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Jingju Cai, Minghua Zhou, Ye Liu, André Savall, Karine Groenen Serrano. Indirect electrochemical oxidation of 2,4-dichlorophenoxyacetic acid using electrochemically-generated persulfate. *Chemosphere*, 2018, 204, pp.163-169. 10.1016/j.chemosphere.2018.04.004 . hal-01949849

**HAL Id: hal-01949849**

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Cai, Jingju and Zhou, Minghua and Liu, Ye<sup>ORCID</sup> and Savall, André<sup>ORCID</sup> and Groenen Serrano, Karine<sup>ORCID</sup> *Indirect electrochemical oxidation of 2,4-dichlorophenoxyacetic acid using electrochemically-generated persulfate.* (2018) *Chemosphere*, 204. 163-169. ISSN 0045-6535

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# Indirect electrochemical oxidation of 2,4-dichlorophenoxyacetic acid using electrochemically-generated persulfate

Jingju Cai <sup>a</sup>, Minghua Zhou <sup>a,\*</sup>, Ye Liu <sup>b</sup>, André Savall <sup>b</sup>, Karine Groenen Serrano <sup>b,\*</sup>

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## H I G H L I G H T S

- 2,4 D can be removed by indirect electrochemical oxidation using persulfate.
- Above 20 °C the decomposition of persulfate occurs during the electrosynthesis of this latter.
- The current efficiency decreases from 96% to 52% with an increase in  $j$  from 5 to 100 mA cm<sup>-2</sup>.
- 2,4 D disappearance follows a first order reaction with a constant rate of 0.22 min<sup>-1</sup>.

## A R T I C L E I N F O

### Keywords:

Boron-doped diamond anode  
Electrochemical oxidation  
Sulfate radical  
Persulfate  
2,4-Dichlorophenoxyacetic acid

## A B S T R A C T

This research investigated persulfate electrosynthesis using a boron doped diamond anode and a chemical reaction of persulfate in its activated form with an herbicide, 2,4 Dichlorophenoxyacetic acid (2,4 D). The first part of this research is dedicated to the influence of the applied current density on the electrosynthesis of persulfate. The first part shows that for a 2 M sulfuric acid, the current efficiency reached 96% for 5 mA/cm<sup>2</sup> and dropped to 52% for a higher current density (100 mA cm<sup>-2</sup>). This fall cannot be explained by mass transfer limitations: an increase in temperature (from 9 to 30 °C) during electrolysis leads to the decomposition of 23% of the persulfate. The second part of this research shows that a quasi complete degradation of the target herbicide can be reached under controlled operating conditions: (i) a high ratio of initial concentrations [Persulfate]/[2,4 D], (ii) a minimum temperature of 60 °C that produces sulfate radicals by heat decomposition of persulfate, and (iii) a sufficient contact time between reactants is required under dynamic conditions.

## 1. Introduction

2,4 dichlorophenoxyacetic acid (2,4 D) is one of the oldest and most widely available herbicides in the world; it has been used since 1945 for the selective control of weeds in gardens and farming. 2,4 D was classified as “possibly carcinogenic to humans, based on inadequate evidence in humans and limited evidence in experimental animals” by the International Agency for Research on Cancer of the World Health Organization (IARC, 2015). In addition, this compound is poorly biodegradable and cannot be decomposed at concentrations higher than 1 mg L<sup>-1</sup> (Hoover et al., 1986).

Pesticide discharges from manufacturing plants, storage sites, accidental spills, and surface runoff may result in the contamination of the aqueous environment. Thus, it is necessary to treat wastewater at source before releasing it into the natural environment. Conventional biological treatment systems (e.g. activated sludge), considered as a cost effective and an environmentally sustainable process, have shown limited success in removing potentially toxic pesticides (Hill et al., 1986; Mangat and Elefsiniotis, 1999).

Among emerging advanced oxidation processes, electrochemical advanced processes, such as electro Fenton (EF) and photoelectro Fenton, have been studied (Brillas et al., 2003; Badellino et al., 2006).

Brillas et al. (2003) have shown that the complete mineralization of 2,4 D can be reached by EF and a general reaction pathway involving all stable intermediates, such as chloro organics, has

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been presented. Oturan (2000) estimated the electrical consumption as 4 kC to mineralize 1 mg of 2,4 D using the electro Fenton process; this high consumption is explained by the fact that the current efficiency sharply decreases during the process from 40% at 40 min (corresponding to 0.5 kC) to 27% at 280 min (corresponding to 1 kC). With the aim of increasing the biodegradability of 2,4 D, Fontmorin et al. (2012) studied the electrochemical pretreatment prior to a biological process. Using a carbon felt as the anode, the quasi complete disappearance of 2,4 D was observed, but only 34% was mineralized. The major issue was the improvement of the biodegradability evaluated through the BOD<sub>5</sub>/COD ratio from 0.04 to 0.25. In addition, electrochemistry can be used for the reductive dechlorination of 2,4 D (Chunan et al., 2009). To reduce such compounds in this way, it is necessary to modify the electrode surface using catalysts, such as palladium or silver. The dechlorination of 2,4 D to phenoxyacetic acid with 78% of current efficiency has been reached using a palladized silver electrode.

In the light of their extraordinary electrochemical properties, the boron doped diamond (BDD) electrodes enable the generation of  $\cdot\text{OH}$  by the electrochemical oxidation of water. The hydroxyl radicals which are physisorbed on the BDD electrode are very reactive and non selective on organics. Because the half life of hydroxyl radicals is very low ( $10^{-9}$  s in water), their action takes place exclusively next to the anode. Consequently, the kinetics of the process is limited by mass transfer, in particular in the case of 2,4 D, which has a low solubility (4 mM). One way to overcome mass transfer limitations is to generate, on the BDD anode, sufficiently strong, stable oxidants, such as peroxy compounds (peroxosulfates, peroxophosphates, peroxocarbonates, etc.) or oxo compounds (ferrate, permanganate, etc.) (Groenen Serrano, 2014). Then, such reactants can diffuse in the solution to react with the organics.

Specifically, persulfate,  $\text{S}_2\text{O}_8^{2-}$ , is a strong oxidizing agent, stable in solutions at ambient temperatures (redox potential 2.1 V/SHE), and can oxidize several organics (Neta et al., 1977). A previous study showed that high current efficiency (95%) for electrosynthesis of peroxodisulfuric acid can be achieved using a BDD anode in concentrated  $\text{H}_2\text{SO}_4$  (>2 M) for moderate temperatures (8–10 °C) (Serrano et al., 2002). The electrosynthesized persulfate can be activated by metal reactions or by supplying energy (heat, UV, etc.) and enables the formation of sulfate radicals (Eq. (1)).



Thermodynamically,  $\text{SO}_4^{\cdot-}$  ( $E^\circ = 2.6 \text{ V/SHE}$ ) is a stronger oxidant than  $\text{S}_2\text{O}_8^{2-}$  ( $E^\circ = 2.01 \text{ V/SHE}$ ).  $\text{SO}_4^{\cdot-}$  can selectively and rapidly react with organics with constant rate values of  $10^9$ – $10^{10} \text{ M}^{-1} \text{ s}^{-1}$  (Neta et al., 1977), while the reaction of  $\text{S}_2\text{O}_8^{2-}$  with many organics is kinetically slow (Osgerby, 2006). Costanza et al. (2010) have studied the oxidation of tetrachloroethylene (PCE) by sodium persulfate in a batch reactor at 50 °C. They showed that PCE was completely dechlorinated with 4 mol of chloride produced per mol of PCE oxidized. This very interesting result evidences that no toxic intermediates in the form of organochlorides were generated using this process.

The approach chosen in this study, in view of treating industrial wastewaters with low concentrations of biorefractory organic species, is to combine both of the following steps:

(i) the electrochemical production of peroxodisulfates and (ii) the oxidation of organics initiated by the conversion of  $\text{S}_2\text{O}_8^{2-}$  into the sulfate radical  $\text{SO}_4^{\cdot-}$  by heat activation. The first step consists of persulfate electrosynthesis, via hydroxyl radicals using a BDD anode at a low temperature. Peroxodisulfate, which is relatively stable, can be produced at high concentrations. In the second step, peroxodisulfate is injected into the preheated solution containing

the target organic compound, 2,4 D, for activation and reaction.

The results are presented in two sections; firstly, the persulfate electrosynthesis and secondly, the coupling processes for the treatment of solutions containing 2,4 D.

## 2. Material and methods

### 2.1. Chemicals

The 2,4 D ( $\geq 98\%$ ) was purchased from Merck. Sulfuric acid (98%) and methanol (HPLC grade) were obtained from Fisher. Acetic acid (100% pure) was purchased from Prolabo.  $\text{KMnO}_4$  ( $\geq 99\%$ ),  $\text{AsNaO}_2$  ( $\geq 90\%$ ),  $\text{Ce}(\text{SO}_4)_2$  and  $\text{Fe}(\text{SO}_4)_2(\text{NH}_4)_2$  were obtained from Sigma. All synthetic solutions were prepared with ultrapure water ( $\rho = 18.2 \text{ M}\Omega \text{ cm}$ ).

### 2.2. Analysis methods

The concentration of 2,4 D was determined by high performance liquid chromatography (Ultimate 3000) with an Acclaim<sup>TM</sup> 120 C18 column (3  $\mu\text{m}$ ,  $3.0 \times 100 \text{ mm}$ ) coupled to a diode array detector at a wavelength of 280 nm. The mobile phase consisted of 60:40 v/v methanol/2% acetic acid. The flow rate was  $0.3 \text{ mL min}^{-1}$  and the volume of injection was 20  $\mu\text{L}$ .

The hydrogen peroxide was determined by  $\text{KMnO}_4$ . The peroxomonosulfuric acid and the hydrogen peroxide were simultaneously determined by back titration with As(III) and Ce(IV). The sum of peroxomonosulfuric acid, hydrogen peroxide and peroxodisulfuric acid was back determined using Fe(II) and  $\text{KMnO}_4$ . The peroxodisulfuric acid was deduced from the two previous results.

The sulfuric acid was measured by ionic chromatography with an ICS 3000 system (Dionex, France). After neutralization with concentrated sodium hydroxide, 25  $\mu\text{L}$  of the sample was injected into the column set at 30 °C. The column was a IonPac<sup>TM</sup> AS11 (Thermo Scientific, Dionex); the mobile phase was 95% of 5 mM NaOH and 5% of 100 mM NaOH; analytical errors were estimated at 6%.

TOC and inorganic carbon ( $\text{HCO}_3^-$  in experimental conditions) were measured with a TOC VCSN instrument (Shimadzu). The concentration of inorganic carbon was measured after acidification and degassing, and automatically performed. TOC was calculated from the difference between the total carbon and inorganic carbon.

### 2.3. Set up

#### 2.3.1. Electrochemical reactor for electrosynthesis

The electrochemical production of peroxodisulfate with a high current efficiency needs the use of a divided cell to avoid the reduction of the peroxodisulfate at the cathode. Therefore, the oxidation of sulfuric acid was performed in a two compartment electrolytic flow cell under galvanostatic conditions. Diamond was used as the anode and zirconium as the cathode. Both electrodes were disks (90 mm diameter) with a geometric area of  $63 \text{ cm}^2$  each. The inter electrode gap was 10 mm. The electrolytes were stored on two 1L thermoregulated glass reservoirs. The electrolyte flow rate was  $100 \text{ L h}^{-1}$  for each compartment. This set up was described in a previous study (Serrano et al., 2002). The electrosynthesis was stopped after reaching a 25% sulfate conversion rate corresponding to a persulfate concentration of 0.2 M. The remaining sulfuric acid concentration was 1.6 M  $\text{H}_2\text{SO}_4$ .

#### 2.3.2. Reactor for the coupling processes

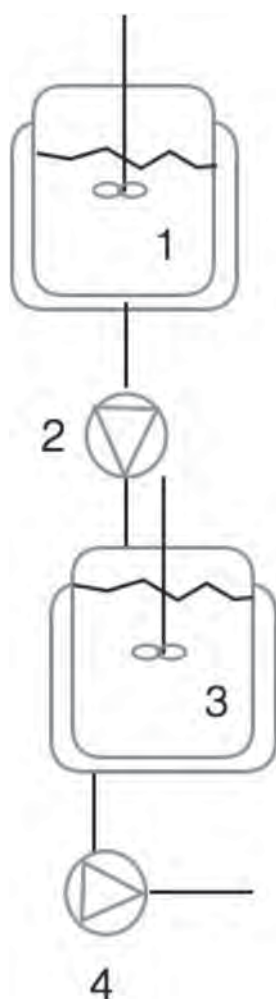
A preliminary study showed that the ratio  $[\text{2,4 D}]/[\text{S}_2\text{O}_8^{2-}]$  plays an important role on the complete disappearance of 2,4 D. Various ratios were tested in the range of 1/60 to 1/8, as shown in the

supplementary data Fig. SM 1. A complete and fast disappearance of 2,4-D was reached for a ratio lower than 1/40. Therefore, the experimental set up was chosen to provide an excess of persulfate over the target organic (Fig. 1). The treated solution containing 2,4-D was stored in a thermostated, stirred tank (1) to maintain a constant temperature of 60 °C. This solution was pumped into a continuous thermostated, stirred tank of 100 mL (3) which initially contained the electro-synthesized persulfate ( $[S_2O_8^{2-}]$  0.2 M,  $[H_2SO_4]$  1.6 M), maintained at 60 °C. A pumping device (4) placed at the outlet of the reactor (3) is used to keep the volume constant in the chemical reactor. The system worked as a continuously stirred tank reactor (CSTR) at a steady state under isothermal conditions. The flow rate of the treated solution was adjusted to match a residence time in the reactor of 2–60 min. Samples were taken regularly in the reactor (3) and filtered through a 0.22  $\mu$ m membrane filter for analysis.

### 3. Results and discussion

#### 3.1. Electrosynthesis of persulfate

A previous study showed that a high current efficiency (95%) for electro-synthesis of peroxodisulfuric acid was achieved in



**Fig. 1.** Set-up used for the disappearance of 2,4-D by reaction with the electro-generated peroxodisulfate. (1) Thermostated, stirred tank containing a 2,4-D solution; (2) pump; (3) Thermostated, stirred tank containing the electro-synthesized persulfate; (4) pump.

concentrated  $H_2SO_4$  (>2 M) for moderate temperatures (8–10 °C) (Serrano et al., 2002). These operating conditions were chosen as a starting point for this study. As shown in Fig. 2, the concentration of sulfuric acid decreases linearly during the electro-synthesis of persulfate. After 300 min, the loss of sulfuric acid concentration is only 12%, confirming that the process is not controlled by mass transfer.

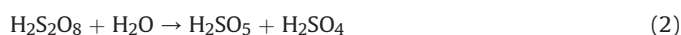
Fig. 3 a shows the variation of persulfate concentration as a function of time for various applied current densities in the range of 5–100  $mA\ cm^{-2}$ . As expected, an increase in current density results in a higher concentration of hydroxyl radicals, which cause a faster increase of the peroxodisulfuric acid concentration. Indeed, the rate of persulfate formation reaches 1.45–16  $\mu M\ min^{-1}\ cm^{-2}$  for a current density that goes from 5 to 100  $mA\ cm^{-2}$ .

In addition, considering the applied electrical charge in the system (Fig. 3 b and inset panel), in the range of 5–100  $mA\ cm^{-2}$ , the conversion rate of persulfate depends on the applied current density. A significant difference is observed with the highest current intensity (100  $mA\ cm^{-2}$ ) showing that a part of the electrical charge is not used for the persulfate electro-synthesis, or that a part of the electro-synthesized persulfate is decomposed.

The faradaic efficiency, defined as the fraction of the current used for the generation of persulfate, is determined assuming a two electron oxidation for converting sulfate into persulfate.

As shown in Fig. 4, the value of the faradaic efficiency decreases as the current density increases. After 180 min's electrolysis, it ranges from 98% to 48.5% for 5–100  $mA\ cm^{-2}$ . To explain this decreasing faradaic efficiency as current density increases, different hypotheses have been established.

Hippauf et al. (2014) observed the same tendency in the concentrated medium (90% of sulfuric acid) and revealed the consumption of persulfate by the detection of oxygen and hydrogen peroxide. Hydrogen peroxide can be formed by a recombination of hydroxyl radicals or by the sequential hydrolysis of persulfate and the Caro acid,  $H_2SO_5$  (Eqs. (2) and (3))



Oxygen can be formed by oxidation of Caro's acid (Eq. (4)):



To explore the possible presence of these secondary reactions,  $SO_5^{2-}$  and  $H_2O_2$  were determined during three electrolyses using different current densities: 5  $mA\ cm^{-2}$ , 20  $mA\ cm^{-2}$  and 100  $mA\ cm^{-2}$ . Results presented in Fig. 5 show that for the lowest applied current density (5  $mA\ cm^{-2}$ ), neither  $SO_5^{2-}$  nor  $H_2O_2$  were detected. For 20  $mA\ cm^{-2}$  and 100  $mA\ cm^{-2}$ , the conversion of persulfate into  $SO_5^{2-}$  reaches a maximum value of 8%. However, for both these current densities,  $H_2O_2$  was not detected. This low amount of Caro's acid can be explained by its oxidation: according to Balej et al. (1980), the oxidation rate of Caro's acid during  $S_2O_8^{2-}$  electro-synthesis is higher than the formation rate of  $H_2SO_5$ .

Another hypothesis that could explain the decline in persulfate yield is a possible reaction with hydroxyl radicals. Indeed, Buxton et al. (1990) measured by radiolysis the kinetic constant of persulfate ions with hydroxyl radicals, which is  $1.2 \cdot 10^7\ M^{-1}\ s^{-1}$ . Electrolysis using a 2 M  $HNO_3$  solution containing 0.2 M persulfate was performed. The concentration of persulfate was analyzed for 350 min' electrolysis. The concentration of persulfate remained stable (2 M) during electrolysis, showing the lack of reaction between persulfate and hydroxyl radicals. The temporal variation of persulfate concentration is shown in supplementary materials (Fig. SM 2).

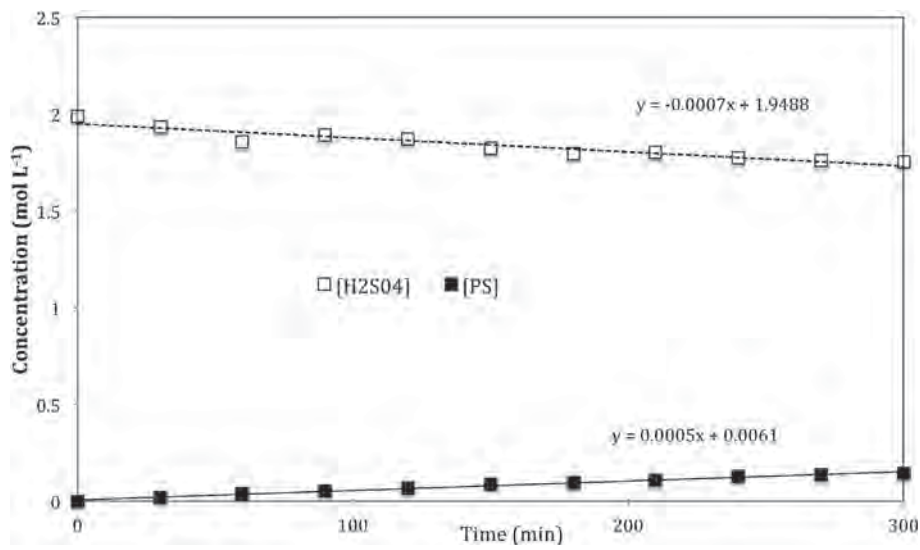


Fig. 2. Concentration of persulfate and sulfuric acid during electrolysis as a function of time. Operating conditions: 1L,  $[H_2SO_4] = 2\text{ M}$ ,  $T = 9^\circ\text{C}$ , flow rate  $100\text{ L h}^{-1}$ , current density:  $40\text{ mA cm}^{-2}$ .

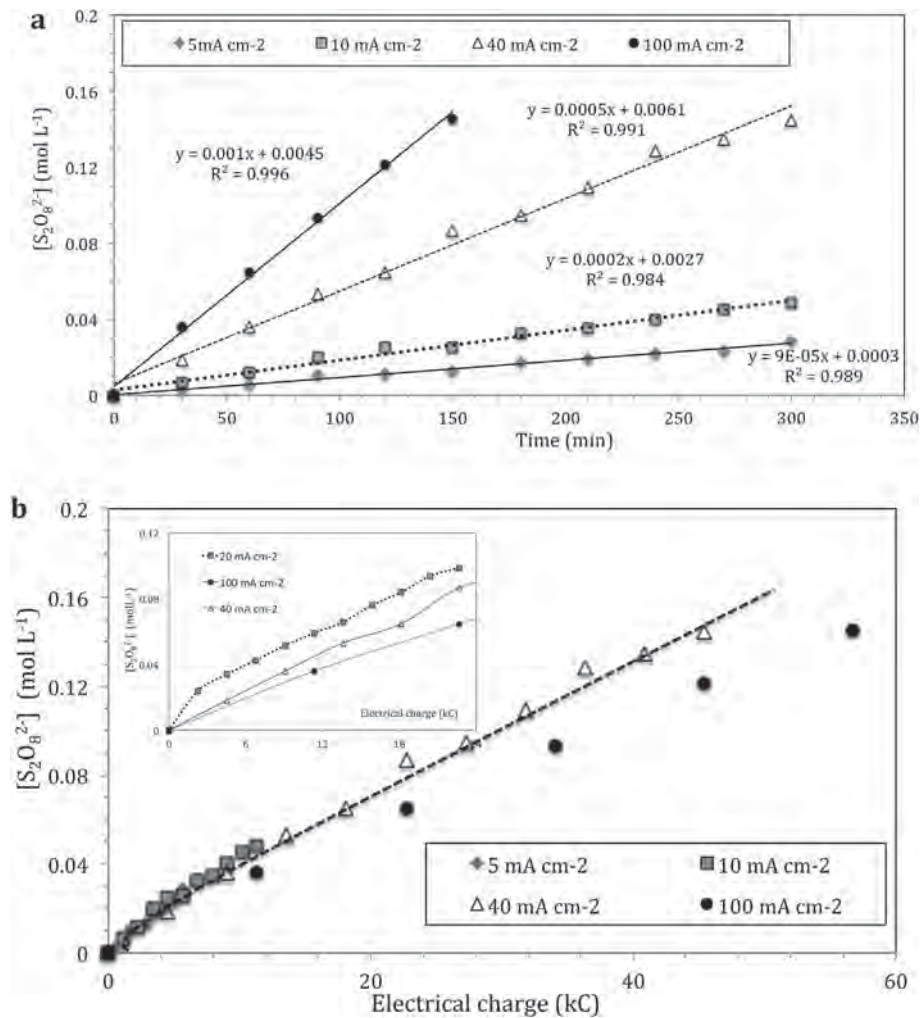


Fig. 3. Concentration of persulfate during electrolysis as a function of (a) time and (b) the applied electrical charge. Inset panel: zoom of the first 25 kC electrolysis. Operating conditions: 1L of  $H_2SO_4$  2 M at  $9^\circ\text{C}$ , flow rate  $100\text{ L h}^{-1}$ , range of current densities:  $5\text{--}100\text{ mA cm}^{-2}$ .

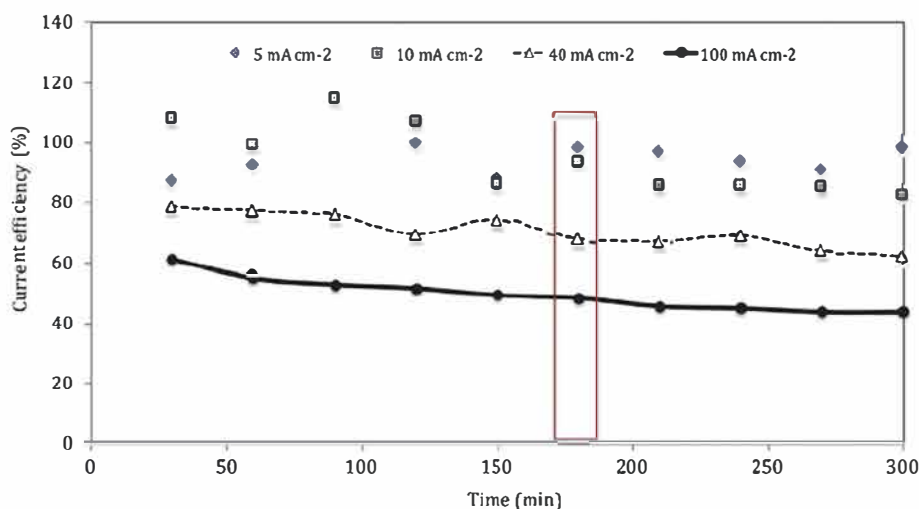


Fig. 4. Effect of current densities on the faradaic efficiency during persulfate electrosynthesis. Operating conditions: 1 L of  $\text{H}_2\text{SO}_4$  2 M at  $9^\circ\text{C}$ , flow rate  $100 \text{ L h}^{-1}$ , range of current densities: 5– $100 \text{ mA cm}^{-2}$ .

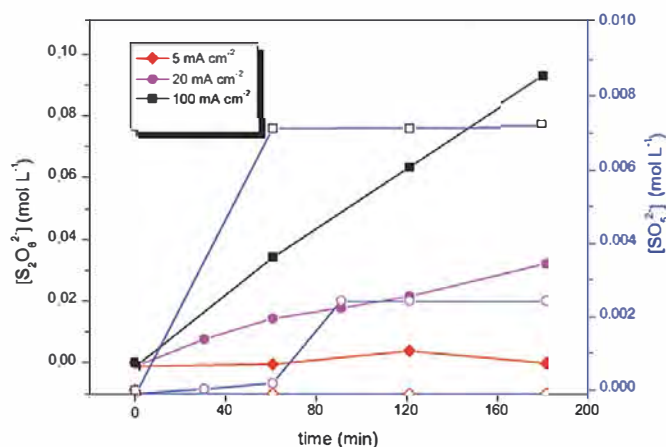


Fig. 5. Concentration of persulfate (full symbols) and Caro's acid,  $\text{SO}_5^{2-}$ , (empty symbols) for 180 min' electrolysis. Operating conditions: 1 L of  $\text{H}_2\text{SO}_4$  2 M at  $9^\circ\text{C}$ , flow rate  $100 \text{ L h}^{-1}$ , range of current densities: 5– $100 \text{ mA cm}^{-2}$ .

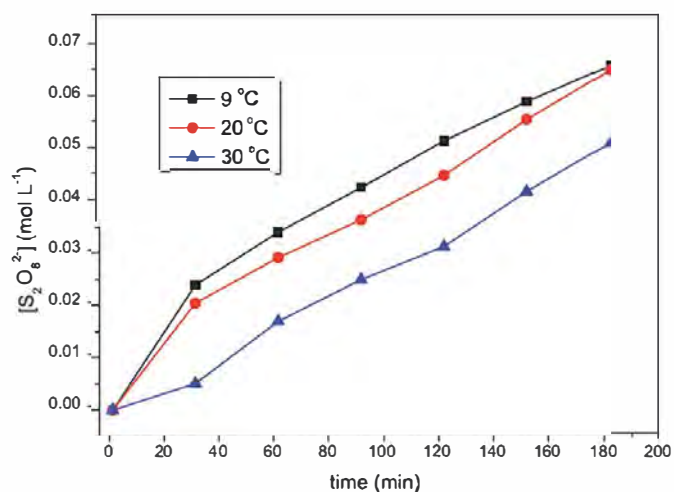


Fig. 6. Concentration of persulfate during 180 min' electrolysis at 9, 20 and  $30^\circ\text{C}$ . Operating conditions: 1 L of  $\text{H}_2\text{SO}_4$  2 M at  $9^\circ\text{C}$ , flow rate  $100 \text{ L h}^{-1}$ , applied current density:  $20 \text{ mA cm}^{-2}$ .

Another plausible explanation for the current efficiency decrease is the decomposition of persulfate caused by an increase in temperature. Indeed, [Serrano et al. \(2002\)](#) showed that the stability of persulfate depends on the temperature. Up to  $20 \text{ mA cm}^{-2}$ , the temperature of the electrolyte remained stable at  $9^\circ\text{C}$ . By contrast, an increase in temperature up to 12 and  $14^\circ\text{C}$  was observed, for the electrolyses carried out under  $40 \text{ mA cm}^{-2}$  and  $100 \text{ mA cm}^{-2}$  respectively. [Fig. 6](#) shows the effect of the temperature on the production of persulfate. After 2 h' electrolysis, corresponding to an electrical charge of 9 kC, an increase in temperature from 9 to  $20^\circ\text{C}$  and from 9 to  $30^\circ\text{C}$  leads to a loss of persulfate concentration of 12% and 23% respectively.

In addition, [Davis et al. \(2014 a,b\)](#) who studied the electrosynthesis of persulfate, obtained a faradaic efficiency close to 60%. Except the temperature, the operating conditions were similar (2.5 M of sulfuric acid,  $j = 20 \text{ mA cm}^{-2}$ ). Davis et al. explained the difference of the efficiency in the previous study (95%, [Serrano et al., 2002](#)) by the fact that the electrosynthesis was performed at  $20^\circ\text{C}$  instead of  $9^\circ\text{C}$ .

In conclusion, even if the process is not limited by the diffusion of sulfate species, it is necessary to control the current density and

temperature to stabilize the electrogenerated persulfate and to avoid the decomposition of persulfate.

### 3.2. Degradation of 2,4 D by electrogenerated peroxodisulfate

Experiments showed that the minimum temperature required to activate persulfate into sulfate radicals is  $60^\circ\text{C}$  (see [Fig. SM 3](#)). This temperature has been chosen for the process of 2,4 D disappearance. As described in section 2.3.2, the treated solution containing the target compound, the 2,4 D at 0.45 mM, was stored in a thermostated, stirred tank at  $60^\circ\text{C}$ . The solution was pumped into a continuous thermostated, stirred tank reactor of 100 mL at  $60^\circ\text{C}$ , which initially contained the oxidizing solution, electro synthesized persulfate. Various flow rates of 2,4 D solution were tested in the range of  $1.66\text{--}50 \text{ mL min}^{-1}$ . The corresponding range of residence time for a 100 mL tank reactor is 2–60 min.

A first series of experiments were performed to study the effect of the residence time of 2,4 D in the chemical reactor on its disappearance. The initial concentrations of 2,4 D in the treated solution and persulfate were set to 0.45 mM and 0.2 M,

respectively. This high ratio of concentrations  $[S_2O_8^{2-}]/[2,4\text{ D}]$  was chosen for its kinetic conditions that can reach the total conversion of 2,4 D, according to a previous study (Fig. SM 1). In these operating conditions, it can be assumed that the oxidizing power of the solution does not vary during the process. The residence time of 2,4 D,  $\tau$ , in the range of 0–60 min was set by controlling the flow rate,  $Q$ . The samples were taken regularly to follow the variation of 2,4 D concentration determined by HPLC.

Fig. 7 a presents the disappearance rate of 2,4 D as a function of the residence time. As expected, for residence times of less than 10 min, the disappearance rate increases as residence time increases, due to a higher contact time between the reagents. For a residence time of more than 10 min, the 2,4 D disappearance rate reaches more than 70%. The quasi complete degradation of 2,4 D is reached for a residence time of 1 h. According to the mass balance obtained in a continuously stirred tank reactor, Eq. (5) is obtained:

$$Q \cdot [2,4\text{ D}]^o - Q \cdot [2,4\text{ D}] + r \cdot V \quad (5)$$

where  $Q$  is the flow rate of the treated solution ( $L\text{ min}^{-1}$ );  $[2,4\text{ D}]^o$  and  $[2,4\text{ D}]$  are the 2,4 D concentrations ( $\text{mol L}^{-1}$ ) at the inlet and outlet of the chemical reactor, respectively;  $r$  is the rate of reaction between 2,4 D and the activated persulfate ( $\text{mol L}^{-1}\text{ min}^{-1}$ ) and  $V$  the volume of the solution in the chemical reactor (L).

According to our previous study, it was found that the degradation of 2,4 D correlated well with a pseudo first order kinetics

model, as described in Eq (6):

$$r = k[2,4\text{ D}] \quad (6)$$

where  $k$  is the constant rate of the reaction between 2,4 D and the activated persulfate ( $\text{min}^{-1}$ ).

Combining Eq. (5) and (6),

$$\frac{[2,4\text{ D}]^o}{[2,4\text{ D}]} = 1 + k \cdot \tau \quad (7)$$

The inset panel of Fig. 7 a enables the determination of the constant of the reaction rate,  $k$ , for these operating conditions, which is  $0.22\text{ min}^{-1}$  at  $60^\circ\text{C}$ .

In parallel, the total organic carbon (TOC) of the solution was measured for each experiment. The shape of the TOC disappearance correlates well with that of the target molecule, 2,4 D. In addition, one can observe that a disappearance of 84% of 2,4 D corresponds to 54% of TOC removal. Unlike the reaction with hydroxyl radicals, this result shows that the reaction of the target molecule with sulfate radicals leads to the formation of intermediates. In general,  $SO_4^{\cdot-}$  is more likely to participate in electron transfer reactions (Neta et al., 1977; Ahmed et al., 2012; Lutze, 2013) than  $\cdot\text{OH}$ , which is more likely to participate in hydrogen abstraction or addition reactions (Minisci et al., 1983; Liang et al., 2007). The former reactions are selective while the latter ones are non selective (Lan et al., 2017).

Solutions containing 2,4 D for concentrations that range from 10 to  $200\text{ mg L}^{-1}$  ( $0.045\text{--}0.9\text{ mM}$ ) have been tested for a residence time of 10 min. Fig. 7 b shows the complete disappearance for  $10\text{ mg L}^{-1}$  of 2,4 D. This rate of disappearance decreases as the initial concentration of 2,4 D increases. Indeed, it reaches less than 60% for  $200\text{ mg L}^{-1}$  of 2,4 D. This indicates a contact time between reactants that is not sufficient.

#### 4. Conclusions

Throughout this study, it has been shown that the complete disappearance of 2,4 D is possible by indirect electrochemical oxidation. This process uses the electro-synthesis of persulfate from a 2 M sulfuric acid solution. The persulfate is then thermally activated to produce sulfate radicals, which are strong and selective oxidants. These radicals react with the target molecule. The efficiency of this process depends on both of the following operating conditions:

When the applied current density is too high,  $100\text{ mA cm}^{-2}$  for 2 M of sulfuric acid, secondary reactions occur.

The complete disappearance of 2,4 D can be reached if the contact time with sulfate radicals is sufficient; the 2,4 D concentration profile follows a first order reaction with an estimated constant rate of  $0.22\text{ min}^{-1}$  under our operating conditions.

The feasibility of the process has been demonstrated. Further studies will be performed to quantify chloride and organic by products.

#### Acknowledgments

The authors would like to thank the French National Center for Scientific Research (PICS Project) for their financial support and Sophie Chambers for proofreading the English manuscript.

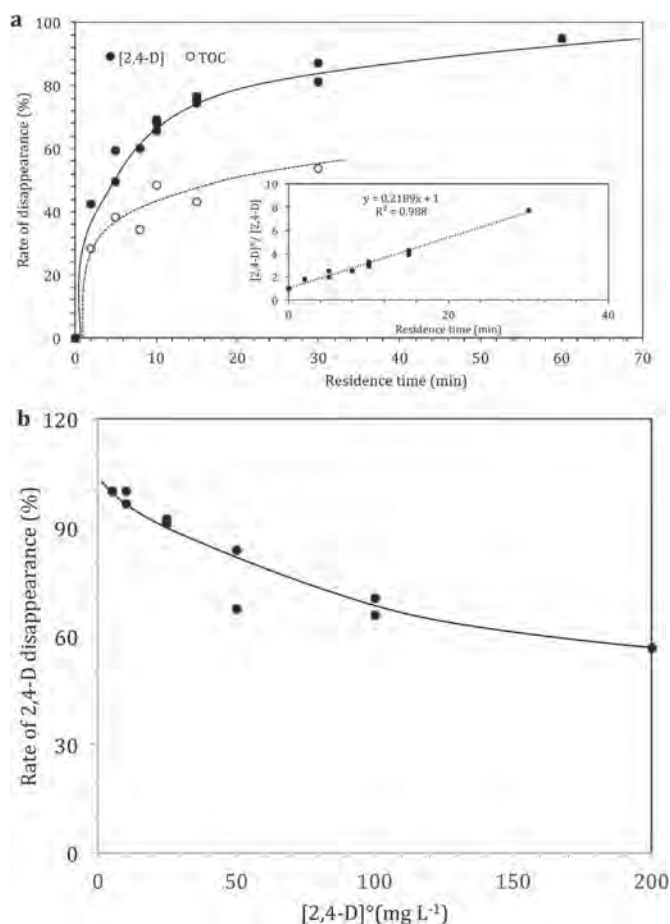


Fig. 7. Influence of (a) the residence time and (b) the initial concentration of 2,4-D on its disappearance. Operating conditions:  $[S_2O_8^{2-}]^o = 0.2\text{ M}$ , temperature of tank (1) and (3)  $60^\circ\text{C}$ ,  $[H_2SO_4]^o = 1.6\text{ M}$ . (a)  $[2,4\text{-D}]^o = 0.45\text{ mM}$ , range of flow rate  $1.6\text{--}50\text{ mL min}^{-1}$  (b)  $[2,4\text{-D}]^o = 0.045\text{--}0.9\text{ mM}$ , residence time of 10 min.



## Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.chemosphere.2018.04.004>.

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