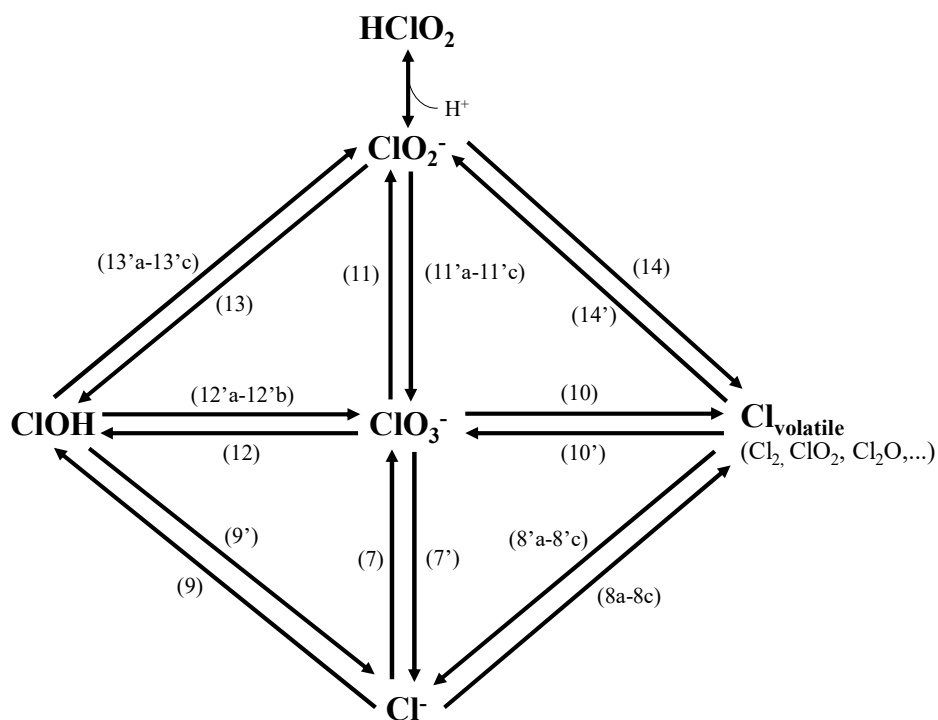


229  
 230 **Fig. 2.** Comparison of simulated (continuous line) and experimental data (×) about the profiles of (a)  
 231 Cl<sup>-</sup>, (b) ClOH, (c) ClO<sub>2</sub><sup>-</sup>, (d) ClO<sub>3</sub><sup>-</sup>, (e) ClO<sub>4</sub><sup>-</sup> and (f) Cl<sub>volatile</sub> in synthetic solutions containing initially a  
 232 mixture of Cl<sup>-</sup>, ClOH, ClO<sub>2</sub><sup>-</sup>, ClO<sub>3</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup> as a function of the applied specific charge during electro-

233 Fenton treatment. Initial conditions: pH 3,  $[\text{Fe}^{2+}] = 0.1 \text{ mM}$ ,  $[\text{Cl}^-] = 4.2 \text{ mM}$ ,  $[\text{ClOH}] = 0.37 \text{ mM}$ ,  
 234  $[\text{ClO}_2^-] = 0.30 \text{ mM}$ ,  $[\text{ClO}_3^-] = 0.24 \text{ mM}$ ,  $[\text{ClO}_4^-] = 0.18 \text{ mM}$ .

235  
 236 The experiments made with single chlorinated compounds and with a mixture of them allowed  
 237 establishing a pathway of the redox cycle of inorganic chlorinated species subjected to electro-  
 238 oxidation/reduction combined to homogeneous Fenton oxidation with carbon felts electrodes in  
 239 synthetic acidic solution (Fig. 3).

240 On the contrary to the pathway given with anodic oxidation using BDD anode [26,51], perchlorate is  
 241 not appearing in this scheme since the oxidation power was not high enough in the present process.  
 242 Moreover, the reduction reactions have been considered as well, since electron transfer could occur at  
 243 both cathode and anode in the electrochemical cell. This reaction pathway highlights the central role of  
 244 chlorate that directly interact with all the inorganic chlorinated species.



245  
 246 **Fig. 3.** Scheme of redox cycle of inorganic chlorinated species under electro-oxidation/reduction  
 247 combined to homogeneous Fenton oxidation with carbon felts electrodes in synthetic acidic solution  
 248 (pH 3). The equations involved are written in brackets.

249  
 250

251 3.1.3. Kinetics analysis of inorganic chlorinated species in a synthetic mixture

252 A kinetic model was proposed based on the results presented in sub-section 3.1.2 that allowed  
253 identifying the main chlorinated species involved during the electro-Fenton process.

254 The order of direct oxidation/reduction reactions was determined according to the initial limiting current  
255 density ( $j_{lim}^{\circ}$ ) (Eq. 15) values compared to the applied current density [52,53].

$$256 \quad j_{lim}^{\circ} = nFk_m C_0 \quad (15)$$

257 where  $n$  is the number of electron exchanged,  $F$  is the Faraday constant ( $96485 \text{ C mol}^{-1}$ ),  $k_m$  is the mass  
258 transport coefficient ( $\text{m s}^{-1}$ ),  $C_0$  is the initial concentration of the electroactive inorganic chlorinated  
259 species (mM).

260 An average  $k_m$  value of  $6 \times 10^{-6} \text{ m s}^{-1}$  has been taken into account, since it is the common value of the  
261 mass transport of species towards electrodes in such electrochemical reactor [39,54]. All the  $j_{lim}^{\circ}$  values  
262 were below  $1.5 \text{ mA cm}^{-2}$ , considering the oxidation of  $\text{Cl}^-$  into  $\text{ClO}_3^-$  (Eq. 7). This reaction involves the  
263 highest number of electrons exchanged and the highest initial concentration of compounds ( $[\text{Cl}^-] = 2.4$   
264 mM), indicating that all other direct oxidation/reduction reactions led to lower  $j_{lim}^{\circ}$ . Thus, the applied  
265 current density ( $2.5 \text{ mA cm}^{-2}$ ) was always higher than  $j_{lim}^{\circ}$ . Consequently, the mass transport was the  
266 rate-limiting step compared to charge transfer mechanism [52,53]. The rate ( $r$ ) of direct  
267 oxidation/reduction reactions under mass transport control can be expressed as follow (Eq. 16) [52,53]:

$$268 \quad r = Ak_m C \quad (16)$$

269 where  $A$  is the surface area of the electrode,  $C$  is the concentration during the electrolysis of the species  
270 that react by direct oxidation/reduction reaction.

271  
272 Considering Eq. 16, the kinetic of reaction is a first order towards  $C$ , the other parameters being  
273 constants. It corroborated the kinetic analysis suggested in previous studies that involved first order  
274 kinetics for direct oxidation/reduction reactions [24,27]. In addition, based on the quasi-steady state  
275 approximation towards  $\cdot\text{OH}$  concentration, a pseudo-first order kinetic model has been also considered  
276 for the reactions between inorganic chlorinated species and  $\cdot\text{OH}$  [27,42].

277 Therefore, the following system of differential equations considering first order kinetics was proposed  
278 to model the reaction kinetics of the species during electrolysis (Eqs. 17-22):

$$279 \quad \frac{d[Cl^-]}{dt} = k'_1[ClO_3^-] + k'_2[Cl_{gas}] + k'_3[ClOH] - (k_1 + k_2 + k_3)[Cl^-] \quad (17)$$

$$280 \quad \frac{d[ClOH]}{dt} = k_3[Cl^-] + k_7[ClO_2^-] + k_6[ClO_3^-] - (k'_3 + k'_6 + k'_7)[ClOH] \quad (18)$$

$$281 \quad \frac{d[ClO_2^-]}{dt} = k'_7[ClOH] + k'_8[Cl_{gas}] + k_5[ClO_3^-] - (k'_5 + k_7 + k_8)[ClO_2^-] \quad (19)$$

$$282 \quad \frac{d[ClO_3^-]}{dt} = k_1[Cl^-] + k'_4[Cl_{gas}] + k'_6[ClOH] + k'_5[ClO_2^-] - (k'_1 + k_4 + k_5 + k_6)[ClO_3^-] \quad (20)$$

$$283 \quad \frac{d[ClO_4^-]}{dt} = 0 \quad (21)$$

$$284 \quad \frac{d[Cl_{gas}]}{dt} = k_2[Cl^-] + k_4[ClO_3^-] + k_8[ClO_2^-] - (k'_2 + k'_4 + k'_8)[Cl_{gas}] \quad (22)$$

285

286 The main reactions implemented in the system are presented in [Table 1](#). The mathematical model has  
 287 been compared with the experimental data for chloride, hypochlorous acid, chlorite, chlorate,  
 288 perchlorate and volatile chlorinated species and the results are displayed in [Fig. 2](#). After calibration of  
 289 the model, the rate constant values (expressed in  $s^{-1}$ ) could be estimated ([Table 2](#)).

290

291

**Table 2.** Estimated kinetic constants values from the model.

Constant	Chlorinated species involved and direction of reaction	Equations involved	Rate constant value ( $s^{-1}$ )
$k_1$	$Cl^- \rightarrow ClO_3^-$	(7)	$1.54 \times 10^{-5}$
$k'_1$	$ClO_3^- \rightarrow Cl^-$	(7')	$3.86 \times 10^{-7}$
$k_2$	$Cl^- \rightarrow Cl_{volatile}$	(8a-8b)	$1.06 \times 10^{-5}$
$k'_2$	$Cl_{volatile} \rightarrow Cl^-$	(8'a-8'b)	$1.74 \times 10^{-5}$
$k_3$	$Cl^- \rightarrow ClOH$	(9)	$1.93 \times 10^{-7}$
$k'_3$	$ClOH \rightarrow Cl^-$	(9')	$9.64 \times 10^{-5}$
$k_4$	$ClO_3^- \rightarrow Cl_{volatile}$	(10)	$1.74 \times 10^{-4}$
$k'_4$	$Cl_{volatile} \rightarrow ClO_3^-$	(10')	$2.89 \times 10^{-5}$
$k_5$	$ClO_3^- \rightarrow ClO_2^-$	(11)	$9.64 \times 10^{-7}$
$k'_5$	$ClO_2^- \rightarrow ClO_3^-$	(11'a-11'c)	$3.86 \times 10^{-4}$
$k_6$	$ClO_3^- \rightarrow ClOH$	(12)	$2.89 \times 10^{-5}$
$k'_6$	$ClOH \rightarrow ClO_3^-$	(12'a-12'b)	$1.54 \times 10^{-4}$
$k_7$	$ClO_2^- \rightarrow ClOH$	(13)	$3.86 \times 10^{-7}$
$k'_7$	$ClOH \rightarrow ClO_2^-$	(13'a-13'c)	$3.86 \times 10^{-5}$
$k_8$	$ClO_2^- \rightarrow Cl_{volatile}$	(14)	$9.64 \times 10^{-4}$
$k'_8$	$Cl_{volatile} \rightarrow ClO_2^-$	(14')	$9.64 \times 10^{-7}$

292

293 The validity of the model was tested to see how well the theoretical curve fit the experimental data by  
 294 calculating the RMSE, ME and IoA. A model that perfectly fits the data would have a RMSE value of  
 295 zero and ME and IoA values of one. The RMSE, ME and IoA values for the model are shown in [Table](#)



296 3. RMSE, ME and IoA were below 0.084 and higher than 0.919 and 0.991, respectively, describing a  
297 good correlation considering the sixteen rate constants that have been taken into account.

298 The estimated values of parameters were ranging from  $1.93 \times 10^{-7} \text{ s}^{-1}$  to  $9.64 \times 10^{-4} \text{ s}^{-1}$ . The highest rate  
299 was attributed to the conversion of  $\text{ClO}_2^-$  into  $\text{Cl}_{\text{volatile}}$  (i.e.  $\text{ClO}_{2(\text{g})}$ ), which corroborates the fast  
300 conversion observed with single species in section 3.1.1. The oxidation of  $\text{ClO}_2^-$  into  $\text{ClO}_3^-$  was also  
301 very quick according to the rate constant ( $3.86 \times 10^{-4} \text{ s}^{-1}$ ), which confirmed the fast decay of  $\text{ClO}_2^-$   
302 compared to the other species during the electrolysis.

303

304 **Table 3.** Efficiency of the kinetic model in comparison with experimental data obtained in synthetic  
305 solution.

	<b>RMSE</b>	<b>ME</b>	<b>IoA</b>
$\text{Cl}^-$ curve	0.042	0.959	0.990
$\text{ClOH}$ curve	0.053	0.940	0.990
$\text{ClO}_2^-$ curve	0.084	0.919	0.941
$\text{ClO}_3^-$ curve	0.025	0.970	0.994
$\text{ClO}_4^-$ curve	0.021	0.992	0.999
$\text{Cl}_{\text{volatile}}$ curve	0.070	0.976	0.989

306

307 The model proposed in this study allowed confirming the pathway proposed in Fig. 3. This scheme and  
308 the model is valid in synthetic solution with inorganic chlorinated species only, considering no  
309 interference with other species that could be present in the effluent. The possible matrix effect has been  
310 studied in the following sections to evaluate these aspects.

311

312 3.2. Influence of additional inorganic species on concentration profile of chlorinated species

313 The possible impact of phosphate ion and inorganic carbon has not been studied previously, though  
314 these species are commonly present in municipal wastewater effluents along with chloride ions [27,39].

315 The influence of phosphate on the oxidation of chloride was determined by comparing the results from  
316 an experiment with initial additions of chloride and phosphate to an experiment with only chloride added  
317 initially (Figs. 4a and 4b). When comparing the normalized chloride concentrations of the experiment  
318 with phosphate to the experiment without phosphate, the values fell within the standard deviation of  
319 each other (Fig. 4a). Both experiments followed a similar trend with a decreasing amount of chloride as  
320 applied specific charge increased until 20% of  $\text{Cl}^-$  removal after  $2.7 \text{ Ah L}^{-1}$ . The kinetics of the evolution

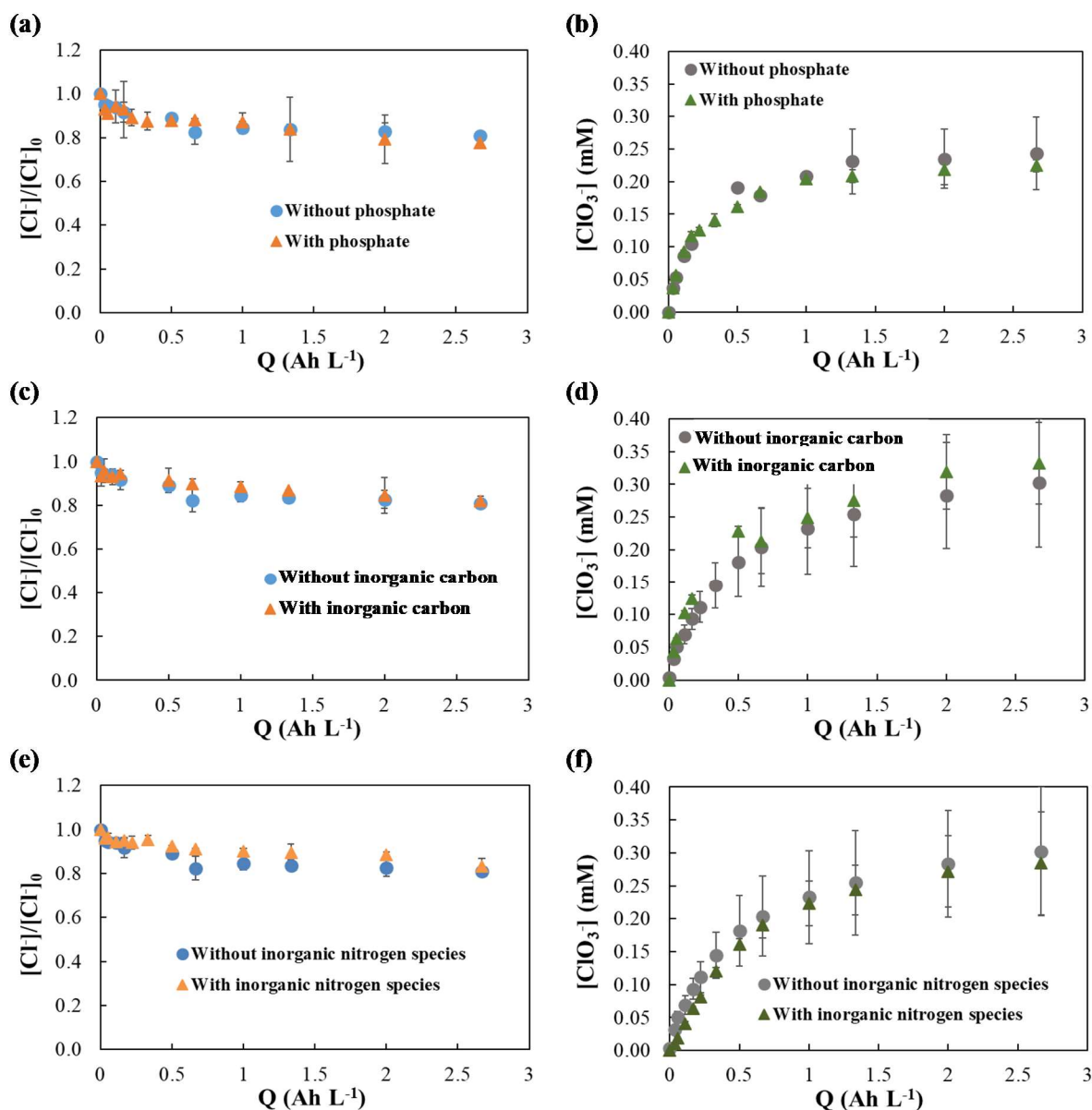
321 of inorganic chlorinated species for both experiments are illustrated in Fig. 4b.  $\text{ClO}_3^-$  was the only  
322 species quantified in the samples in both experiments, which is in agreement with single chloride  
323 experiments (Fig. 1a). Both experiments followed the same trend and the same kinetics considering the  
324 standard deviation, i.e. absence of chlorate initially and increasing over applied specific charge until a  
325 plateau around 0.24 mM. Therefore, phosphate did not have any impact on the redox evolution of  
326 inorganic chlorinated species in such electro-Fenton conditions. It seems that perphosphate ( $\text{P}_2\text{O}_8^{4-}$ ) was  
327 not produced during the electrolysis unlike in advanced electro-oxidation process (Eqs. 23-24) as the  
328 phosphate concentration remained constant all along the treatment and  $\text{P}_2\text{O}_8^{4-}$  could have oxidized  
329 chlorinated species.



332

333 The operating conditions may not be strong enough to allow  $\text{PO}_4^{3-}$  oxidation. It is also important to note  
334 that the predominant species at pH 3 are phosphoric acid ( $\text{H}_3\text{PO}_4$ ) and  $\text{H}_2\text{PO}_4^-$  whose pKa is 2.15. In this  
335 context, the oxidation of  $\text{H}_3\text{PO}_4$  or  $\text{H}_2\text{PO}_4^-$  species could be more difficult.

336



337  
 338 **Fig. 4.** Effect of phosphate ((a) and (b)), inorganic carbon ((c) and (d)) and inorganic nitrogen species  
 339 ((e) and (f)) contents on the decay of  $\text{Cl}^-$  normalized to the initial  $\text{Cl}^-$  concentration ( $[\text{Cl}^-]_0$ ) ((a), (c) and  
 340 (e)) and on the generation of  $\text{ClO}_3^-$  ((b), (d) and (f)) in synthetic solutions as a function of the applied  
 341 specific charge during electro-Fenton treatment. Initial conditions: pH 3,  $[\text{Fe}^{2+}] = 0.1 \text{ mM}$ ,  $[\text{Cl}^-] = 4.2$   
 342  $\text{mM}$ ;  $[\text{PO}_4^{3-}] = 0.21 \text{ mM}$  ((a) and (b)),  $[\text{CO}_3^{2-}] = 0.33 \text{ mM}$  ((c) and (d)),  $[\text{NH}_4^+] = 0.8 \text{ mM}$  ((e) and (f)),  
 343  $[\text{NO}_3^-] = 0.37 \text{ mM}$  ((e) and (f)),  $[\text{NO}_2^-] = 0.19 \text{ mM}$  ((e) and (f)).

344  
 345 Similarly, the effect of inorganic carbon on the concentration profiles of inorganic chlorinated species  
 346 was also negligible (Figs. 4c and 4d). In acidic condition the predominant inorganic carbon species  
 347 present in solution is carbonic acid ( $\text{H}_2\text{CO}_3$ ), according to the pKa of  $\text{H}_2\text{CO}_3/\text{HCO}_3^-$  couple that equal

348 6.3. Both acidic and milder oxidative stress conditions compared to the anodic oxidation technology  
349 might limit the formation of percarbonate (Eqs. 25-26) that could have played a role in the oxidation of  
350 chlorinated species otherwise.



353

354 It further highlights that in this acidic condition, the formation of calcium carbonate ( $\text{CaCO}_3$ ) at the  
355 cathode due to local pH increase [26] can be avoided. In the presence of  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$ , which is the  
356 case of reclaimed wastewater [27,39], this local precipitation is frequent and cause scaling effect that  
357 can impede the electrolysis.

358 The influence of inorganic nitrogen species has been also tested using concentration of 0.8 mM, 0.37  
359 mM and 0.19 mM for  $\text{NH}_4^+$ ,  $\text{NO}_3^-$  and  $\text{NO}_2^-$  respectively, which corresponds to the concentration  
360 employed in a previous study [27]. The results are shown in Figs. 4e and 4f and the same trends and  
361 kinetics of chloride and chlorate concentrations were observed regardless of the presence or absence  
362 of nitrogen species. However, the kinetics evolution of nitrogen species is impacted by the presence of  
363 chlorinated species as previously shown in electro-Fenton condition [27]. The ammonia tends to  
364 decrease due to the formation of monochloramine ( $\text{NH}_2\text{Cl}$ ), dichloramine ( $\text{NHCl}_2$ ) and trichloramine  
365 ( $\text{NCl}_3$ ) with  $\text{ClOH}$ , while nitrate tends to accumulate in solution [27].

366

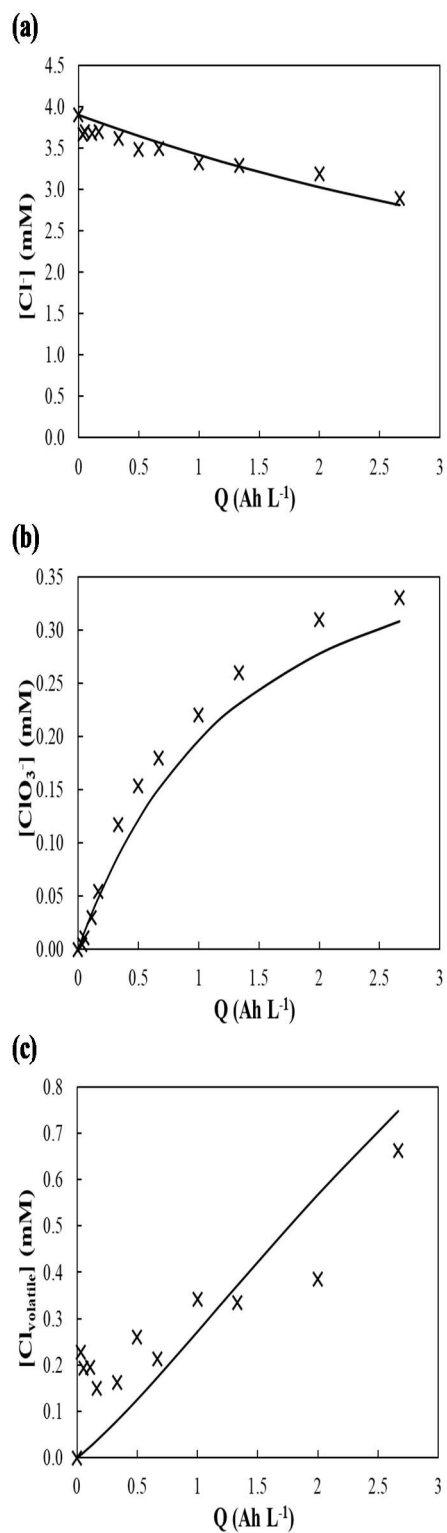
367 Thus, the presence in the initial effluent of phosphate, inorganic carbon and inorganic nitrogen species  
368 should not affect the concentration profiles and the proposed pathway of the inorganic chlorinated  
369 species in electro-Fenton condition. This is verified in reclaimed wastewater in the following section  
370 3.3.

371

372 3.3. Validation of the suggested model on the concentration profiles of inorganic chlorinated  
373 species in reclaimed wastewater

374 Experiments have been performed with reclaimed wastewater from the outlet of a municipal wastewater  
375 treatment plant in Reims, France. The characteristics of the initial effluent are given in a previous paper  
376 [27]. The inorganic chlorinated species have been monitored and only chloride and chlorate were

377 detected in the samples from the wastewater electrolysis and their concentrations are graphed in [Fig. 5a](#)  
378 and [Fig. 5b](#), while  $Cl_{\text{volatile}}$  is plotted in [Fig. 5c](#). The model that has been proposed in section 3.1.2 has  
379 been applied for the experiments with real effluent and the results are depicted in [Figs. 5a-c](#). The same  
380 kinetic rate constant values and ordinary differential equations were used. The model fitted quite well  
381 the experimental concentrations of the chlorinated species. RMSE, ME and IoA were lower than 0.071  
382 and higher than 0.910 and 0.937, respectively ([Table 4](#)). It further confirmed that phosphate, inorganic  
383 carbon contents and nitrogenous species were not impacting the fate of chloride and chlorate species.  
384 The pathway proposed in [Fig. 3](#) could be then validated with real wastewater.  
385



386

387 **Fig. 5.** Comparison of simulated (continuous line) and experimental data (x) about the profiles of (a)  
 388 Cl<sup>-</sup>, (b) ClO<sub>3</sub><sup>-</sup> and (c) Cl<sub>volatile</sub> in reclaimed wastewater as a function of the applied specific charge  
 389 during electro-Fenton treatment. Initial conditions: pH 3, [Fe<sup>2+</sup>] = 0.1 mM.

390

391

392

**Table 4.** Validation of the kinetic model applied for reclaimed wastewater.

	<b>RMSE</b>	<b>ME</b>	<b>IoA</b>
Cl <sup>-</sup> curve	0.059	0.990	0.991
ClO <sub>3</sub> <sup>-</sup> curve	0.034	0.990	0.997
Cl <sub>volatile</sub> curve	0.071	0.910	0.937

393

394

#### 395 4. Conclusions

396 For the first time, the concentration profiles of inorganic chlorinated species in synthetic and reclaimed  
 397 municipal wastewater in electro-Fenton process have been investigated in detail. The redox cycles of  
 398 chloride, hypochlorous acid, chlorite, chlorate, perchlorate and volatile chlorinated species have been  
 399 established. A kinetic model considering first order kinetics and sixteen rate constants has been  
 400 proposed. After calibration and validation of the model with experimental data obtained in synthetic  
 401 solution, the model has been further validated with a real solution. A reaction pathway has been  
 402 suggested for both synthetic and reclaimed wastewater.

403 The acidic and mild oxidation conditions compared to anodic oxidation with non-active anode permit  
 404 to avoid the interference of phosphate, carbonate and inorganic nitrogen species with the redox cycles  
 405 of inorganic chlorinated species. Furthermore, perchlorate could not accumulate unlike in advanced  
 406 electro-oxidation. However, chlorate and volatile chlorinated species were still accumulating with the  
 407 applied specific charge for all tested solutions. In this context, these intermediates need to be carefully  
 408 assessed during the electro-Fenton treatment of real chlorinated effluents.

409

410

#### 411 References

- 412 [1] UNESCO, Wastewater, The Untapped Resource. United Nations World Water Development  
 413 Report, 2017.
- 414 [2] S.D. Richardson, S.Y. Kimura, Water Analysis: Emerging Contaminants and Current Issues,  
 415 Anal. Chem. 88 (2016) 546–582.
- 416 [3] R.I.L. Eggen, J. Hollender, A. Joss, M. Schärer, C. Stamm, Reducing the discharge of  
 417 micropollutants in the aquatic environment: The benefits of upgrading wastewater treatment  
 418 plants, Environ. Sci. Technol. 48 (2014) 7683–7689.

- 419 [4] L. Kovalova, H. Siegrist, U. von Gunten, J. Eugster, M. Hagenbuch, A. Wittmer, R. Moser, C.S.  
420 McArdell, Elimination of micropollutants during post-treatment of hospital wastewater with  
421 powdered activated carbon, ozone, and UV., *Environ. Sci. Technol.* 47 (2013) 7899–7908.
- 422 [5] F.C. Moreira, R.A.R. Boaventura, E. Brillas, V.J.P. Vilar, Electrochemical advanced oxidation  
423 processes: A review on their application to synthetic and real wastewaters, *Appl. Catal. B*  
424 *Environ.* 202 (2017) 217–261.
- 425 [6] C.A. Martínez-Huitle, M.A. Rodrigo, I. Sirés, O. Scialdone, Single and coupled electrochemical  
426 processes and reactors for the abatement of organic water pollutants : A critical review, *Chem.*  
427 *Rev.* 115 (2015) 13362–13407.
- 428 [7] E. Mousset, N. Oturan, M.A. Oturan, An unprecedented route of OH radical reactivity evidenced  
429 by an electrocatalytical process: Ipso-substitution with perhalogenocarbon compounds, *Appl.*  
430 *Catal. B Environ.* 226 (2018) 135–146.
- 431 [8] N. Oturan, E. Brillas, M.A. Oturan, Unprecedented total mineralization of atrazine and cyanuric  
432 acid by anodic oxidation and electro-Fenton with a boron-doped diamond anode, *Environ. Chem.*  
433 *Lett.* 10 (2012) 165–170.
- 434 [9] P. Cañizares, R. Paz, C. Sáez, M.A. Rodrigo, Costs of the electrochemical oxidation of  
435 wastewaters: a comparison with ozonation and Fenton oxidation processes., *J. Environ. Manage.*  
436 90 (2009) 410–420.
- 437 [10] E. Mousset, N. Oturan, E.D. van Hullebusch, G. Guibaud, G. Esposito, M.A. Oturan, Influence  
438 of solubilizing agents (cyclodextrin or surfactant) on phenanthrene degradation by electro-  
439 Fenton process - Study of soil washing recycling possibilities and environmental impact, *Water*  
440 *Res.* 48 (2014) 306–316.
- 441 [11] H. Monteil, Y. Péchaud, N. Oturan, M.A. Oturan, A review on efficiency and cost effectiveness  
442 of electro- and bio-electro-Fenton processes: Application to the treatment of pharmaceutical  
443 pollutants in water, *Chem. Eng. J.* (2018) 1–30.
- 444 [12] L. Feng, N. Oturan, E.D. van Hullebusch, G. Esposito, M.A. Oturan, Degradation of anti-  
445 inflammatory drug ketoprofen by electro-oxidation: comparison of electro-Fenton and anodic  
446 oxidation processes., *Environ. Sci. Pollut. Res. Int.* 21 (2014) 8406–8416.
- 447 [13] S. Garcia-Segura, R. Salazar, E. Brillas, Mineralization of phthalic acid by solar photoelectro-



- 448 Fenton with a stirred boron-doped diamond/air-diffusion tank reactor: Influence of  $\text{Fe}^{3+}$  and  $\text{Cu}^{2+}$   
449 catalysts and identification of oxidation products, *Electrochim. Acta.* 113 (2013) 609–619.
- 450 [14] I.F. Mena, S. Cotillas, E. Díaz, C. Sáez, Á.F. Mohedano, M.A. Rodrigo, Influence of the  
451 supporting electrolyte on the removal of ionic liquids by electrolysis with diamond anodes, *Catal.*  
452 *Today.* 313 (2018) 203–210.
- 453 [15] E. Mousset, D. Huguenot, E.D. Van Hullebusch, N. Oturan, G. Guibaud, G. Esposito, M.A.  
454 Oturan, Impact of electrochemical treatment of soil washing solution on PAH degradation  
455 efficiency and soil respirometry, *Environ. Pollut.* 211 (2016) 354–362.
- 456 [16] N. Oturan, E.D. Van Hullebusch, H. Zhang, L. Mazeas, H. Budzinski, K. Le Menach, M.A.  
457 Oturan, Occurrence and removal of organic micropollutants in landfill leachates treated by  
458 electrochemical advanced oxidation processes, *Environ. Sci. Technol.* 49 (2015) 12187–12196.
- 459 [17] S. Garcia-Segura, J.D. Ocon, M.N. Chong, Electrochemical oxidation remediation of real  
460 wastewater effluents — A review, *Process Saf. Environ. Prot.* 113 (2018) 48–67.
- 461 [18] E. Mousset, Z. Wang, H. Olvera-Vargas, O. Lefebvre, Advanced electrocatalytic pre-treatment  
462 to improve the biodegradability of real wastewater from the electronics industry — A detailed  
463 investigation study, *J. Hazard. Mater.* 360 (2018) 552–559.
- 464 [19] E. Mousset, N. Oturan, E.D. van Hullebusch, G. Guibaud, G. Esposito, M.A. Oturan, Treatment  
465 of synthetic soil washing solutions containing phenanthrene and cyclodextrin by electro-  
466 oxidation. Influence of anode materials on toxicity removal and biodegradability enhancement,  
467 *Appl. Catal. B Environ.* 160–161 (2014) 666–675.
- 468 [20] N. Barhoumi, N. Oturan, H. Olvera-Vargas, E. Brillas, A. Gadri, S. Ammar, M.A. Oturan, Pyrite  
469 as a sustainable catalyst in electro-Fenton process for improving oxidation of sulfamethazine.  
470 Kinetics, mechanism and toxicity assessment, *Water Res.* 94 (2016) 52–61.
- 471 [21] A. Kapalka, L. Joss, Á. Anglada, C. Comninellis, K.M. Udert, Direct and mediated  
472 electrochemical oxidation of ammonia on boron-doped diamond electrode, 12 (2010) 1714–  
473 1717.
- 474 [22] A. Kapalka, S. Fierro, Z. Frontistis, A. Katsaounis, S. Neodo, O. Frey, N. de Rooij, K.M. Udert,  
475 C. Comninellis, Electrochemical oxidation of ammonia ( $\text{NH}_4^+/\text{NH}_3$ ) on thermally and  
476 electrochemically prepared  $\text{IrO}_2$  electrodes, *Electrochim. Acta.* 56 (2011) 1361–1365.

- 477 [23] E. Lacasa, J. Llanos, P. Cañizares, M.A. Rodrigo, Electrochemical denitrification with chlorides  
478 using DSA and BDD anodes, *Chem. Eng. J.* 184 (2012) 66–71.
- 479 [24] G. Pérez, R. Ibáñez, A.M. Urtiaga, I. Ortiz, Kinetic study of the simultaneous electrochemical  
480 removal of aqueous nitrogen compounds using BDD electrodes, *Chem. Eng. J.* 197 (2012) 475–  
481 482.
- 482 [25] M.J.M. De Vidales, M. Millán, C. Sáez, P. Cañizares, M.A. Rodrigo, What happens to inorganic  
483 nitrogen species during conductive diamond electrochemical oxidation of real wastewater?,  
484 *Electrochem. Commun.* 67 (2016) 65–68.
- 485 [26] Y. Lan, C. Coetsier, C. Causserand, K. Groenen Serrano, On the role of salts for the treatment of  
486 wastewaters containing pharmaceuticals by electrochemical oxidation using a boron doped  
487 diamond anode, *Electrochim. Acta.* 231 (2017) 309–318.
- 488 [27] E. Mousset, S. Pontvianne, M.-N. Pons, Fate of inorganic nitrogen species under homogeneous  
489 Fenton combined with electro-oxidation/reduction treatments in synthetic solutions and  
490 reclaimed municipal wastewater, *Chemosphere.* 201 (2018) 6–12.
- 491 [28] H. Bergmann, A.S. Koparal, The formation of chlorine dioxide in the electrochemical treatment  
492 of drinking water for disinfection, *Electrochim. Acta.* 50 (2005) 5218–5228.
- 493 [29] M.E.H. Bergmann, J. Rollin, T. Iourtchouk, The occurrence of perchlorate during drinking water  
494 electrolysis using BDD anodes, *Electrochim. Acta.* 54 (2009) 2102–2107.
- 495 [30] H. Bergmann, A.T. Koparal, A.S. Koparal, F. Ehrig, The influence of products and by-products  
496 obtained by drinking water electrolysis on microorganisms, *Microchem. J.* 89 (2008) 98–107.
- 497 [31] M.E.H. Bergmann, J. Rollin, Product and by-product formation in laboratory studies on  
498 disinfection electrolysis of water using boron-doped diamond anodes, *Catal. Today.* 124 (2007)  
499 198–203.
- 500 [32] M.E.H. Bergmann, A.S. Koparal, T. Iourtchouk, Electrochemical Advanced oxidation processes,  
501 formation of halogenate and perhalogenate species: A critical review, *Crit. Rev. Environ. Sci.*  
502 *Technol.* 44 (2014) 348–390.
- 503 [33] C.D.N. Brito, D.M. de Araújo, C.A. Martínez-Huitle, M.A. Rodrigo, Understanding active  
504 chlorine species production using boron doped diamond films with lower and higher  $sp^3/sp^2$  ratio,  
505 *Electrochem. Commun.* 55 (2015) 34–38.

- 506 [34] J. Llanos, S. Cotillas, P. Cañizares, M.A. Rodrigo, Conductive diamond sono-electrochemical  
507 disinfection (CDSED) for municipal wastewater reclamation., *Ultrason. Sonochem.* 22 (2015)  
508 493–498.
- 509 [35] A. Cano, P. Cañizares, C. Barrera, C. Sáez, M.A. Rodrigo, Use of low current densities in  
510 electrolyses with conductive-diamond electrochemical — Oxidation to disinfect treated  
511 wastewaters for reuse, *Electrochem. Commun.* 13 (2011) 1268–1270.
- 512 [36] A. Cano, P. Cañizares, C. Barrera-Díaz, C. Sáez, M.A. Rodrigo, Use of conductive-diamond  
513 electrochemical-oxidation for the disinfection of several actual treated wastewaters, *Chem. Eng.*  
514 *J.* 211–212 (2012) 463–469.
- 515 [37] M. Panizza, M.A. Oturan, Degradation of Alizarin Red by electro-Fenton process using a  
516 graphite-felt cathode, *Electrochim. Acta.* 56 (2011) 7084–7087.
- 517 [38] A. Dirany, I. Sirés, N. Oturan, A. Ozcan, M.A. Oturan, Electrochemical treatment of the  
518 antibiotic sulfachloropyridazine: kinetics, reaction pathways, and toxicity evolution, *Environ.*  
519 *Sci. Technol.* 46 (2012) 4074–4082.
- 520 [39] E. Mousset, M. Puce, M.-N. Pons, Advanced electro-oxidation with boron-doped diamond for  
521 acetaminophen removal from real wastewater in a microfluidic reactor – Kinetics and mass  
522 transfer studies, *ChemElectroChem.* 6 (2019) 2908–2916.
- 523 [40] E. Mousset, Z. Wang, O. Lefebvre, Electro-Fenton for control and removal of micropollutants –  
524 process optimization and energy efficiency, *Water Sci. Technol.* 74 (2016) 2068–2074.
- 525 [41] M. Panizza, G. Cerisola, Direct and mediated anodic oxidation of organic pollutants, *Chem. Rev.*  
526 109 (2009) 6541–6569.
- 527 [42] E. Brillas, I. Sirés, M.A. Oturan, Electro-Fenton process and related electrochemical  
528 technologies based on Fenton’s reaction chemistry, *Chem. Rev.* 109 (2009) 6570–6631.
- 529 [43] I. Sirés, E. Brillas, M.A. Oturan, M.A. Rodrigo, M. Panizza, Electrochemical advanced oxidation  
530 processes: today and tomorrow. A review., *Environ. Sci. Pollut. Res.* 21 (2014) 8336–8367.
- 531 [44] E. Mousset, L. Frunzo, G. Esposito, E.D. van Hullebusch, N. Oturan, M.A. Oturan, A complete  
532 phenol oxidation pathway obtained during electro-Fenton treatment and validated by a kinetic  
533 model study, *Appl. Catal. B Environ.* 180 (2016) 189–198.
- 534 [45] Y.J. Jung, K.W. Baek, B.S. Oh, J.W. Kang, An investigation of the formation of chlorate and

- 535 perchlorate during electrolysis using Pt/Ti electrodes: The effects of pH and reactive oxygen  
536 species and the results of kinetic studies, *Water Res.* 44 (2010) 5345–5355.
- 537 [46] E. Mostafa, P. Reinsberg, S. Garcia-Segura, H. Baltruschat, Chlorine species evolution during  
538 electrochlorination on boron-doped diamond anodes: In-situ electrogeneration of Cl<sub>2</sub>, Cl<sub>2</sub>O and  
539 ClO<sub>2</sub>, *Electrochim. Acta.* 281 (2018) 831–840.
- 540 [47] G.M. Brown, The reduction of chlorate and perchlorate ions at an active titanium electrode, *J.*  
541 *Electroanal. Chem.* 198 (1986) 319–330.
- 542 [48] M. Tian, L. Yang, J. Wang, Z. Li, S. Chen, Degradation of p-nitrophenol affected by synergy of  
543 indirect and direct electrooxidation, *Adv. Mater. Res.* 518–523 (2012) 295–298.
- 544 [49] B. Michele, P.S. Fair, D.P. Hautman, Occurrence of chlorate in hypochlorite solutions used for  
545 drinking water disinfection, *Environ. Sci. Technol.* 26 (1992) 1663–1665.
- 546 [50] A. Sánchez-Carretero, C. Sáez, P. Cañizares, M.A. Rodrigo, Electrochemical production of  
547 perchlorates using conductive diamond electrolyses, *Chem. Eng. J.* 166 (2011) 710–714.
- 548 [51] B.P. Chaplin, Critical review of electrochemical advanced oxidation processes for water  
549 treatment applications., *Environ. Sci. Process. Impacts.* 16 (2014) 1182–1203.
- 550 [52] M. Panizza, P.A. Michaud, G. Cerisola, C. Cominellis, Anodic oxidation of 2-naphthol at  
551 boron-doped diamond electrodes, *J. Electroanal. Chem.* 507 (2001) 206–214.
- 552 [53] E. Mousset, Y. Pechaud, N. Oturan, M.A. Oturan, Charge transfer/mass transport competition in  
553 advanced hybrid electrocatalytic wastewater treatment: Development of a new current efficiency  
554 relation, *Appl. Catal. B Environ.* 240 (2019) 102–111.
- 555 [54] E.V. dos Santos, S.F.M. Sena, D.R. da Silva, S. Ferro, A. De Battisti, C.A. Martínez-Huitile,  
556 Scale-up of electrochemical oxidation system for treatment of produced water generated by  
557 Brazilian petrochemical industry, *Environ. Sci. Pollut. Res.* 21 (2014) 8466–8475.

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