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**An unprecedented route of $\cdot\text{OH}$ radical reactivity evidenced by an
electrocatalytical process: ipso-substitution with
perhalogenocarbon compounds**

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ABSTRACT

Hydroxyl radical ($\cdot\text{OH}$) is ubiquitous in the environment and in metabolism. It is one of the most powerful oxidants and can react instantaneously with surrounding chemicals. Currently, three attack modes of $\cdot\text{OH}$ have been identified: hydrogen atom abstraction, addition to unsaturated bond and electron transfer. Perhalogenocarbon compounds such as CCl_4 are therefore supposed to be recalcitrant to $\cdot\text{OH}$ as suggested by numerous authors due to the absence of both hydrogen atom(s) and unsaturated bond(s). Here, we report for the first time a fourth attack mode of $\cdot\text{OH}$ through ipso-substitution of the halogen atom. This breakthrough offers new scientific insight for understanding the mechanisms of $\cdot\text{OH}$ oxidation in the related research areas of research. It is especially a great progress in organic contaminants removal from water. In this study, CCl_4 is successfully degraded and mineralized in aqueous media using a green and efficient electrocatalytical production of homogeneous and heterogeneous $\cdot\text{OH}$. Maximum degradation rate of 0.298 min^{-1} and mineralization yield of 82% were reached. This opens up new possibilities of emerging water pollutants elimination such as fluorosurfactants.

Keywords: carbon tetrachloride; anodic oxidation; electrocatalysis; electro-Fenton; oxidation pathway.

1. INTRODUCTION

The omnipresence of hydroxyl radical ($\cdot\text{OH}$) is now well established in various types of environments including natural waters, atmosphere in which it plays a role of “detergent”, interstellar space as well as biological systems where $\cdot\text{OH}$ has an important role in immunity metabolism [1–4]. It makes $\cdot\text{OH}$ as the most important free radical in chemistry and biology because of its multiple implications and applications [5,6].

In water media, $\cdot\text{OH}$ is the second strongest oxidizing agent after fluorine with a standard redox potential of 2.8 V/SHE [7]. The presence of unpaired electron on oxygen atom makes $\cdot\text{OH}$ a very reactive species with a mean lifetime estimated as only a few nanoseconds in water [8]. It destroys most of organic and organometallic pollutants until total mineralization, i.e. conversion into CO_2 , H_2O , and inorganic ions; hence the interest of its use in water treatment area. Indeed, the occurrence of hazardous and toxic pollutants into the water compartments led the water and wastewater regulatory requirements to become more stringent regarding the release of such compounds. Being xenobiotic, these contaminants cannot be removed by conventional wastewater treatment plant and therefore an advanced physicochemical treatment is required. Thus, since more than 30 years the outstanding properties of $\cdot\text{OH}$ have been tested for water purification in the so-called advanced oxidation processes (AOPs) [9]. AOPs have gained increasing interests as they constitute promising, efficient and environmental-friendly methods to remove persistent organic pollutants (POPs) from waters [10,11]. Several types of AOPs have been developed based on the *in situ* formation of $\cdot\text{OH}$ by means of various chemical, photochemical, sonochemical, or electrochemical reactions. Then, the $\cdot\text{OH}$ formed can react according to three possible reaction modes proposed in literature: (i) hydrogen atom abstraction (dehydrogenation), (ii) electrophilic addition to an unsaturated bond (hydroxylation) and (iii) electron transfer (redox) reactions [6,10]. The first mode is typical for alkanes and alcohols (Eq. 1) with rate

constants in the range 10^6 - 10^8 $M^{-1} s^{-1}$ [12], whereas the second mode occurs especially with aromatics (ArH) (Eqs. 2a-2b) with rate constants as high as 10^8 - 10^{10} $M^{-1} s^{-1}$ [12] while the third mode is generally given with oxidizable inorganics such as cation (Fe^{2+} (Eq. 3a)) as well as anions (Eq. 3b) (Cl^- , NO_2^- , HCO_3^-) and organics (Eq. 4) [1]:



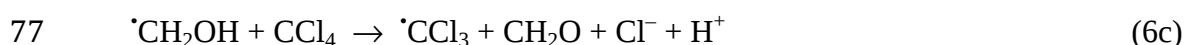
Therefore, $\cdot OH$ s are very active species that can oxidize even the most recalcitrant chemicals. However, $\cdot OH$ have been considered in several studies as unreactive with perhalogenated alkanes (C_xX_y) water contaminants that contain only carbon and halogen atoms such as carbon tetrafluoride (CF_4), carbon tetrachloride (CCl_4), hexafluoroethane (C_2F_6) and hexachloroethane (C_2Cl_6) that are widely used as etchant in semiconductor manufacturing and as refrigerants. Indeed, these pollutants do not have any hydrogen atom as well as no unsaturated bond. Thus, no one of the three above-mentioned modes of $\cdot OH$ actions can occur.

Interestingly, several authors intended to be able to degrade perhalogenocarbon compounds by applying some AOPs but in the presence of an organic precursor. Cho et al. [13,14] succeeded to degrade CCl_4 with a heterogeneous photocatalysis (UV/ TiO_2) process in the presence of surfactant as organic precursor. It was proposed as a hypothesis that a complex formation between the surfactant functional groups and TiO_2 surface was responsible for the

69 weak visible light absorption and the subsequent photo-induced electron transfer to CCl₄
 70 (Eqs. (5a)-(5b)):



73 Gonzalez et al. [15] employed methanol as precursor to mineralize CCl₄ by H₂O₂ photolysis
 74 according to the following reactions sequence (Eqs. (6a)-(6c)):



78 In addition, some authors applying other AOPs also demonstrated the degradation of CCl₄ by
 79 suggesting the formation of additional inorganic species that were responsible for its
 80 decomposition. Thus, it was considered that sonication decomposes water molecules into
 81 hydrogen radical ($\cdot\text{H}$) and $\cdot\text{OH}$ and then CCl₄ reacts with $\cdot\text{H}$ [16,17]:



84 In a modified chemical Fenton's treatment it was suggested that the superoxide ion ($\text{O}_2^{\cdot-}$) was
 85 responsible for the decomposition of CCl₄ [18–20]. $\text{O}_2^{\cdot-}$ is a weak nucleophile and reductant
 86 that was suggested to be able to degrade CCl₄ in aprotic media such as dimethyl sulfoxide and
 87 dimethylformamide as organic precursor [21,22] and more recently in aqueous media by
 88 using high concentration of H₂O₂ (>0.1 M) in a Fenton-like process.

However, an important feature is that at the operated Fenton pH (pH 3 initially), hydroperoxyl ion ($\text{HO}_2^\cdot$), a weak oxidant ($E^\circ = 1.65 \text{ V/SHE}$), predominate in such acidic conditions ($pK_a = 4.8$) instead of $\text{O}_2^{\cdot-}$ [23]. Therefore, the role of $\text{O}_2^{\cdot-}$ has to be reconsidered.

Recently, electrochemical advanced oxidation processes (EAOPs) for generating $^\cdot\text{OH}$ in a catalytic and continuous mode have gained increasing interests [23–27]. They are not only more environmentally friendly as electron is a clean reagent but also more efficient as they can even degrade the most recalcitrant compounds [28–34] such as cyanuric acid known to be resistant to $^\cdot\text{OH}$ oxidation in more conventional AOPs [35]. Another advantage is that EAOPs are modular process according to the electrodes materials to be used which lead to different oxidizing/reducing species formed [23,36–40]. In other words, the nature of the electrogenerated species can be controlled by the adequate electrode materials and operating conditions. Therefore, the oxidative degradation of perhalogenated compounds such as CCl_4 has never been studied by EAOPs, it appears important to carry out it as it can bring novel tremendous scientific insights on the mechanism of degradation of such molecules according to the electrode material employed.

2. EXPERIMENTAL

2.1. Chemicals

All the chemicals were of analytical grade, and were used without any further purification. Carbon tetrachloride (CCl_4), titanium tetrachloride (TiCl_4), potassium hydrogen phthalate, hydrogen peroxide (H_2O_2) (30% w/w) and sodium sulfate (Na_2SO_4) were purchased from Sigma-Aldrich. Heptahydrated ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), sulfuric acid (H_2SO_4) and phosphoric acid (H_3PO_4) (85% w/w) were supplied by Acros Organics. In all experiments, the

solutions were prepared with ultrapure water from a Millipore Simplicity 185 (resistivity > 18 MΩ cm at room temperature).

2.2. Electrochemical reactor set-up

Electrolysis experiments with CCl₄ aqueous solutions (0.2 mM) were run at controlled temperature (22.0 ± 0.1 °C), in a 0.20 L closed-undivided glass electrochemical reactor under current-controlled conditions. The cathode was either a 150 cm² carbon felt (CF) piece (Carbone-Lorraine, France) or a 28 cm² plate of stainless steel (SS) (GoodFellow, France). Either a Pt grid (5 cm height cylindrical (i.d. = 3 cm)) or boron-doped diamond (BDD) coated on a Niobium (Nb) plate (28 cm²) (Condias, Germany) was employed as an anode material with an electrode distance of 3.5 cm. The electrochemical cell was monitored by a power supply HAMEG 7042-5 (Germany) and the applied current was set to 1000 mA. An inert supporting electrolyte (Na₂SO₄ at 0.050 M) was added to the medium to ensure a constant ionic strength (0.15 M). The pH of the initial solution was adjusted to a pH of 3 [41]. The solutions were continuously stirred to assure homogeneous mixing. FeSO₄·7H₂O was added (0.05 mM) as a source of catalyst (Fe²⁺) to implement Fenton's reaction in EF process. Compressed air was bubbled initially before starting the experiment and before adding CCl₄ compound [42]. This was to saturate the aqueous solution in O₂ as a source of H₂O₂ production (Eq. 9) while avoiding the volatilization of CCl₄. The reactor set-up for electrolysis experiments is illustrated in Fig. 1. The same reactor was employed to perform H₂O₂ oxidation experiments, except that the electrodes were absent.

2.3. Analytical methods

2.3.1. Cyclic voltammetry (CV)

CV experiments were performed to evaluate the electroactivity of CCl_4 in aqueous media with a potentiostat/galvanostat PGP201 VoltaLab (Radiometer Analytical S.A.) in a three-electrode system. Either Pt (1 mm diameter) or glassy carbon (3 mm diameter) was employed as working electrode while a Pt wire was used as counter electrode. A saturated calomel electrode (SCE) was employed as reference electrode; therefore, all the voltage values given in the text are expressed in V/SCE, unless stated otherwise. Sodium sulfate (0.050 M) was used as electrolyte and the solutions were acidified to pH 3.0, the optimal EAOPs conditions. The CV experiments were performed in a voltage range of -3.0 V to +3.0 V and at a scan rate of 10 mV s^{-1} .

2.3.2. Hydrogen peroxide experiments and analysis

The oxidation power of H_2O_2 onto CCl_4 was evaluated by adding initially H_2O_2 in excess (100 mM) into CCl_4 (0.2 mM) aqueous solution before starting the experiments. The amount of H_2O_2 accumulated in bulk solution was determined by performing electrolysis experiments in the same conditions than EAOPs treatments, except that no Fe^{2+} was added to avoid Fenton's reaction to occur [37]. H_2O_2 was quantified by colorimetry using TiCl_4 [43]. The absorbance of the pertitanic acid complex formed was measured with a Perkin Elmer (USA) Lambda 10 UV-VIS spectrophotometer at a wavelength of 410 nm. An external calibration curve was obtained with standards of H_2O_2 , giving a molar extinction coefficient of around $935 \pm 2 \text{ L mol}^{-1} \text{ cm}^{-1}$. The H_2O_2 concentrations were then calculated according to the Beer-Lambert law.

2.3.3. Total organic carbon (TOC) measurements

TOC analyses were performed to quantify the mineralization degree during the different kind of treatments. The solution TOC values were determined by thermal catalytic oxidation (680

°C in presence of Pt catalyst) using a Shimadzu (Japan) V_{CSH} TOC analyzer. All samples were acidified to pH 2 with H₃PO₄ (25% w/w) to remove inorganic carbon. The injection volumes were 50 µL. Calibrations were performed by using potassium hydrogen phthalate solutions (50 mg C L⁻¹) as standard. All measured TOC values were given with a coefficient of variance below to 2%.

Mineralization yields (r_{min}) were considered equivalent to TOC removal percentage and can be determined according to the following Eq. 8:

$$r_{min}(\%) = \frac{(\Delta TOC)_t}{TOC_0} \times 100 \quad (8)$$

where $(\Delta TOC)_t$ is the difference between the initial TOC (TOC_0) and TOC at time t .

2.3.4. Ionic chromatography analysis

The inorganic ions released in the treated solutions were determined by ion chromatography using a Dionex ICS-1000 basic ion chromatography system (USA). The analysis of anions was monitored using an IonPac AS4A-SC (25 cm × 4 mm) anion-exchange column linked to an IonPac AG4A-SC (5 cm × 4 mm) column guard. The system was equipped with a DS6 conductivity detector containing a cell heated at 35 °C. The mobile phase contained 1.8 mM Na₂CO₃ and 1.7 mM NaHCO₃. The flow rate was set to 2 mL min⁻¹. The suppressor SRS (Self Regenerating Suppressor) needed to prevent the influence of the eluent ions in the detector signal was at a current of 30 mA.

2.3.5. Kinetic model for CCl₄ degradation

The decay rate of CCl₄ can be written as follow (Eq. 9):

$$\frac{d[CCl_4]}{dt} = -k_{CCl_4}[\cdot OH][CCl_4] \quad (9)$$

184 where $[CCl_4]$ is the concentration of CCl_4 , k_{CCl_4} is the decay rate constant of CCl_4 and $[\cdot OH]$
 185 is the concentration of $\cdot OH$ radical.

186 Considering that the degradation of one mole of CCl_4 produce four moles of Cl^- , the following
 187 equivalence of chemical rate can be obtained (Eq. 10):

$$188 \quad -\frac{d[CCl_4]}{dt} = +\frac{1}{4} \frac{d[Cl^-]}{dt} \quad (10)$$

189 By inserting Eq. 10 into Eq. 9, the Eq. 11 is given:

$$190 \quad \frac{d[Cl^-]}{dt} = 4k_{CCl_4}[\cdot OH][CCl_4] \quad (11)$$

191 By considering that $[Cl^-] = [CCl_4]_0 - [CCl_4]$, that $[CCl_4] = [CCl_4]_0 - [Cl^-]_{meas}$ and that
 192 $[Cl^-] = 4[Cl^-]_{meas}$, the following Eq. 12 is retrieved from Eq. 11:

$$193 \quad \frac{d[Cl^-]_{meas}}{dt} = k_{CCl_4}[\cdot OH]([CCl_4]_0 - [Cl^-]_{meas}) \quad (12)$$

194 where $[CCl_4]_0$ is the initial concentration of CCl_4 and $[Cl^-]_{meas}$ is the measured concentration
 195 of Cl^- released into the solution.

196 By considering the quasi-steady state approximation towards the $\cdot OH$ concentration evolution,
 197 a pseudo-first order kinetic model can be assumed [23]:

$$198 \quad \frac{d[Cl^-]_{meas}}{dt} = k_{app}([CCl_4]_0 - [Cl^-]_{meas}) \quad (13)$$

199 where $k_{app} = k_{CCl_4}[\cdot OH]$ is the apparent decay rate constant of CCl_4 oxidation by $\cdot OH$.

200 After integration of Eq. 13, the semi-logarithmic Eq. 14 is obtained:

$$201 \quad \ln\left(\frac{[CCl_4]_0}{[CCl_4]_0 - [Cl^-]_{meas}}\right) = \ln\left(\frac{[CCl_4]_0}{[CCl_4]_t}\right) = k_{app}t \quad (14)$$

202 where $[CCl_4]_t$ is the concentration of CCl_4 at time t .

203

3. RESULTS AND DISCUSSION

3.1. Evaluation of electroactivity of CCl₄

Before studying the possibility of CCl₄ degradation by $\cdot\text{OH}$ produced by EAOPs, it appeared important to preliminary verify the electroactivity of CCl₄ to check if it can be degraded by direct electron transfer at anode or cathode surface. Cyclic voltammetry (CV) have been therefore performed in voltage window ranging from -3 V to +3 V in Na₂SO₄ (0.050 M) solution at pH 3. Either platinum (Pt) or glassy carbon was used as working electrode, since both electrode materials were later employed in the EAOPs. As anticipated, neither electro-oxidation nor electro-reduction of CCl₄ occurred by using Pt as working electrode (Fig. 2A). Whatever the presence or not of CCl₄, no peak of current was observed except the oxidation of H₂O into O₂ (anode) and its reduction into H₂ (cathode). Employing vitreous carbon as working electrode further demonstrated the non-electroactivity of CCl₄ at the potential range studied (Fig. 2B). A difference was noticed between Pt and carbon electrode, since a cathodic peak, attributed to the formation of H₂O₂ (Eq. 15), was noticed at -0.6 V with the latter. This peak is expected because carbonaceous cathodes are well-known to promote the formation of H₂O₂ from 2-electron reduction of O₂ [44]:



To further investigate the oxidative inaction of H₂O₂ towards CCl₄, experiments were performed by initially spiking H₂O₂ in excess (100 mM) in a 0.2 mM CCl₄ aqueous solution in a hermetic seal batch reactor (Fig. 2C and Fig. 1). As expected H₂O₂ was not able to degrade CCl₄ as no Cl⁻ were released in solution while the total organic carbon (TOC) values remained unchanged along the experiment. The H₂O₂ concentration measurements depicted in Fig. 3 highlights the absence of H₂O₂ consumption during oxidation experiments with CCl₄, as it remained constant (around 100 ± 0.1 mM) all along the experiment. H₂O₂ is known to be

a relatively weak oxidant ($E^\circ(\text{H}_2\text{O}_2/\text{H}_2\text{O}) = 1.8 \text{ V/SHE}$) [45] that has relatively poor redox abilities which explain its unreliability to oxidize CCl_4 .

3.2. Degradation of CCl_4 by EAOPs

3.2.1. Role of BDD anode: production of heterogeneous $\cdot\text{OH}$

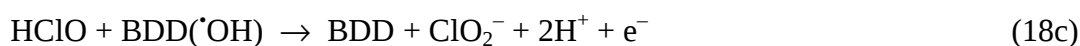
The performance of EAOPs to degrade CCl_4 (0.2 mM) has been tested. Guided by the hypothesis described in section 3.1 regarding the role of $\cdot\text{OH}$ in the CCl_4 degradation, an anodic oxidation (AO) experiment was first performed with a SS cathode and a BDD anode (AO-SS/BDD cell) in order to check this assumption (Fig. 4A). The experiments were performed in aqueous media, in absence of any other organic compound that could play a role of precursor for $\cdot\text{CCl}_3$ formation. Moreover, the electrolysis was carried out in dark conditions to avoid any photo-activity. To check whether H_2O_2 formation occurred at SS cathode, the accumulation of H_2O_2 in bulk solution during electrolysis using SS cathode and Pt anode has been performed and the results are represented in Fig. 5. It is shown that the H_2O_2 concentration could not reach higher value than 0.041 mM, which is very low. This is attributed to the SS material that do not favor the two electrons-oxygen reduction reaction (ORR) pathway to form H_2O_2 and will rather promote the four electron-ORR pathway that produce H_2O (Eq. 16) as previously stated [23,43]:

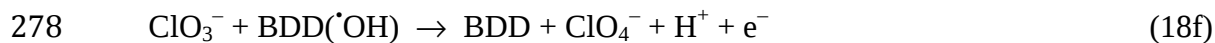
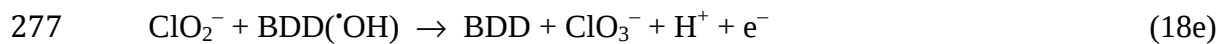


Therefore, the use of SS cathode limited the formation of H_2O_2 through O_2 reduction (Eq. 15) (Fig. 5) while the BDD anode ensured the heterogeneous generation of BDD($\cdot\text{OH}$) thanks to its high O_2 evolution overvoltage (2.3 V/SHE) [46,47].

Excitingly, Fig. 4A highlights the release of Cl^- ions into the solution by performing an AO-SS/BDD experiment. Upon control experiments results showing, as expected, the absence of

Cl^- ions in solution when no current intensity was applied, CCl_4 was successfully degraded by
 $\text{BDD}(\cdot\text{OH})$ generated in AO process. It can further be noticed that the amount of Cl^- formed
could not reach the maximal Cl^- theoretical concentration ($[\text{Cl}^-]_{\text{max,th}}$) that could be released.
In fact, the rate of chloride formation was in competition with the rate of its oxidation into Cl_2
as highlighted by the decrease of $[\text{Cl}^-]$ after 40 min of treatment (Fig. 4A). Indeed, Cl_2 react
quickly with H_2O to form HOCl [48] that undergoes further oxidation reactions to be
converted into chlorate (ClO_3^-) and perchlorate (ClO_4^-) at BDD surface as shown by ionic
chromatograms in Fig. 6. Thus, the chromatograms of anions evolution during EF treatment
with BDD anode at different treatment time (0 min, 20 min, 40 min, 60 min, 120 min, and
240 min) display Cl^- peaks at retention time around 1.3 min and major peaks of SO_4^{2-} at
retention time of 3.1 min. Interestingly, two more peaks could be distinguished at retention
times of 2.2 min and 7.4 min, respectively. These peaks are ascribed to chlorine oxyanions
such as ClO_3^- and ClO_4^- , respectively. These anions can be formed by Cl^- oxidation into Cl_2
gas at BDD anode due to its high oxidation ability with physisorbed $\cdot\text{OH}$ formed at its surface
($\text{BDD}(\cdot\text{OH})$) (Eqs. 17-18a). Cl_2 reacts quickly with H_2O to form the hypochlorous acid
(HClO) (Eq. 8b) in the bulk. Since the pH remained between 2.4 and 3.0 during the whole
electrolysis, HClO is the predominant species as compared to ClO^- knowing the acid
dissociation constant value of HClO ; $pK_a = 7.54$ (at 25 °C). HClO is then oxidized into ClO_2^-
(Eq. 18c) which is quickly oxidized into ClO_3^- (Eqs. 18d-18e) and then into ClO_4^- (Eq. 18f)
as end-product having the maximal oxidation state [49,50]:





Chlorite ion was not observed in the electrolysis with BDD because the high applied current density (35.7 mA cm⁻² as reported to the BDD anode surface area) favor the rapid oxidation of ClO₂⁻ into ClO₃⁻ as noticed previously [51], especially in BDD experiments performed at 30 mA cm⁻² [52].

As it can be seen at the detailed view of Cl⁻ peak evolution (Fig. 6B), a maximal peak area could be noticed at 20 min of electrolysis, while it started decreasing after longer treatment. At this time the peaks area of ClO₃⁻ increase until 60 min of treatment and start decreasing after electrolysis time longer than 120 min. In the meanwhile, peaks area of ClO₄⁻ start raising from 120 min until 240 min of treatment. The subsequent increase/decrease trends observed from Cl⁻ evolution concentration to ClO₃⁻ and then to ClO₄⁻ corroborated the reactions sequence (Eqs. 18a-18e).

In addition, the chromatogram of SO₄²⁻ (Fig. 6C) highlights a slight decrease of SO₄²⁻ peak right after the starting of the EF-CF/BDD treatment, corresponding to a SO₄²⁻ concentration decrease from 50 mM to 47.1 ± 0.9 mM. This is attributed to the reaction of SO₄²⁻ with high reactive BDD surface producing sulfate radical (SO₄^{•-}) (Eq. 19a) and persulfate (S₂O₈²⁻) (Eq. 19b) as previously stated [53,54].



The oxidation power of SO₄^{•-} and S₂O₈²⁻ are lower than that of the [•]OH, with standard reduction potentials of 2.6 and 2.01 V/SHE, respectively [23]. It has been previously demonstrated that SO₄^{•-} radical could not react with CCl₄, since it was found as one of the end-

product during oxidation of chlorinated phenol by $\text{SO}_4^\bullet$ radical [55]. It means that $\text{OH}^\bullet$ is the only species responsible for the oxidation of CCl_4 .

It is important to note that the same trends were observed with all BDD experiments (AO-SS/BDD, AO-CF/BDD and EF-CF/BDD) as these phenomenon depends on the use of BDD anode material itself.

3.2.2. Influence of CF cathode: production of homogeneous $\text{OH}^\bullet$ by peroxone reaction

Interestingly, when a CF cathode was employed (AO-CF/BDD cell), the concentration of Cl^- released could reach $[\text{Cl}^-]_{\text{max,th}}$ (0.8 mM), highlighting a better degradation of CCl_4 (Fig. 4A). To better understand this behavior, the accumulation of H_2O_2 in bulk solution during electrolysis using CF cathode and Pt anode is represented in Fig. 7. It was first noticed a transient phase followed by a steady state. This phenomenon is typical in undivided cell study and is referred to the competition reactions between H_2O_2 electrogeneration and H_2O_2 decomposition at the anode (Eqs. 20a-20b), at the cathode (Eq. 21) and in a lesser extent decomposition in bulk solution (Eq. 22) as stated previously by numerous authors [23]:



It was further emphasized that in presence of CF cathode the maximal amount of H_2O_2 accumulated in bulk solution was 1 mM, which was 24 times higher than with SS cathode. It was attributed to the nature of cathode material itself and to its surface area. Indeed, carbon-based cathodes have high H_2 evolution overpotential and low catalytic activity for H_2O_2 decomposition. Moreover, CF has a 3D porous structure that dramatically increases its

specific surface area as compared to the SS material employed. This property makes increase the number of active sites for O₂ adsorption before its subsequent reduction into H₂O₂. Therefore, the enhancement obtained with AO-CF/BDD cell as compared to AO-SS/BDD cell could be due to the additional source of [•]OH formed by peroxone reaction between H₂O₂ electrogenerated at CF cathode and O₃ produced at the anode surface (Eq. 23) [56], as previously shown in several studies performed in similar electrolysis conditions [57–59], thus confirming the role of [•]OH in the degradation process.



Indeed the high oxidation power of BDD anode allows also generating O₃ from water oxidation at its surface (Eq. 24) [49].



It is worthy to specify that O₃ itself is a moderately strong oxidant ($E^\circ(\text{O}_3/\text{O}_2) = 2.1 \text{ V/SHE}$) [45] compared to [•]OH and has no direct oxidation effect on CCl₄ as stated by a previous study [19].

3.2.3. Role of iron catalyst: production of homogeneous [•]OH by Fenton reaction

The addition of Fe²⁺ (0.1 mM) in order to produce [•]OH through Fenton's reaction (Eq. 25) [23] was further investigated by performing electro-Fenton (EF) treatment with CF cathode and BDD anode (EF-CF/BDD cell).



The presence of ferrous ion could even enhance better the degradation of CCl₄ by reaching faster $[\text{Cl}^-]_{\text{max,th}}$ value as seen in Fig. 4A.

This enhancement in CCl₄ degradation rate is due to the formation of homogeneous [•]OH formed in bulk solution that react directly with CCl₄, in addition to BDD([•]OH) formed at anode surface. In this process, Fenton's reaction (Eq. 25) is electrocatalyzed by continuous regeneration of Fe²⁺ (catalyst) from electro-reduction of Fe³⁺ ions (Eq. 26) formed by Fenton's reaction [48]:



The difference of efficiency between AO-CF/BDD and EF-CF/BDD experiments was therefore mainly attributed to the action of supplementary [•]OH generated in the bulk solution by Fenton reaction (Eq. 25).

Furthermore, when Pt was used as anode instead of BDD in EF process (EF-CF/Pt cell), the dechlorination rate and yield were higher compared with AO-SS/BDD cell (Fig. 4A). It was also noticed that a plateau of Cl⁻ concentration was observed in EF-CF/Pt cell experiment, highlighting the accumulation of Cl⁻ in the solution. In order to better understand this evolution, the chromatograms of anions evolution during EF treatment with Pt anode at different treatment time (0 min, 5 min, 10 min, 20 min, 40 min, 60 min, 120 min, 180 min, 240 min) have been recorded and are represented in Fig. 8. Fig. 8A displays Cl⁻ peaks at retention time around 1.3 min and major peaks of SO₄²⁻ from the supporting electrolyte (Na₂SO₄) at retention time of 3.1 min, as observed with BDD anode electrolysis. To have a better view of the Cl⁻ chromatograms, an enlarged picture allows observing the evolution of Cl⁻ peaks area and height in Fig. 8B. From 0 min to 40 min of EF treatment, it is clearly seen an increase of peak area, meaning that CCl₄ is progressively degraded into Cl⁻. After 40 min of treatment the peaks area barely change, because at this time, the concentration of Cl⁻ has reached its theoretical level value (0.8 mM). Moreover, no other peak could be observed on the chromatogram whatever the time of treatment, meaning that chloride ions could not be

further oxidized into Cl₂, chlorate, perchlorate species on the contrary to BDD experiments. It is also interesting to note that the peaks area of SO₄²⁻ remain the same (50 ± 0.1 mM) whatever the treatment time (Fig. 8C), which underlines that the electrolyte stayed unreactive during the treatment, unlike with BDD treatments. This is in accordance with the low oxidation power of Pt that has a low O₂ evolution overvoltage (1.6 V/SHE) [60]. In this case, [•]OH at Pt surface (Pt([•]OH)) is chemisorbed and O₂ evolution is the main reaction (Eqs. 27a-27b) [47]:



In addition, [Cl⁻]_{max,th} (0.8 mM) was reached only after 120 min against around 20 min with AO-CF/BDD and EF-CF/BDD cells. The superiority of AO-CF/BDD cell over EF-CF/Pt cell was attributed to the higher oxidation power of BDD and to the second source of [•]OH from peroxone reaction as discussed in section 3.2.2.

Thus, the only source of [•]OH was coming from the electro-Fenton process through Fenton's reaction in EF-CF/Pt cell. It further emphasized the primary role of homogeneous [•]OH formed by Fenton's reaction as compared to heterogeneous [•]OH formed at BDD surface in AO-SS/BDD cell, because in such diluted solution the electrolysis is controlled by mass transfer rate.

3.2.4. Quantitative comparison between oxidation mechanisms with kinetic rate constants

In order to compare quantitatively each applied condition, a kinetic model has been established (section 2.3.5). The kinetic rate constants of CCl₄ degradation (*k*_{app}) have been

determined considering a pseudo-first order kinetics for the reaction between CCl_4 and $\cdot\text{OH}$ by assuming a quasi-stationary state for $\cdot\text{OH}$ concentration.

Based on Eq. 14, a linear regression allowed determining k_{app} values from the slope of the straight lines (Fig. 4B) that were ranked as follow: AO-SS/BDD ($0.004 \pm 0.001 \text{ min}^{-1}$) < EF-CF/Pt ($0.072 \pm 0.003 \text{ min}^{-1}$) < AO-CF/BDD ($0.171 \pm 0.002 \text{ min}^{-1}$) < EF-CF/BDD ($0.298 \pm 0.001 \text{ min}^{-1}$). All correlation coefficient (R^2) were higher than 0.989, highlighting the good fitting between experimental data and the pseudo-first order kinetic model. This rank was corroborating the dechlorination results. It highlights again the primary role of BDD($\cdot\text{OH}$) / $\cdot\text{OH}$ while EF-CF/BDD depicted more than 4 times quicker degradation kinetics due to the three sources of hydroxyl radicals generation (e.g. Fenton, peroxone and anodic oxidation mechanisms co-contributions).

3.3. Mineralization of CCl_4 by EAOPs

The mineralization of CCl_4 was evaluated by monitoring the TOC in the same experimental conditions, e.g. AO-SS/BDD, AO-CF/BDD, EF-CF/BDD and EF-CF/Pt cells (Fig. 9). After 8 h of electrolysis, the following mineralization rank was obtained: AO-SS/BDD ($24 \pm 1.2 \%$) < EF-CF/Pt ($55 \pm 1.8 \%$) < AO-CF/BDD ($74 \pm 0.9 \%$) < EF-CF/BDD ($82 \pm 1.4 \%$) (Fig. 9A). In addition, by assuming a pseudo-first order kinetic model for TOC decay [61], the same rank was noticed: AO-SS/BDD ($0.123 \pm 0.011 \text{ h}^{-1}$) < EF-CF/Pt ($0.220 \pm 0.013 \text{ h}^{-1}$) < AO-CF/BDD ($0.772 \pm 0.012 \text{ h}^{-1}$) < EF-CF/BDD ($0.806 \pm 0.010 \text{ h}^{-1}$) (Fig. 9B). All correlation coefficient (R^2) values were higher than 0.989, highlighting again the good fitting between experimental data and the pseudo-first order kinetic model.

Knowing that the control experiment has shown negligible TOC removal (2% in 8 h-electrolysis), we could first conclude that CCl_4 was successfully mineralized even with AO-

SS/BDD giving the lower production of $\cdot\text{OH}$ as mentioned previously. Moreover, these ranks of mineralization efficiency were corroborating the degradation kinetics results, demonstrating again the superiority of EF-CF/BDD.

3.4. Proposed reaction pathway

Based on the above finding a reaction pathway for $\cdot\text{OH}$ action on CCl_4 is proposed (Fig. 10A). For the sake of simplicity, hydroxyl radicals were presented by $\cdot\text{OH}$ without making explicit the O-H bond. First, the presence of Cl atom favors the formation of a dipole between $\text{C}(\delta^+)$ and $\text{Cl}(\delta^-)$, atoms due to the higher electronegativity of Cl (3.16) compared to C (2.55) according to Pauling scale. Being a strong electrophilic species, $\cdot\text{OH}$ reacts by ipso-substitution on the C atom (Eq. 28a) leading to the subsequent formation of trichloromethanol (CCl_3OH) (Eq. 28b). Trichloromethanol is then decomposed in water into phosgene (CCl_2O) (Eq. 29) [62]. Finally CCl_2O is quickly hydrolyzed in water by forming CO_2 , Cl^- and H^+ (Eq. 30) [63].



Taking into account these considerations, a reaction pathway was therefore proposed for complete degradation of CCl_4 until mineralization, leading to a new attack mode of $\cdot\text{OH}$ (Fig. 10B). Over the existing attack $\cdot\text{OH}$ modes, e.g. dehydrogenation, hydroxylation and electron transfer [6,64], a fourth mode, namely “**ipso-substitution**” is proposed. It generally consists of the oxidation of perhalogenocarbon compounds (C_xX_y) into trihalo-alcohol ($\text{C}_x\text{X}_{y-1}\text{OH}$) in

a first step. Furthermore, it has been observed a slight continuous decrease of pH during the EAOPs treatments from an initial pH of 3.0 to a final pH of around 2.4 ± 0.2 after 8 h electrolysis with a standard deviation of 0.2 which is due to the kind of applied treatment. This is an evidence of the accumulation of protons formed through the mechanism proposed.

4. CONCLUSIONS

In summary, the treatment of CCl_4 in aqueous solution with EAOPs has been investigated for the first time. Upon successful degradation and mineralization of CCl_4 with the unique presence of $\cdot\text{OH}$ produced by anodic oxidation a new attack mode of $\cdot\text{OH}$ was proposed on perhalogenocarbon compounds by ipso-substitution of halogen atom with $\cdot\text{OH}$. The decrease of pH during the electrolysis corroborated the proposed mechanism. The use of electro-Fenton process enhanced significantly the removal efficiency due to generation of supplementary $\cdot\text{OH}$ in the bulk solution.

This fourth oxidation pathway of $\cdot\text{OH}$ should be considered in other areas of research such as in atmospheric studies as some of these perhalogenocarbons are known to be volatile and can be subjected to $\cdot\text{OH}$ reactions.

Furthermore, this new finding opens up many opportunities in environmental protection by offering possibilities of degrading and mineralizing such recalcitrant perhalogenocarbons compounds that are used as solvents, refrigerant, aerosol propellant and representing an environmental issue, such as carbon tetrafluoride, hexafluoroethane, carbon tetrachloride, hexachloroethane, perfluorohexane, and so on, but also cyclic perfluoroalkanes like perfluorooctane, perfluoro-1,3-dimethylcyclohexane and perfluorodecalin. More recently fluorosurfactants such as perfluorooctanesulfonic acid, perfluorononanoic acid and perfluorooctanoic acid have been found into the environment and especially into water

464 bodies. They are employed by some textile companies in emulsion polymerization process to
465 produce fluoropolymers but they have caught recently the attention of regulatory agencies has
466 they are persistent in the environment, toxic and bioaccumulate in the food chain.

467 In short, this study highlights that perhalogenocarbons compounds should be considered to be
468 eliminated by $\cdot\text{OH}$ generated in EAOPs.

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648
649

FIGURE CAPTIONS

Fig. 1. Reactor set-up for H₂O₂ oxidation and electrolysis experiments.

Fig. 2. Evaluation of CCl₄ electroactivity and reactivity with H₂O₂. (A), cyclic voltamogrammes in absence or presence of CCl₄ with Pt working electrode (Pt counter electrode); (B), cyclic voltamogrammes in absence or presence of CCl₄ with glassy carbon working electrode (Pt counter electrode), (C), oxidative treatment of CCl₄ with hydrogen peroxide.

Fig. 3. Hydrogen peroxide concentration evolution during spiking experiment.

Fig. 4. Degradation of CCl₄ by AO and EF treatments using different cathodes and anodes. (A), chloride concentration ([Cl⁻]) evolution normalized by the maximal theoretical Cl⁻ concentration ([Cl⁻]_{max,th}) and (B), determination of the apparent rate constants for CCl₄ decay assuming a pseudo-first order kinetic model (SI, Eq. 15). EF, electro-Fenton; AO, anodic oxidation; CF, carbon felt; SS, stainless steel; BDD, boron-doped diamond.

Fig. 5. Hydrogen peroxide accumulation using SS cathode and Pt anode. Conditions: $I = 1000$ mA, [Na₂SO₄] = 50 mM, V = 200 mL, pH 3.

Fig. 6. Chromatograms of anions evolution during EF treatments of CCl₄ with BDD anode (EF-CF-BDD) at different treatment time (0 min, 20 min, 40 min, 60 min, 120 min, 240 min). (A), ionic chromatograms. (B), Cl⁻ peaks evolution. (C), SO₄²⁻ peaks evolution. Conditions: $I = 1000$ mA, [Na₂SO₄] = 50 mM, [Fe²⁺] = 0.05 mM, V = 200 mL, pH 3.

Fig. 7. Hydrogen peroxide accumulation using CF cathode and Pt anode. Conditions: $I = 1000$ mA, [Na₂SO₄] = 50 mM, V = 200 mL, pH 3.

Fig. 8. Chromatograms of anions evolution during electro-Fenton treatments of CCl₄ with Pt anode (EF-CF/Pt) at different treatment time (0 min, 5 min, 10 min, 20 min, 40 min, 60 min, 120 min, 180 min, 240 min). (A), ionic chromatograms. (B), Cl⁻ peaks evolution. (C), SO₄²⁻ peaks evolution. Conditions: $I = 1000$ mA, $[\text{Na}_2\text{SO}_4] = 50$ mM, $[\text{Fe}^{2+}] = 0.05$ mM, $V = 200$ mL, pH 3.

Fig. 9. Mineralization of CCl₄ by anodic oxidation and electro-Fenton treatments using different cathodes and anodes. (A), normalized TOC evolution by the initial TOC. (B), determination of the TOC decay rate constants assuming a pseudo-first order kinetic model. EF, electro-Fenton; AO, anodic oxidation; CF, carbon felt; SS, stainless steel; BDD, boron-doped diamond.

Fig. 10. Pathways of organic compounds oxidation by [•]OH. (A), CCl₄ oxidation by ipso-substitution with [•]OH. (B), schematic description of the four attack modes of [•]OH with organic compounds. RH, alkane; ArH, aromatic; C_xX_y, perhalogenocarbon compounds.

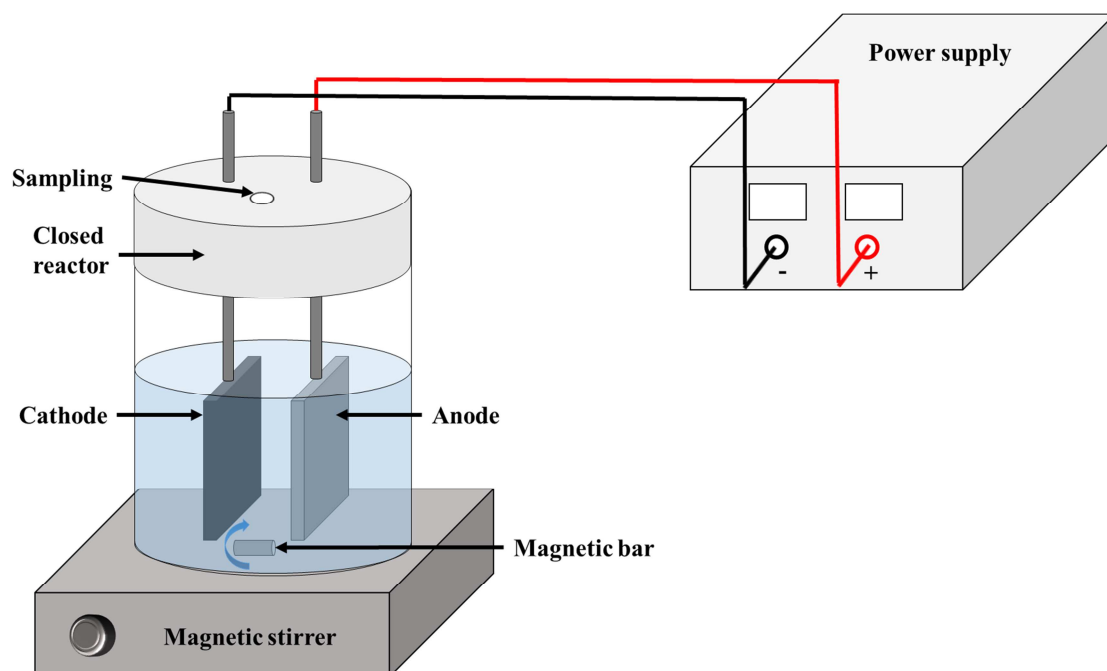


Fig. 1

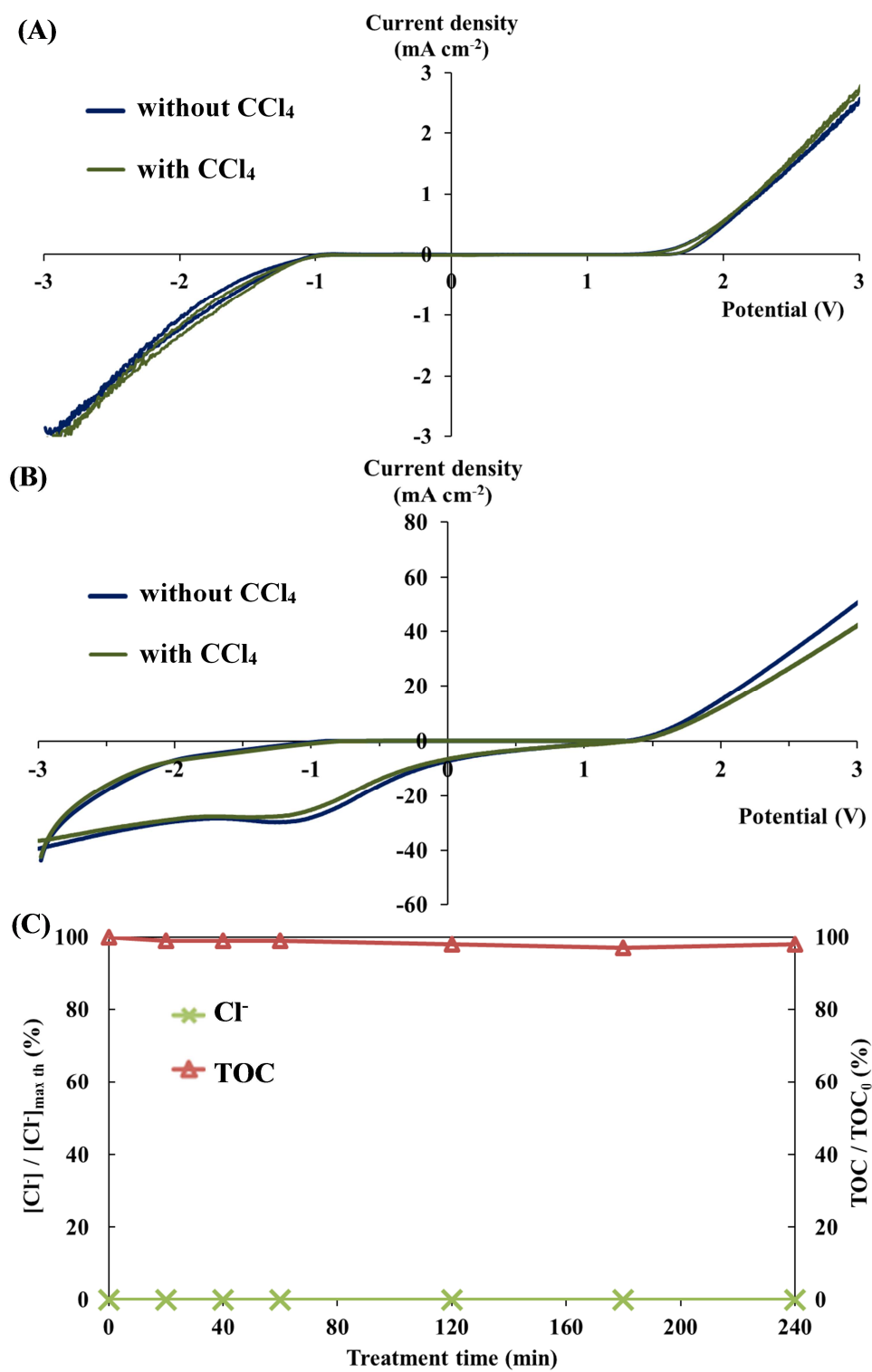


Fig. 2

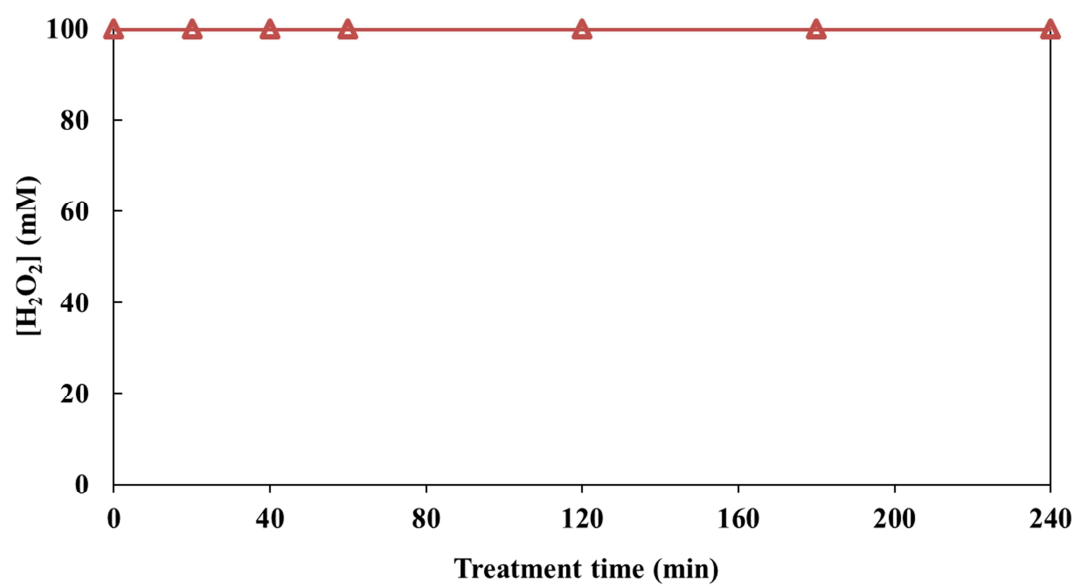


Fig. 3

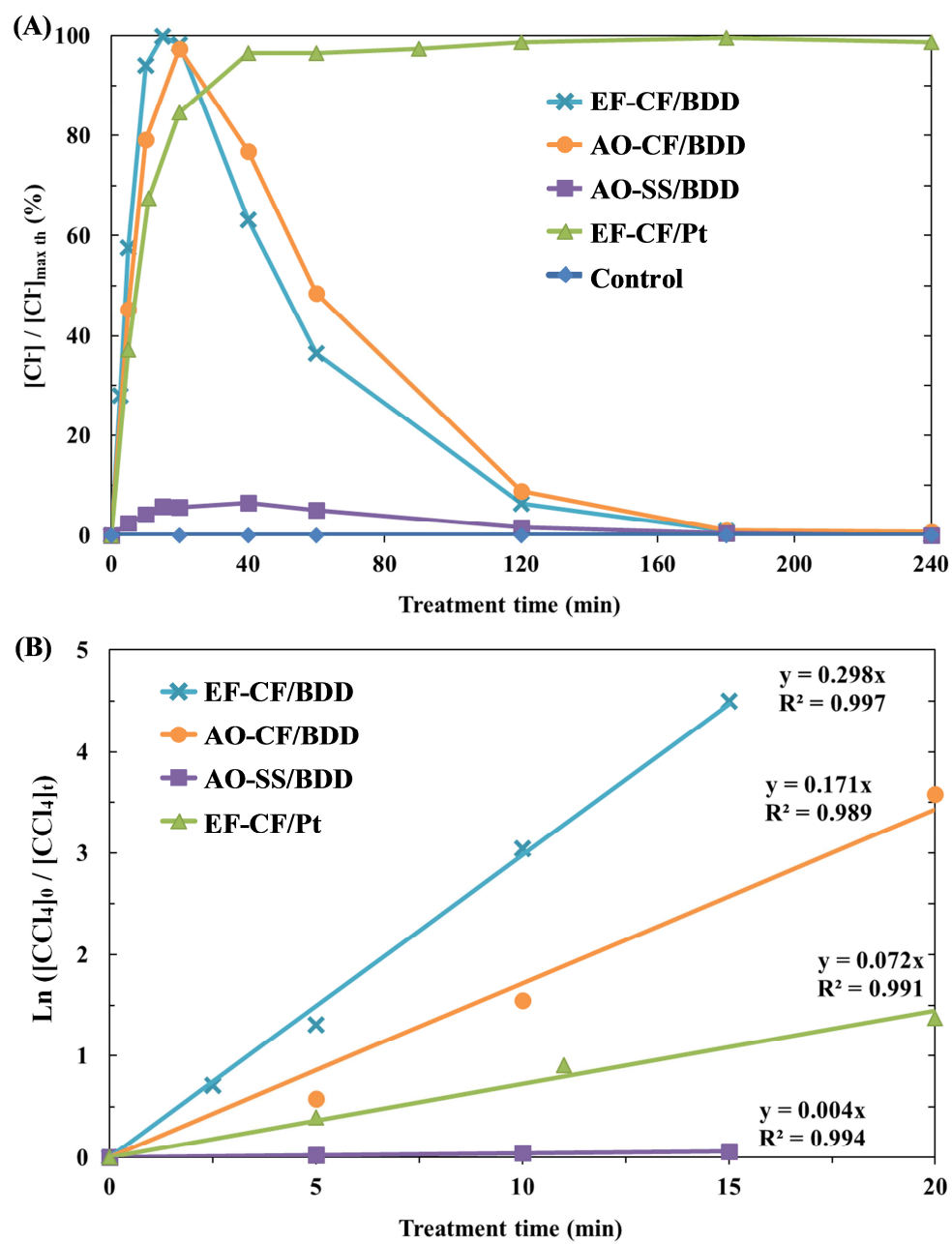


Fig. 4

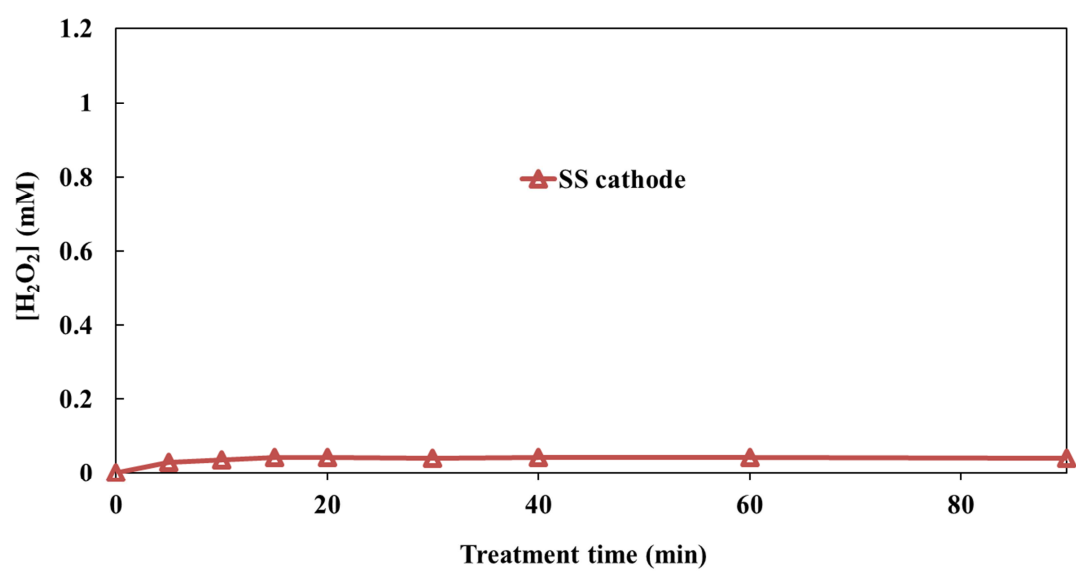


Fig. 5

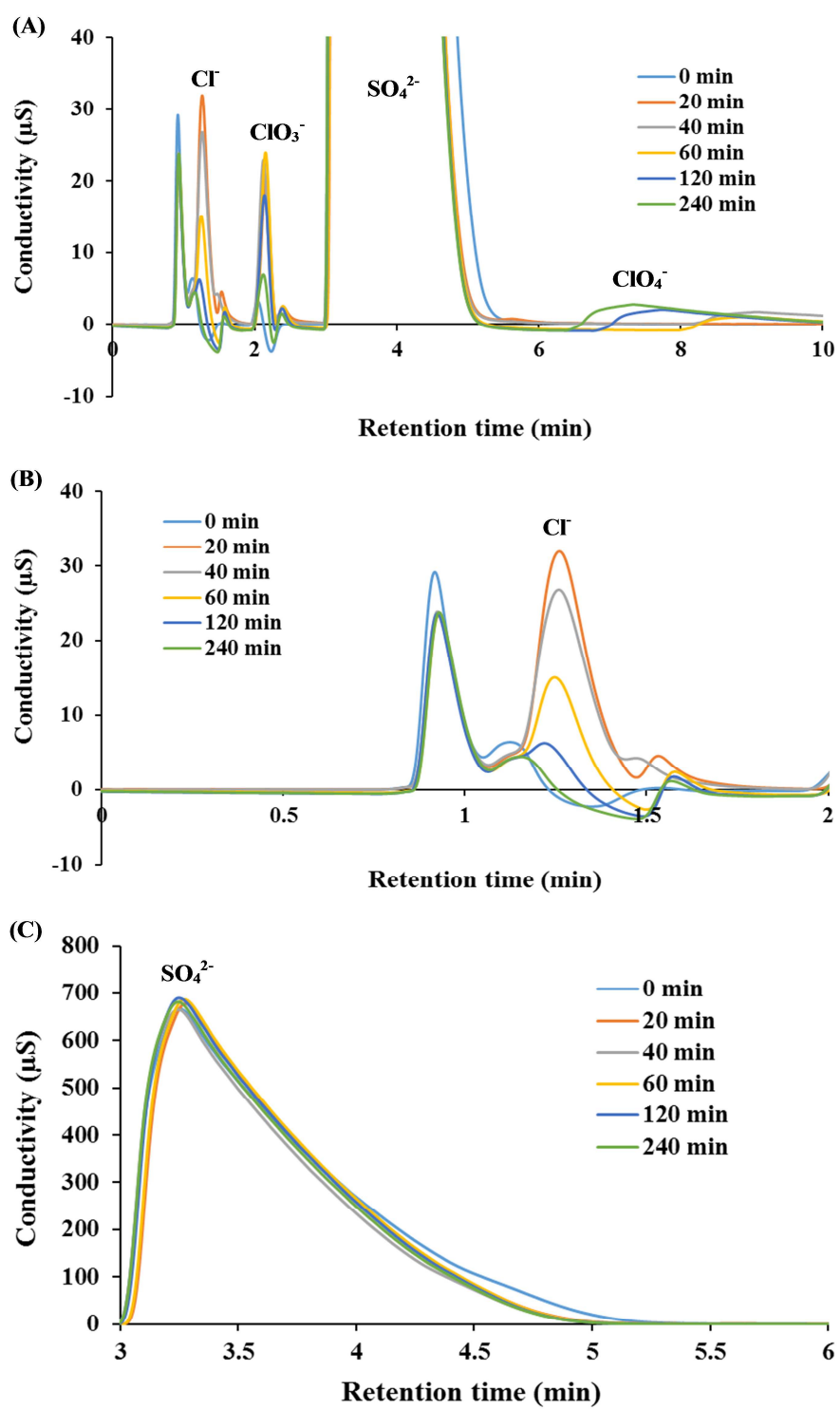


Fig. 6

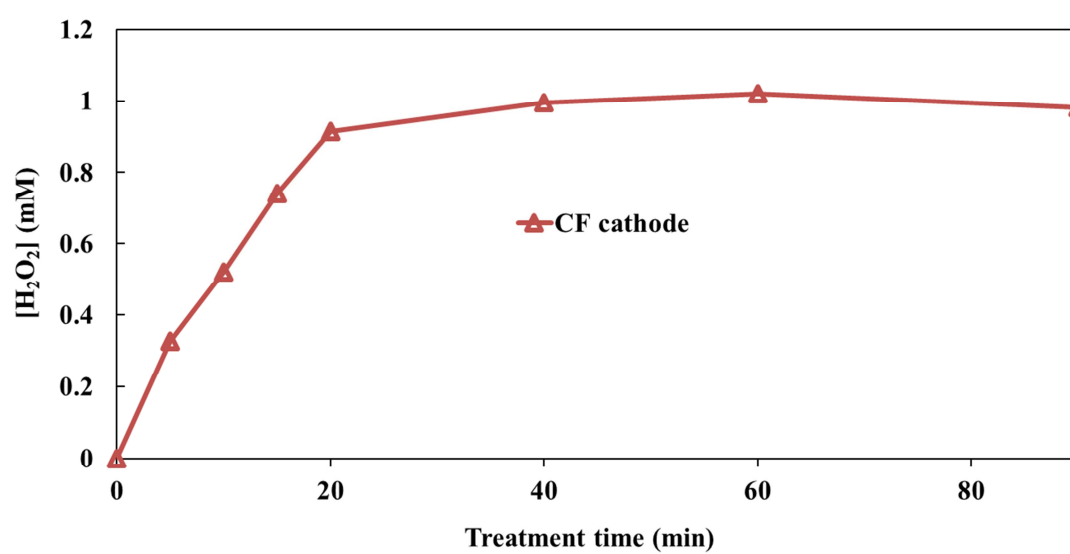


Fig. 7

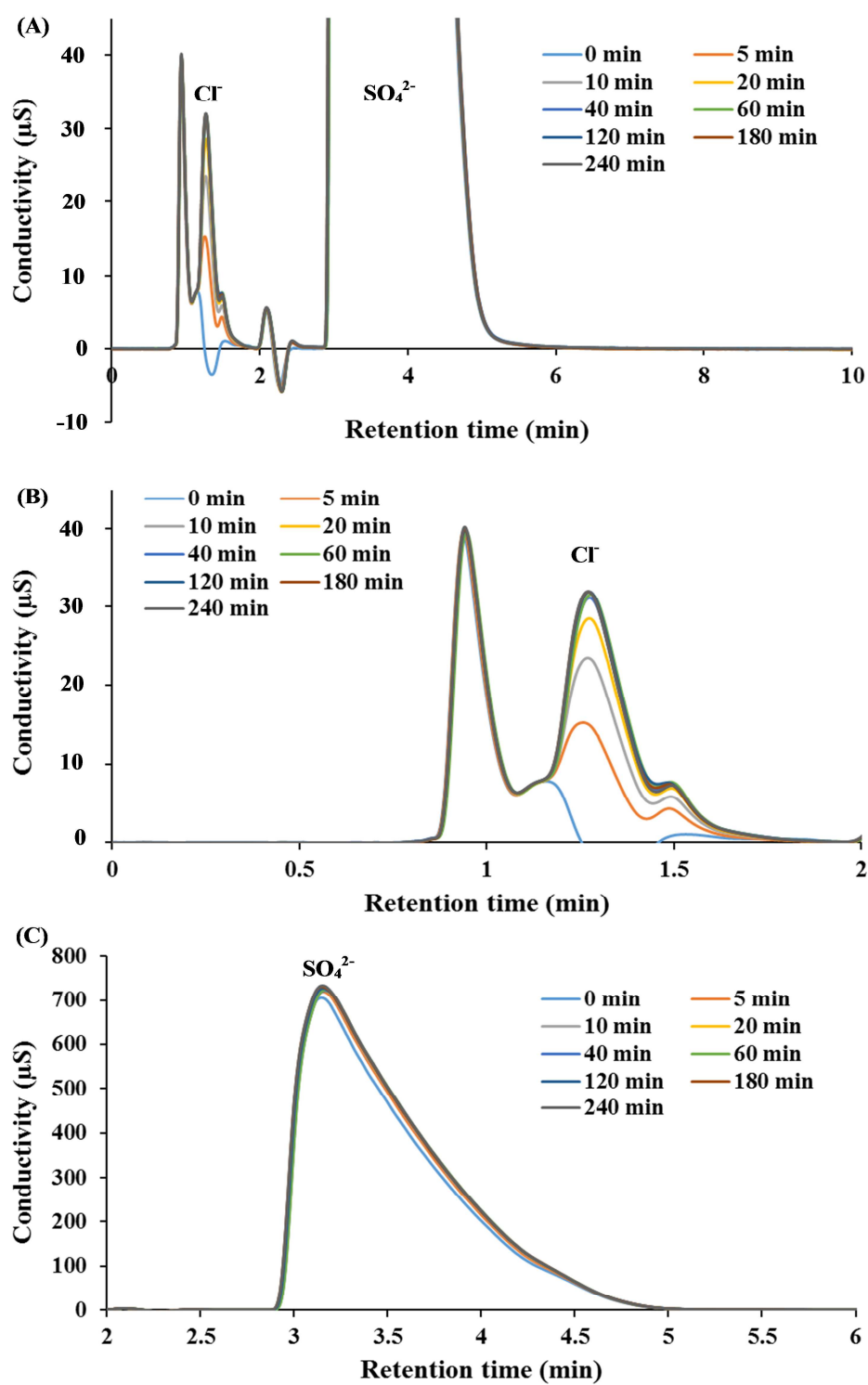


Fig. 8

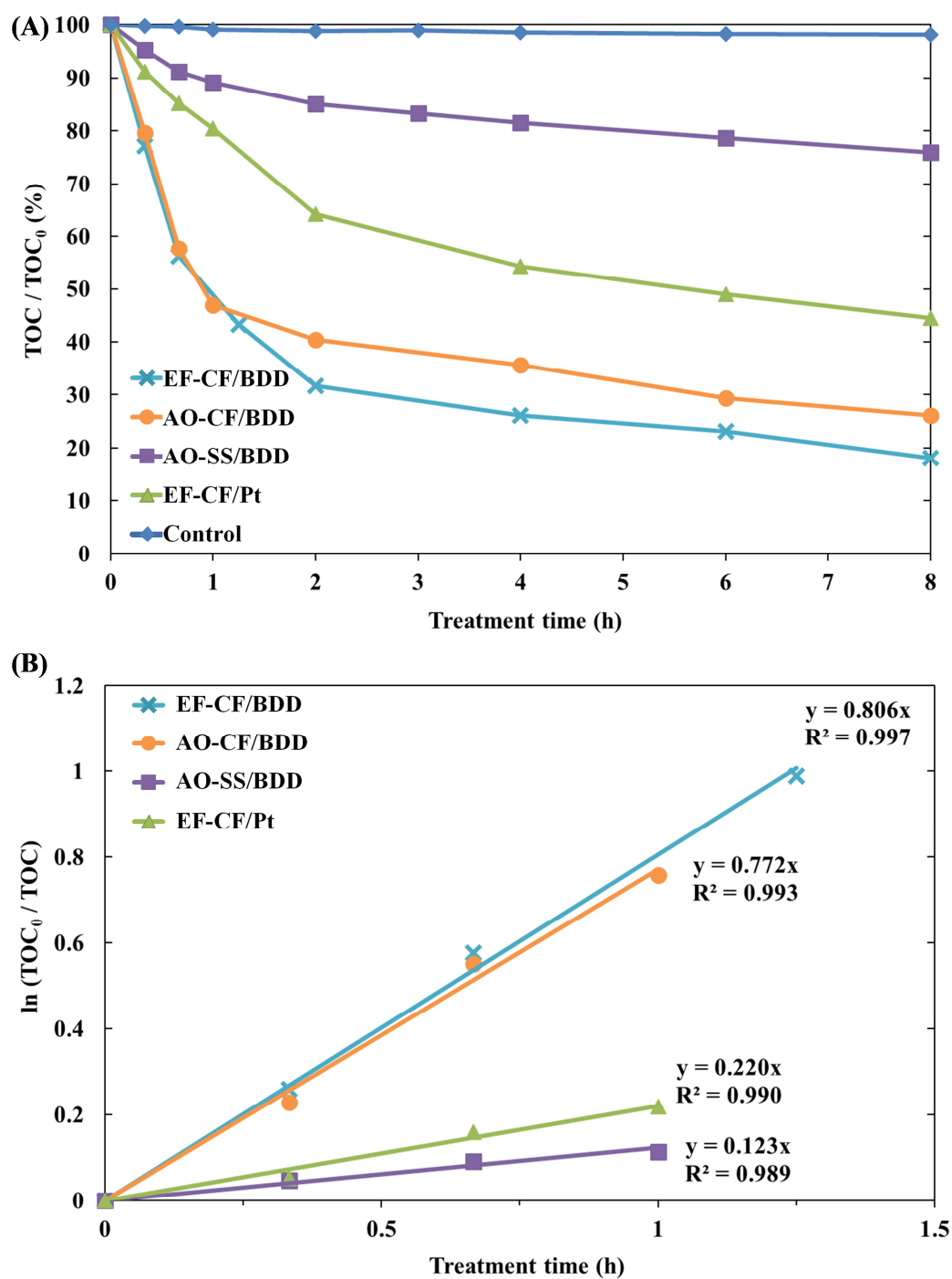
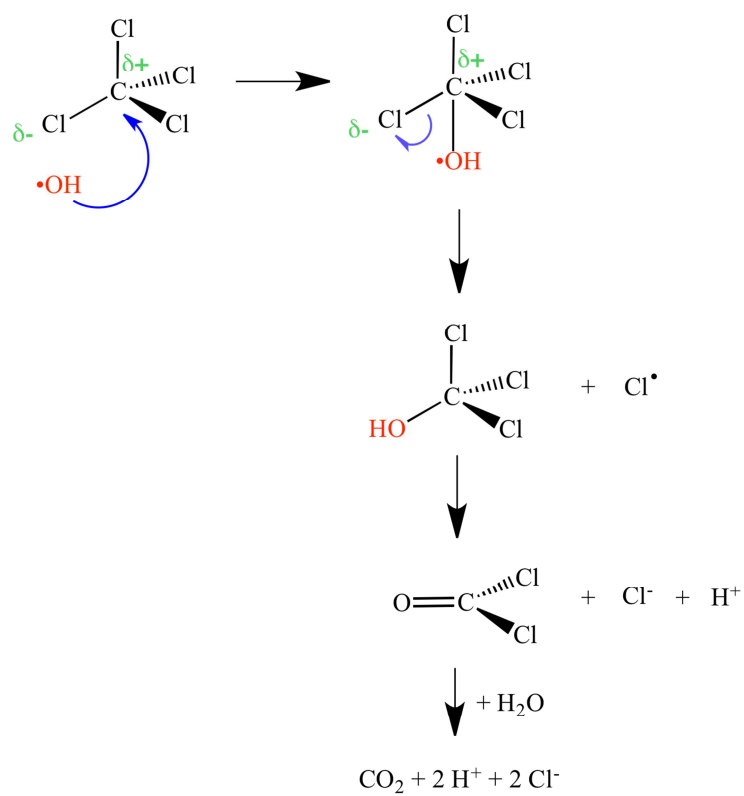


Fig. 9

(A)



(B)

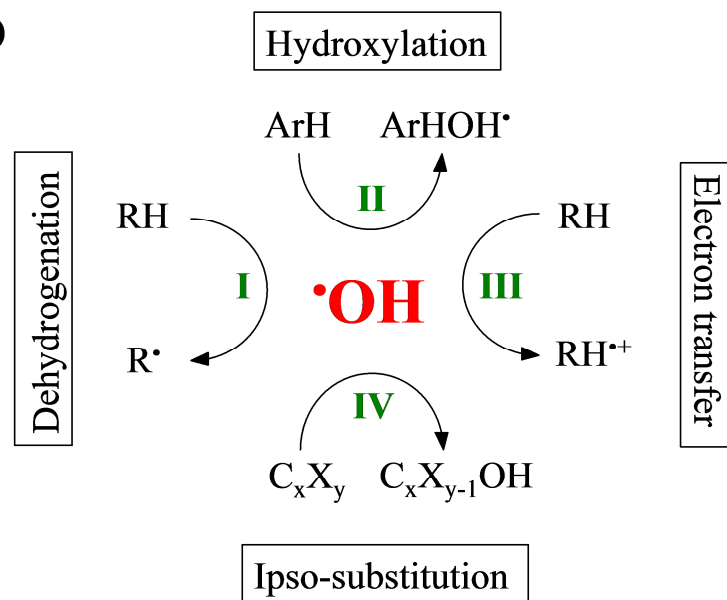


Fig. 10