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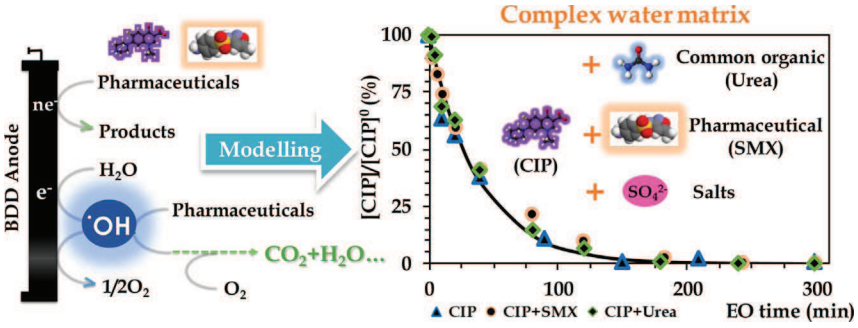
GRAPHICAL ABSTRACT



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ABSTRACT

This paper deals with an experimental and modelling study on the electrochemical oxidation of refractory pharmaceuticals using a boron-doped diamond (BDD) anode. Different parameters have been investigated, such as the role of salts (sulfates), the presence of other organics, and the influence of applied current intensity. Ciprofloxacin (CIP), Sulfamethoxazole (SMX) and Salbutamol (SALBU) were used for models of pharmaceuticals, and urea as a model for a common organic. The complete removal of pharmaceuticals was observed in all electrolyses under galvanostatic conditions. The presence of common organic waste or other pharmaceutical has no significant impact on the degradation of the CIP target molecule. A mathematical model predicting the temporal concentration variation of organics with electroxidation time has been developed. In this model, different oxidation pathways have been considered: the transfer of electrons (direct oxidation) or of oxygen atoms via the reaction with either hydroxyl radicals or/and with strong electrogenerated oxidants. Excellent correlation with experiments is obtained under all experimental conditions.

1. Introduction

The world-wide consumption of antibiotics is estimated to be between 100 000 and 200 000 tons over the last 50 years [1]. Because most pharmaceuticals, especially antibiotics, are only partially biodegradable, or even resistant to the conventional activated sludge process of a wastewater treatment plant (WWTP), they are released directly into the environment [2–4]. Consequently, the spread and accumulation of pharmaceuticals in the aquatic system [5–10] pose significant threats to the sustainability of eco-systems and the safety of drinking water [11–13]. It is therefore crucial to develop and apply more efficient water treatment technologies for the removal of refractory pharmaceuticals from effluents.

Although the industrial scale is still under development,

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Abbreviations

A	electrode surface (m^2)
C	concentration (mol m^{-3})
C^0	initial concentration (mol m^{-3})
C_s	concentration at the electrode (mol m^{-3})
j	current density (A m^{-2})
j_{lim,ne^-}	limiting current density of direct transfer of electrons (A m^{-2})
$j_{lim,^{\cdot}OH}$	limiting current density corresponding to the total mineralization of the specie i (A m^{-2})
Kd	mass transfer coefficient (m s^{-1})
k_i	rate constant of chemical reaction involving $^{\cdot}OH$ and i
k_{SE}	pseudo-first-order constant rate due to salt effect (s^{-1})
n	number of exchanged electrons
V	volume (m^3)

Greek letters

γ	equivalent number of exchange electrons necessary to achieve complete mineralisation
Γ	total rate of organic destruction
Γ_e^-	rate of direct oxidation (electron transfer)
Γ_{OH}	reaction rate of organic with hydroxyl radicals
Γ_{SE}	reaction rate of organic with electrogenerated oxidant

electrochemical oxidation is a promising alternative technology for the elimination of pharmaceuticals from water, in particular using a boron-doped diamond anode (BDD) [14]. The strong ability of BDD anodes for organic oxidation is well known and attributed to the electrogeneration of hydroxyl radicals (·OH) from water discharge (Eq. (1)). Hydroxyl radicals are the most powerful oxidants in water (standard potential E_0 = 2.74 V/SHE [15]). They react unselectively and rapidly with a large variety of organics (i.e. kinetic constant > 10^9 M^{-1} s^{-1}) [16].

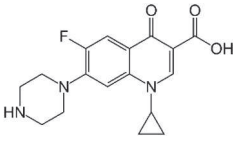
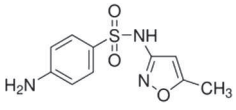
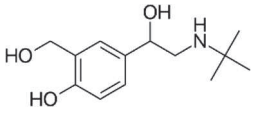
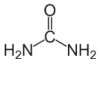
$$H_2O \rightarrow {}^{\cdot}OH + H^+ + e^- \quad (1)$$

Due to the wide electrode potential window of BDD anodes, direct transfer reactions of electrons are also available. They constitute an important additional mechanism for the oxidation of organics. Numerous studies have shown that a combination of direct transfer of electrons and ·OH oxidation are involved in the oxidation pathways of various organic compounds. Through these oxidation pathways, electrochemical oxidation processes have demonstrated their great ability to efficiently degrade a wide range of refractory pharmaceuticals, such as paracetamol [17], atenolol [18], trimethoprim [19] and sulfachloropyridazine [20]. Nevertheless, almost all of these studies were performed in an aqueous solution that contained only a single pharmaceutical compound. The composition of wastewater is more complex, it often contains common organics, such as urea or other refractory pharmaceuticals [21,22]. With the aim of the industrial application of the electrochemical processes, the consequence of the presence of organics on the degradation of a target pharmaceutical should be studied.

Modelling is an important approach in the understanding of the oxidation process. Several models have been developed to describe the electroxidation of organic pollutants at the BDD anode. A theoretical model presented by Panizza et al. [23] predicts the temporal decay of the global parameter, which is the chemical oxygen demand (COD). This model, based on the unselectivity of hydroxyl radicals is very useful. Scialdone et al. [24] have extended this model, by taking into consideration species, like oxalic acid. This type of specie is directly oxidized by the transfer of electrons, due to the slow kinetics of the chemical reaction between oxalic acid and hydroxyl radical: 9.2 10^{-6} L mol^{-1} s^{-1}. Cañizares et al. [25] have investigated a model which describes the evolution of the concentration of one organic involved in the oxidation processes. The kinetics of organic oxidation were described by pseudo first-order reactions. To reduce the mathematical complexity, the concentration of the organic compound was considered as dependent only temporally, not spatially. The approach used by Mascia et al. [26,27] focused on the phenomena close to the anode by using a diffusion-reaction model. The aim was to evidence the effects of the operating conditions (hydrodynamics of the cell, current density, influence of the salts, namely chlorides) on the kinetics of the phenolic compounds oxidation. Kapalka et al. [28] investigated the temporal and spatial variations of concentration of a single organic compound and hydroxyl radicals. In this model, a single zone is defined comprising electrode and solution. In order to highlight the role of hydroxyl radicals and their action zone, we have developed a model containing three zones [29]: (i) the action zone of ·OH close to the electrode (ii) the diffusion zone where the concentration of organics linearly varies with the distance (iii) the bulk zone where the organic concentration is homogenous. This model evidenced the role of ·OH in the competition of organics.

The present study, based on an experimental and modelling approach, aims to investigate the degradation of pharmaceutical pollutants by electrochemical oxidation on the BDD anode. The contributions of the oxidation pathways are emphasized: transfer of electrons (direct oxidation), transfer of oxygen atoms via a reaction with either hydroxyl radicals or/and with a strong electrogenerated oxidant. For this purpose, the chosen target pollutants are: two antibiotics (ciprofloxacin and sulfamethoxazole), one beta-agonist (salbutamol), and a common organic compound (urea). All these compounds are frequently detected in groundwater [4,30–32]. An easy-to-use model is put forward and compared with the experimental results obtained in various operating conditions: concentration of sulfate, various current densities, presence of electroactive and electroinactive organics in the solution.

Table 1
Organics used in the synthetic solution.

	Ciprofloxacin (CIP)	Sulfamethoxazole (SMX)	Salbutamol (SALBU)	Urea
Formula	$C_{17}H_{18}FN_3O_3$	$C_{10}H_{11}N_3O_3S$	$C_{13}H_{21}NO_3$	CH_4N_2O
Type	Antibiotic	Antibiotic	Beta-agonist	Organic
M (g mol^{-1})	331.3	253.3	239.3	60.06
Structure				

2. Materials and method

2.1. Chemicals

The pharmaceuticals: ciprofloxacin (≥98% purity), sulfamethoxazole (≥98% purity) and salbutamol (Salbutamol·sulfate ≥ 99% purity) were purchased from Alfa Aesar and Fluka. Urea was laboratory reagent grade from Fisher chemical. All synthetic solutions were prepared with ultrapure water (ρ = 18.2 MΩ cm). Potassium sulfate (≥99% purity), as the supporting electrolyte for electrochemical oxidation in the synthetic solution, was analytical grade and supplied by Fisher Science. Other chemicals, organics or solvents, were HPLC or analytical grade(Table 1).

The range of concentration of the pharmaceuticals (CIP, SMX, SALBU) used in this study was chosen according to the concentration of refractory organics detected in the nanofiltration concentrate of a biological-treated hospital wastewater [33].

2.2. Analytical methods

Pharmaceutical concentrations were measured by high performance liquid chromatography (HPLC) and a UV detector using an Agilent ZORBAX Eclipse Plus C18 column (3.5 µm, 3 mm × 100 mm) from Agilent Technologies. The UV wavelength detection was set to 278 nm. The mobile phase was a mixture of a gradient of ultrapure water (with 0.1% formic acid) and acetonitrile (with 0.1% formic acid) which was thermoregulated at 30 °C. The flow rate was 0.4 mL min^{-1} and the volume of injection was 10 µL. The gradient for the mobile phase is reported in the Table 2.

5.1, 9.9 and 12.1 min were the retention times of SALBU, CIP and SMX, respectively. The detection limit of CIP and SMX was 10 µg L^{-1} and of SALBU was 100 µg L^{-1}. The analytical errors ranged from 0.2% to 1%.

Concentrations of urea were determined by a L-Arginine/Urea/Ammonia kit (Nzytech, Portugal). The principle of the measure is shown in Eqs. (2) and (3). The amount of nicotinamide adenine dinucleotide phosphate ($NADP^+$, measured at UV 340 nm) was formed through the combined action of urease (URE) and glutamate dehydrogenase (GlDH).

$$Urea + H_2O \xrightarrow{URE} 2NH_3 + CO_2 \quad (2)$$

$$2\text{–}Oxoglutarate + NADPH + NH_4^+ \xrightarrow{GIDH} L\text{–}Glutamate + NADP^+ + H_2O \quad (3)$$

The sensitivity of the assay was based on 0.005 absorbance units and a sample volume of 2.00 ml. The detection limit of urea was 0.13 mg L^{-1}. The relative standard deviation of the urea test was 3%.

2.3. Electrochemical cell and reactor

Cyclic voltammograms were carried out in a conventional three-electrode cell of 100 mL capacity using a computer-controlled Autolab potentiostat Model 30. A BDD anode of 0.196 cm^2 from Adamant (Switzerland) was used as the working electrode, a Pt wire as the counter electrode and a $Hg/Hg_2Cl_2/Cl^-$ (sat) electrode (SME) as the reference electrode. Before each experiment, the electrode was pretreated using anodic polarisation at 2.84 V/SHE for 40 s into a 1 M H_2SO_4 solution.

Electrolyses were conducted at 30 °C in a one-compartment flow filterpress reactor (3) under galvanostatic conditions. The experimental solution was stored in a 1-litre thermoregulated glass reservoir (1) and circulated through the electrolytic cell using a centrifugal pump (2) (Fig. 1). The flow rate was 360 L h^{-1}.

The electrodes were two discs of 69 cm^2 of active surface each, separated by 10 mm between them. The BDD anode from Adamant (Switzerland) was elaborated by chemical vapour deposition on a conductive substrate of silicium. The thickness of BDD is 2–3 µm, the boron concentration is 500 ppm and the initial sp3/sp2 ratio is in the range of 100–300. The cathode was a 1-mm thick disc of zirconium. The current was supplied by an ELCAL 924 power supply. Before each electrolysis, the working electrodes were anodically pretreated (40 mA cm^{-2} for 30 min in a 0.1 M K_2SO_4 solution) to clean their surfaces of any possible adsorbed impurities. Then the system was rinsed with ultrapure water. Samples were taken at regular intervals in the tank. The overall volume of samples was less than 10% of the total volume. K_2SO_4 was used in this study as the electrolyte at two different concentrations and pH: 0.1 M at pH = 4 (adjusted with concentrated H_2SO_4) and 0.02 M at pH = 6.

In the present study, the flow rate was 360 L h^{-1} at 30 °C. At 360 L h^{-1}1, the mass transfer coefficient has been estimated to be 2.30×10^{-5} m s^{-1} at 30 °C in a preceding study [34].

3. Theory and mathematical model

A general illustration of the possible pathways of electroxidation of organics with the BDD anode is shown in Fig. 2. The oxidation reactions can occur at the anode surface by direct transfer of electrons (1) for an electroactive organic or by unselective oxygen transfer via the hydroxyl radicals, ·OH (4), generated by water discharge (2). Because of the weak interaction between the surface of BDD anode and the hydroxyl radical, ·OH can be considered as quasi free on the surface [28]. If the amount of available ·OH is higher than that required for the mineralization of organics, complete mineralization can be reached (7). Otherwise, it is possible to generate organic radicals (5) with chain reactions [35]. Oxidation via direct exchange of electrons occurs only at the anode surface and the reaction with ·OH happens in a narrow zone adjacent to the electrode surface (< 1.0 µm).

3.1. Model description

The direct electroxidation can be written according to Eq. (4):

$$Organic \rightarrow Product + ne^- \quad (4)$$

The corresponding limiting current density (j_{lim,ne^-}) which depends on the mass transfer coefficient k_d (m s^{-1}) and the concentration of the electroactive specie, *C(t),* can be defined by Eq. (5).

$$j_{lim,ne^-} = nFk_dC(t) \quad (5)$$

where j_{lim,ne^-} is the initial limiting current density of direct transfer of electrons (A m^{-2}), n is the number of exchanged electrons, F is Faraday constant (96485 C mol^{-1}) and C(t) is concentration of electroactive species in the solution (mol m^{-3}).

Consequently, the initial limiting current density (j^0_{lim,ne^-}) can be written as Eq. (6).

$$j^0_{lim,ne^-} = nFk_dC^0 \quad (6)$$

C^0 is the initial concentration of the electroactive specie in the solution (mol m^{-3}).

When the current density, *j*, is lower than j_{lim,ne^-}, the oxidation process is controlled by electron transfer. Whereas when *j* is higher than

Table 2
Gradient of the mobile phase for analysis of pharmaceuticals with ZORBAX Eclipse Plus C18 column.

Time (min)	acetonitrile% (with 0.1% formic acid)
0	5
3	5
18	95
21	5
30	5

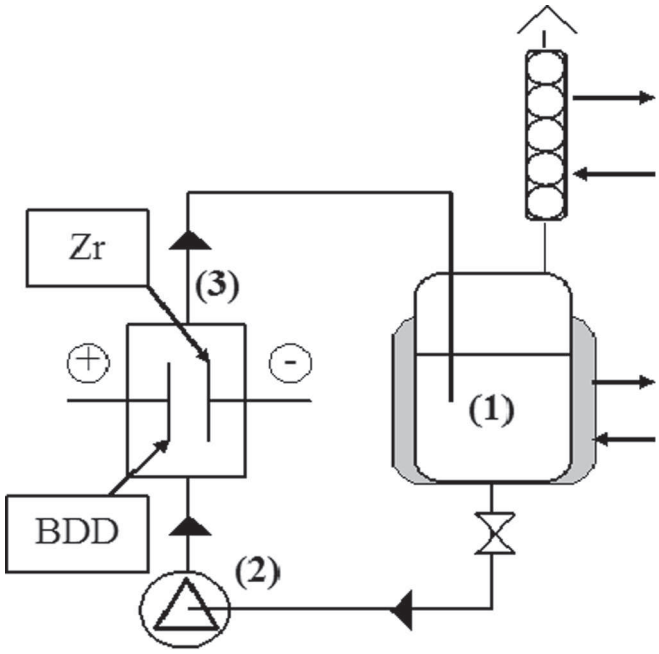


Fig. 1. Discontinuous process with a single-compartment electrochemical reactor, (1) tank, (2) pump, (3) electrochemical cell.

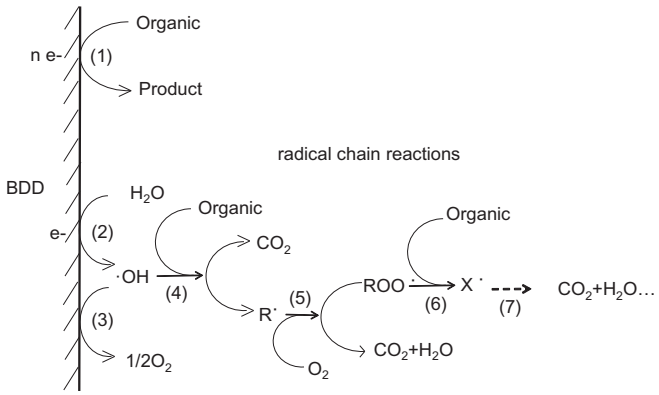


Fig. 2. Oxidation pathways of organics in a BDD anode system: (1) direct exchange of electrons, (2) electrogeneration of ·OH, (3) generation of oxygen (4) formation of organic radicals via reactions between organics and hydroxyl radicals, (5) reactions between O_2 and organic radicals, (6) reaction between peroxy radicals and organics in the solution, (7) complete mineralization.

j_{lim,ne^-}, the oxidation of water occurs and hydroxyl radicals are generated (Eq. (1)). Because these radicals are quasi free at the electrode surface, they can react actively with the organics, reaching complete mineralization. The equivalent number of exchanged electrons can be calculated with Eq. (7):

$$C_xH_yO_z + (2x-z)H_2O \rightarrow xCO_2 + (4x + y-2z)H^+ + (4x + y-2z)e^- \quad (7)$$

The equivalent number of exchanged electrons γ, is calculated by Eq. (8):

$$\gamma = 4x + y-2z \quad (8)$$

In this case, the initial limiting current density that corresponds to the total mineralization of the organic specie ($j^0_{lim,\cdot OH}$, A m^{-2}) can be defined: it is a function of γ, k_d and C^0.

$$j^0_{lim,\cdot OH} = (4x + y-2z)Fk_dC^0 \quad (9)$$

When several organics are present in the solution, the limiting current density that corresponds to the total mineralization of the organic matter is calculated from the sum of the limiting current densities of each organic, *i*.

$$j^0_{lim,\cdot OH} = \sum_i j^0_{lim,\cdot OH}(i) = Fk_d \sum_i \gamma_i C_i^0 \quad (10)$$

This model is based on the variation of the organic concentration, C(t), which depends only on the rate of organic oxidation, Γ, involving direct transfer of electrons and/or oxygen atom transfer:

$$V\frac{dC(t)}{dt} = -\Gamma A \quad (11)$$

V is the volume of the solution, A is the electrode surface (m^2), Γ is the total rate of organic destruction.

Depending on the value of the concentration of organics and the applied current density, three different regimes can be considered.

a) $j \leq j_{lim,ne^-}$
b) $j_{lim,ne^-} < j < j_{lim,\cdot OH}$
c) $j > j_{lim,\cdot OH}$

In this study, because the removal of organics using a BDD anode is efficient in the presence of ·OH, the study model will be focused on the regions (b) and (c) where ·OH are electrogenerated.

(a) $j \leqslant j_{lim,ne^-}$

In this regime, only direct exchanged electron occurs, the rate of organic destruction corresponds to the direct electrochemical oxidation rate, Γ_{e-}. This oxidation, governed by electron transfer, depends on the applied current density *j*:

$$\Gamma = \Gamma_{e^-} = \frac{j}{nF} \quad (12)$$

In the case of $j = j_{\mathrm{lim,ne-}}$, Γ_{e-} can be written by Eq. (13)

$$\Gamma_{e^-} = \frac{j^0_{lim,ne^-}}{nF} \quad (13)$$

(b) $j_{lim,ne^-} < (j < j_{lim,\cdot OH}$

For a current density higher than j_{lim,ne^-}, the oxidation of water occurs. Then the rate of organic oxidation is expressed by the sum of the rate of electrons transfer, Γ_{e-}, and the rate of reaction with ·OH, $\Gamma_{\cdot OH}$.

$$\Gamma = \Gamma_{e^-} + \Gamma_{OH} \quad (14)$$

The mass balance of the organic specie can be expressed by Eq. (15).

$$V\frac{dC(t)}{dt} = -(\Gamma_{e^-} + \Gamma_{OH})A \quad (15)$$

here, the part of the current density used to generate ·OH, $j_{\cdot OH}$, represents the difference between the applied current density and j_{lim,ne^-}:

$$J_{\cdot OH} = j - j_{lim,ne^-} \quad (16)$$

According to Eqs. (7) and (8), the mineralization of one mol of $C_xH_yO_z$ consumes γ mol of ·OH. The reaction rate of organics with ·OH ($\Gamma_{\cdot OH}$) can be written by Eq. (17).

$$\Gamma_{OH} = \frac{j_{\cdot OH}}{\gamma F} \quad (17)$$

Combining Eqs. (12), (14) and (17),

$$V\frac{dC(t)}{dt} = -\left(\frac{j^0_{lim,ne^-}}{nF} + \frac{j_{\cdot OH}}{\gamma F}\right)A \quad (18)$$

$n \ll \gamma$ (see Table 4) for mainly organics, it can be assumed that $j_{OH} = j$, in this context combining Eq. (5), Eq. (18) and, t = 0, C = C^0 gives the temporal variation of C:

$$C(t) = -\frac{j_{\cdot OH}}{\gamma F k_d} + K\ exp\left(-\frac{Ak_d}{V}t\right) \quad (19)$$

where K is a constant defined by Eq. (20).

$$K = C^0 + \frac{j_{\cdot OH}}{\gamma F k_d} \quad (20)$$

This expression applies until a critical time (t_{cr}), at which the applied current density (j) equals the limiting current density for mineralization, $j_{lim,\cdot OH}$.

A characteristic parameter α is defined as

$$\alpha = \frac{j}{j^0_{lim,\cdot OH}} \quad (21)$$

The concentration of organics on critical time is C_{cr} defined by Eq. (22)

$$C_{cr} = \alpha C^0 \quad (22)$$

Substituting Eq. (22) for Eq. (19), the critical time can be calculated as

$$t_{cr} = -\frac{V}{Ak_d} ln\left(\frac{2\alpha\gamma - \alpha n}{\gamma + \alpha\gamma - n}\right) \quad (23)$$

As $n \ll \gamma$, the function can be simplified:

$$t_{cr} = -\frac{V}{Ak_d} ln\left(\frac{2\alpha}{1+\alpha}\right) \quad (24)$$

In this region, the non-electroactive organics can be oxidized only via the chemical reaction with hydroxyl radicals. The reaction rate is written as

$$\Gamma = \Gamma_{\cdot OH} \quad (25)$$

Then, the variation of concentration of organics is expressed as:

$$C(t) = C^0 - \frac{Aj_{\cdot OH}}{\gamma FV}t \quad (26)$$

(c) $j > j_{lim,\cdot OH}$

When the applied current density exceeds the limiting current density for complete mineralization $j > j_{lim,\cdot OH}$, the ˙OH chain-reaction rate is controlled by mass transfer. Under these experimental conditions, the flux of ·OH is always higher than that required for the mineralization of organics. Consequently, the concentration of organic on the anode surface (C_s (t)) is zero. The reaction of organics for ·OH radical-chain reactions is written as:

$$\Gamma_{\cdot OH} = k_d(C(t) - C_s(t)) = k_d C(t) \quad (27)$$

Combining Eqs. (5), (13), and (27), Eq. (15) is written as Eq. (28)

$$V\frac{dC(t)}{dt} = -2Ak_d C(t) \quad (28)$$

Consequently, the temporal variation of organics can be calculated from Eq. (28).

$$C(t) = C^0 exp\left(-\frac{2Ak_d}{V}t\right) \quad (29)$$

For non-electroactive organics,

$$C(t) = C^0 exp\left(-\frac{Ak_d}{V}t\right) \quad (30)$$

The theoretical expressions for the temporal variation of the organic concentration in all conditions are summarized in Table 3.

3.2. Determination of model parameters

To validate the model, experiments were performed using different pharmaceutical compounds: ciprofloxacin (CIP), sulfamethoxazole (SMX) and salbutamol (SALBU), or a common organic compound (urea). The experimental data obtained from electrolysis were compared with the proposed model for which the parameters were preliminarily investigated. These parameters include the number of exchanged electrons, n, and the equivalent electrons for complete mineralization, γ, depending on the electro -activity of the studied molecule on the BDD anode.

A typical cyclic voltamogram of a solution containing CIP is shown in Fig. 3. An irreversible oxidation peak of CIP appears before the water discharge at 1 V/SCE. Similar electrochemical behaviour was obtained by Boudreau et al. [36] and Karuwan et al. [37] in a synthetic solution of SMX and SALBU on a BDD anode, respectively. For both cases, the authors observed the deposition of a polymeric film on the anode, before the water discharge. The organic compounds undergo electron transfer at the anode, form phenolic radicals, recombine themselves and finally form a polymer. The activity of the electrode can be restored using an applied current density (or potential) that is sufficiently high to produce hydroxyl radicals, the “cleansing agent”.

In addition, An et al. [38] studied the chemical reaction between the hydroxyl radical and CIP. They reported a kinetic constant of $k_{\cdot OH} = 2.15\ 10^{10}\ mol^{-1}\ L^{-1}\ s^{-1}$. The constant rate for the reaction of OH radicals and SMX is also high and reaches $5.5\ 10^{9}\ mol^{-1}\ L^{-1}\ s^{-1}$ [39].

Consequently these three pharmaceuticals can be oxidized following two pathways: direct transfer of electrons and oxygen transfer via hydroxyl radicals.

By contrast, Cataldo Hernández et al. [40] showed that urea is not electroactive because no direct transfer of electrons was observed on the BDD electrode.

The reaction of mineralization of CIP, SMX, SALBU and urea is presented by Eq. (31)–(35). All nitrogen atoms derived from organics are assumed to be converted into NO_3^-. During the mineralization of organics, the number of exchanged electrons, n, and the equivalent electrons for complete mineralization, γ, are reported in Table 4.

$$C_{17}H_{18}FN_3O_3 + 40H_2O \rightarrow 17CO_2 + 3NO_3^- + F^- + 98H^+ + 94e^- \quad (31)$$

$$C_{10}H_{11}N_3O_3S + 30H_2O \rightarrow 10CO_2 + 3NO_3^- + SO_4^{2-} + 71H^+ + 66e^- \quad (32)$$

$$C_{13}H_{21}NO_3 + 26H_2O \rightarrow 13CO_2 + NO_3^- + 73H^+ + 72e^- \quad (33)$$

$$CH_4N_2O + 7H_2O \rightarrow CO_2 + 2NO_3^- + 18H^+ + 16e- \quad (34)$$

4. Results and discussion

4.1. Influence of salts

Previous studies have shown that the presence of salts in the solution, such as chloride and sulfate, can induce an increase in the removal

Table 3
Temporal variation of organic concentrations in all conditions.

Operating current	Electro activity	Concentration	
$j_{lim,ne^-} < j < j_{lim,\cdot OH}$	Yes	$C(t) = -\frac{j_{\cdot OH}}{\gamma F k_d} + K exp\left(-\frac{Ak_d}{V}t\right)$	(19)
	No	$C(t) = C^0 - \frac{Aj_{\cdot OH}}{\gamma FV}t$	(26)
$j > j_{lim,\cdot OH}$	Yes	$C(t) = C^0 exp\left(-\frac{2Ak_d}{V}t\right)$	(29)
	No	$C(t) = C^0 exp\left(-\frac{Ak_d}{V}t\right)$	(30)

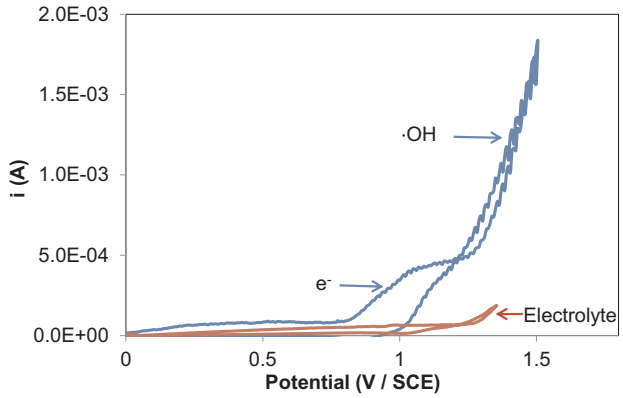


Fig. 3. Cyclic voltammogram of CIP 0.068 mM in 0.1 M H_2SO_4. Working electrode: BDD (0.196 cm^2), Counter electrode: Pt (1 cm^2), Reference electrode: SCE. Scan rate: 100 mVs^{-1}, ω = 800 rpm.

Table 4
Parameters used for model validation for CIP, SMX, SALBU and Urea.

	Ciprofloxacin (CIP)	Sulfamethoxazole (SMX)	Salbutamol (SALBU)	Urea
Electroactivity	Yes	Yes	Yes	No
n	2 [41]	1 [42]	1 [37]	–
γ	94	66	72	16

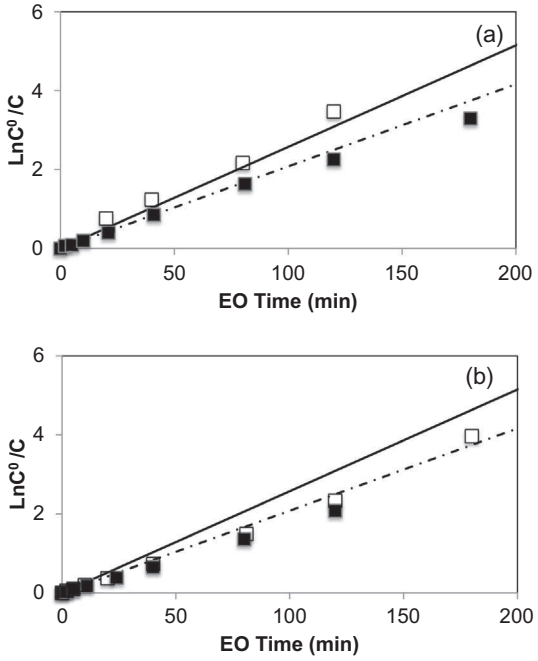


Fig. 4. The normalized concentration of CIP (a) and SALBU (b) during electrolyses: symbols: experimental data, line: model, $j = 1.45\ mA\ cm^{-2}$, $j > j^0_{lim}$, $k_{SE} = 1.1 \times 10^{-4}\ s^{-1}$, T = 30 °C, in □$K_2SO_4$ 0.1 M, pH = 4, range of potential difference: 3.7–4.0 V; ■ K_2SO_4 0.02 M, pH range = 6.4–4, range of potential difference: 4.1–4.3 V, Simulated values calculated from: Eq. (38): – continuous line; from Eq. (29) — dashed line.

rate of pharmaceuticals [42–44]. In fact, strong oxidants can be electrogenerated from salts during electrochemical oxidation, in particular using a BDD anode. These oxidants react chemically with organics. $SO_4^{\cdot -}$ can react selectively and rapidly with pharmaceuticals that are close to the anode surface, with in an order of 10^9–$10^{10}\ M^{-1}\ s^{-1}$ [43]. For example, Radjenovic et al. [44] showed that the rate of SMX oxidation was 6 times higher in a sulfate anolyte compared to a nitrate

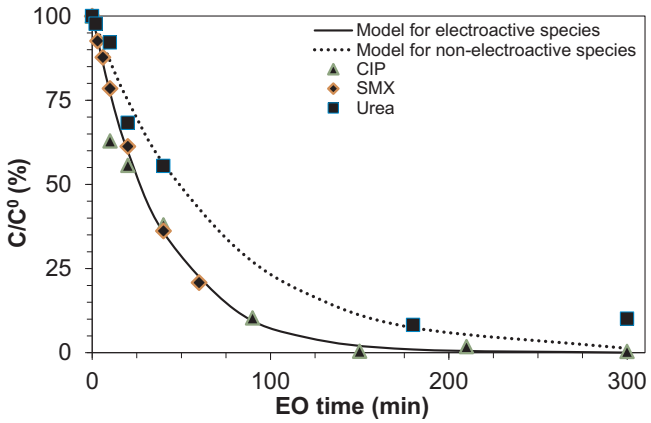


Fig. 5. Experimental (symbol) and simulated (line) concentrations of CIP, SMX, UREA values over time. Simulated values calculated from Eq. (29): – continuous line; Eq. (30) — dashed line. For $j > j^0_{lim,{}^{\cdot}OH}$, range of potential difference: 4.5–4.8 V, $k_d = 2.3 \times 10^{-5}\ m\ s^{-1}$, $k_{SE} = 1.1 \times 10^{-4}\ s^{-1}$, T = 30 °C, pH = 4, [$K_2SO_4$] = 0.1 M. ▲ $[CIP]^0 = 53\ \mu M$, $j^O_{lim,{}^{\cdot}OH} = 1\ mA\ cm^{-2}$, $j = 7.2\ mA\ cm^{-2}$. ● $[SMX]^0 = 59\ \mu M$, $j^O_{lim,{}^{\cdot}OH} = 1\ mA\ cm^{-2}$, $j = 7.2\ mA\ cm^{-2}$. O $[Urea]^\circ = 630\ \mu M$, $j^0_{lim,{}^{\cdot}OH} = 2.5\ mA\ cm^{-2}$, $j = 7.2\ mA\ cm^{-2}$.

anolyte. By using scavengers of radicals (t-BuOH for ˙OH and EtOH for both ˙OH and $SO_4^{\cdot -}$), [45] experimentally evidenced that $SO_4^{\cdot -}$ radicals take part in the oxidation of CIP as well as ˙OH. In addition, it has been shown that the presence of sulfates accelerates the removal of CIP and SMX but their presence had no effect on the oxidation of SALBU [33]. This latter result highlights the selectivity of the reaction between organics and sulfate radicals.

Consequently, our model has been implemented with the consideration of these reactions. The total oxidation rate of organics is expressed by the sum of the rate of electron transfer, $\Gamma_e -$, the rate of reaction with ˙OH, $\Gamma_{\cdot OH}$ and the rate of reaction with $SO_4^{\cdot -}$ (called salt effect: SE), Γ_{SE}.

$$\Gamma = \Gamma_{e-} + \Gamma_{OH} + \Gamma_{SE} \tag{35}$$

The reaction rate, Γ_{SE} (mol s^{-1}), is described by a pseudo first-order kinetic:

$$\Gamma_{SE} = k_{SE} C(t) \tag{36}$$

k_{SE} (s^{-1}) is the pseudo-first-order constant rate due to SE.

Taking into account the additional oxidation of the active electrolyte, the oxidation rate is expressed by combining Eqs. (28) and (36):

$$\frac{dC(t)}{dt} = -\frac{2Ak_d}{V} C(t) - k_{SE} C(t) \tag{37}$$

In the case of $j > j_{lim,{}^{\cdot}OH}$, the temporal variation of organics can be calculated from Eq. (38):

$$C(t) = C^0 exp\left(-\left(\frac{2Ak_d}{V} + k_{SE}\right)t\right) \tag{38}$$

For non-electroactive organics,

$$C(t) = C^0 exp\left(-\left(\frac{Ak_d}{V} + k_{SE}\right)t\right) \tag{39}$$

To investigate the role of sulfate species and validate the implemented model (Eq. (39)), the results obtained from experiments were compared with the model using two concentrations of sulfate. Indeed, a previous study [33] showed that the amount of sulfate radicals is negligible in 0.02 M K_2SO_4 in comparison with that of 0.1 M K_2SO_4 at pH = 4. Fig. 4 shows the comparison of the temporal variation of the normalized CIP concentration, using both electrolytes.

The acceleration of CIP oxidation is observed when the sulfate anolyte concentration is the highest. In 100 min, 94% of CIP was removed

Table 5
Applied current density, initial limiting current and the calculated critical time for the electrolyses.

	[CIP]^0 (μM)	j (mA cm^{-2})	$j^0_{lim,ne-}$ (mA cm^{-2})	$j^0_{lim,^{\cdot}OH}$ (mA cm^{-2})	α	t_{cr} (min)
$j^0_{lim,ne-} < j < j^0_{lim,^{\cdot}OH}$	52	0.72	0.023	0.90	0.8	34
$j > j^0_{lim,^{\cdot}OH}$	62	1.45	0.027	1.07	1.36	–
	59	7.24	0.026	1.02	7.10	–

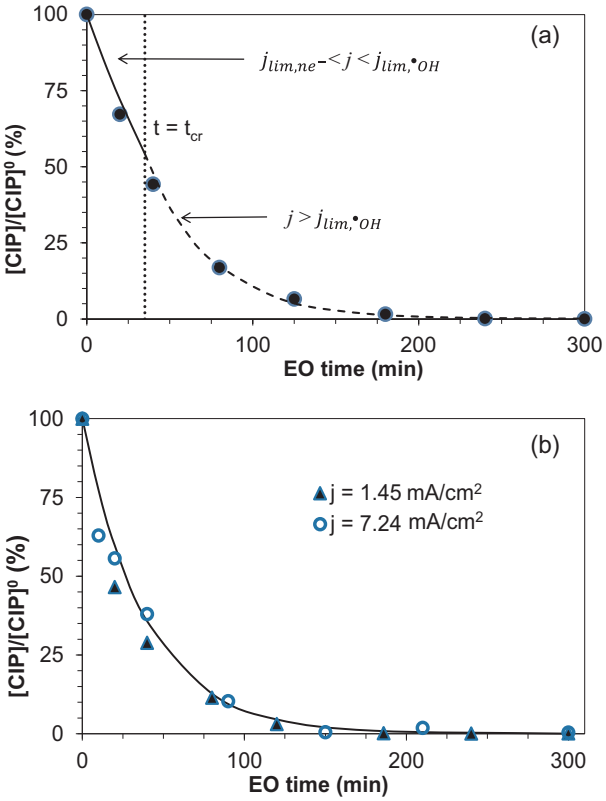


Fig. 6. Experimental (symbol) and simulated (line) values of concentration versus electroxidation time $k_d = 2.3 \times 10^{-5}$ m s^{-1}, $k_{SE} = 1.12 \times 10^{-4}$ s^{-1}, T = 30 °C, pH = 4, [K_2SO_4] = 0.1 M, [CIP]^0 = 0.052 mM. (a) $j^0_{lim,ne-} < j < j^0_{lim,OH}$ (Eq. (19)), continuous line – ; $j > j_{lim,^{\cdot}OH}$ (Eq. (29)), dashed line —, j = 0.72 mA cm^{-2}, range of potential difference: 3–3.9 V. (b) $j > j^0_{lim,^{\cdot}OH}$ simulated values calculated from Eq. (38), j = 1.45 and 7.24 mA cm^{-2}, range of potential difference: 3.7–4.0 and 4.5–4.8 V.

Table 6
Composition of solutions, limiting and applied current density of electrolysis of Fig. 7.

	Organics	Electro-activity	C^0 (μM)	$j^0_{lim,^{\cdot}OH}$ (mAcm^{-2})	j (mAcm^{-2})
Single solution	CIP	Yes	69	1.20	7.24
Multi-Component solutions	CIP	Yes	42	1.30	7.24
	Urea	No	90		
	CIP	Yes	76	2.51	7.24
	SMX	Yes	60		

in the highest concentration of K_2SO_4 whereas it takes 150 min to reach the same removal rate in 0.02 M K_2SO_4. Inversely, Fig. 4(b) shows that the SALBU oxidation is independent of the K_2SO_4 concentration, which confirms that the sulfate radical is selective for the reaction with organics.

The modelling degradation of pharmaceuticals, taking into account the active salt effect (0.1 M K_2SO_4) is calculated from Eq. (38). k_{SE} in this equation was experimentally estimated by electroxidation of SMX in K_2SO_4 0.1 M and 0.02 M electrolytes. Details are provided in

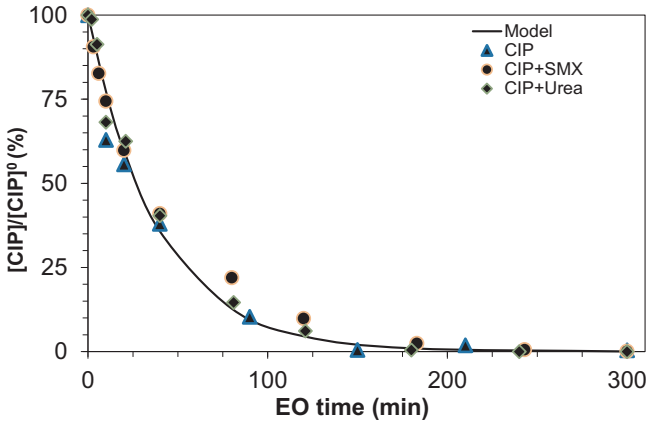


Fig. 7. Experimental (symbol) and simulated (line) concentrations of CIP during electrolysis of solutions (given in Table 5) at $j > j^0_{lim,^{\cdot}OH}$, $k_d = 2.3 \times 10^{-5}$ m s^{-1}, $k_{SE} = 1.12 \times 10^{-4}$ s^{-1}, T = 30 °C, pH = 4, range of potential difference: 4.5–4.8 V, electrolyte: K_2SO_4 0.1 M.

Supplementary Materials S1. A value of 1.1×10^{-4} s^{-1} was found for k_{SE}. This value is very close to the one provided in the literature: 1.3×10^{-4} s^{-1} [44].

The comparison of the experimental data and the model taking into account the reaction of CIP with the "activated" electrolyte (in the case of 0.1 M K_2SO_4) or without (in the case of 0.02 M K_2SO_4) shows a good correlation. In addition, the model confirms the non-reaction between sulfate radicals and SALBU.

4.2. Influence of the electroactivity

Three electrolyses were performed with a solution containing a single organic: CIP, SMX and urea under mass transfer control conditions ($j > j_{lim,^{\cdot}OH}$, 4.5–4.8 V was the measured difference of potential, this value was stable during the electrolysis. Fig. 5 illustrates the temporal variation of concentrations of these organics over electroxidation time. As expected, the complete removal of the electroactive organics (CIP and SMX) was obtained with quite similar degradation rates. In addition, the excellent correlation between the experimental data and predicted values with Eq. (29) is observed for electroxidation of all tested electroactive organics.

However, the degradation of the non-electroactive specie, urea, shows a lower rate, comparing to two electroactive pharmaceuticals under the same operating conditions. Indeed, the two pharmaceuticals, which are electroactive, can be oxidized through two pathways: direct and indirect exchange of electrons via $^{\cdot}OH$, while urea, which is non electro-active, reacts only with hydroxyl radicals. There is a good correlation between experimental degradation of urea and the model for non-electroactive organics.

4.3. Influence of the current density

In order to investigate the influence of the applied current density on the degradation of pharmaceuticals, the electroxidation of CIP was performed at various applied current densities corresponding to different regimes, $j^\circ_{lim,ne-} < j < j^\circ_{lim,^{\cdot}OH}$ and $j > j^\circ_{lim,^{\cdot}OH}$. The operating

conditions of each electrolysis are presented in Table 5 and the variation of CIP during electrolysis is shown in Fig. 6. It can be observed in Fig. 6 (a) that the model correlates well with the experimental data for both regimes: $j^0_{lim,ne-} < j < j^0_{lim,^{\cdot}OH}$ and $j > j^0_{lim,^{\cdot}OH}$. Fig. 6 (b) shows that for two current densities (j = 1.45 and 7.24 mA cm^{-2}), CIP concentration decreases with the same rate and 100% of CIP was removed after 180 min of electrolysis. The removal rate of CIP is unlikely to depend on the applied current intensity when operating in the regime of $j > j^0_{lim,^{\cdot}OH}$. Furthermore the model is validated for all applied current densities.

4.4. In the presence of other organics

Electrolyses were performed in two multicomponent solutions containing pharmaceuticals or common organic. The variation of the CIP concentration during electrolysis has been compared with the one obtained in a single solution. For each case, the electrolysis was controlled by mass transfer ($j > j^0_{lim,^{\cdot}OH}$). The operating conditions are shown in Table 6.

Fig. 7 presents the experimental and simulated variation of the CIP concentrations during electrolysis in different solutions (single and multi-component solutions).

After 180 min the removal of CIP is complete for all solutions, which indicates that the presence of other compounds (SMX or Urea) has no significant impact on the CIP oxidation rate. Excellent correlation of experimental and modelling simulation were obtained.

It can be expected that this model can be applied to wastewater that contains more organics to predict the temporal concentration of various target organic compounds.

5. Conclusion

An easy-to-use model has been proposed and validated by the experimental results to predict the variation of the concentration of a target organic in the electrochemical oxidation process using a BDD anode. The contribution of the types of transfers in the oxidation process has been emphasized: electrons (direct oxidation), atoms of oxygen via the reaction with either hydroxyl radicals or with strong electrogenerated oxidants. The proposed model showed a strong correlation between the experimental data obtained for various operating conditions : concentrations of sulfate, current densities.

Because real solutions always contain other organic compounds, a study was performed by taking into account the presence of another pharmaceutical compound (SMX) or a common organic compound (urea). In each case, the experiment and the modelling showed that the presence of such compounds did not affect the degradation of the target compound, ciprofloxacin.

In addition, this model was implemented to take into account the effect of salts. Indeed, the presence of some anions, under polarization, can generate powerful oxidants and so accelerate the degradation of target molecules. For example, it was shown that 50% gain in time for electrolysis was obtained in the presence of sulfate for the complete removal the CIP antibiotic.

In summary, regarding the target molecule, to use this model, the input parameters are: the number of exchanged electrons for direct oxidation, n; the electroactivity on BDD; in the case of the presence of electroactive salts (such as sulfate), the reaction rate with the electrogenerated oxidants from salts (described and estimated by a pseudo-first-order kinetic in this study). The excellent correlation between experimental results and predicted values from the model simulations in all conditions indicate that this model enables a wide application to predict the oxidation behaviour of electroactive and non-electroactive organics at various applied current densities in single and mixed solutions.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cej.2017.09.164.

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