



Electrochemical treatment of aqueous solutions containing one or many organic pollutants at boron doped diamond anodes. Theoretical modeling and experimental data

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ABSTRACT

The electrochemical oxidation of organics in water at boron doped diamonds (BDD) was experimentally investigated with the aim to discuss the correlations among the conversion of the pollutants and the instantaneous current efficiency *ICE* with the operative conditions. A simple theoretical model previously developed for the oxidation of oxalic acid accounting for the cases of mass transfer control, oxidation reaction control and mixed kinetic regimes was adopted and extended to challenge its predictive capability in the case of organics of different nature and in systems with more pollutants. A quite good agreement, between theoretical predictions and experimental data pertaining to the electrochemical oxidation of numerous organics, including some carboxylic acids and aliphatic chlorides, was observed, both for experiments performed in the presence of one or more organics. Results clearly indicate that such a simple model can be used to describe properly the “direct oxidation” (including oxidation by anodic electron transfer or by means of hydroxyl radicals) of organics at BDD. The comparison between the theoretical model and the experimental data strongly sustained the hypothesis that oxalic acid is oxidized by anodic electron transfer exchange while formic and maleic acids by reaction with hydroxyl radicals.

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1. Introduction

The electrochemical oxidation of organics has been widely investigated for both synthetic and environmental purposes [1–4]. It has been demonstrated that the performances of environmental remediation processes, in terms of final abatement of the pollutants and current efficiencies, depend dramatically on the nature of the anode material. Boron doped diamond (BDD) films are among the more promising anodic materials for the complete oxidation of organics in water (e.g., “electrochemical incineration”) and the more cited in the recent pertaining literature [5–7]. Thus, a very large series of organics can be successfully oxidized to carbon dioxide at BDD anodes that are very stable for long times also in quite aggressive media. For a given electrode, the performances of the process depend on many operative conditions such as the composition of the aqueous stream, the pollutant concentrations, the current density, the flowdynamic regime and the adopted reactor configuration. Quite often the high number of operative parameters which may be adjusted makes an empirical investigation exceedingly onerous in order to individuate the conditions which allow

the optimization of the electrochemical process. In this perspective, theoretical models can offer useful strategies for both the individuation of the parameters that affect more the competition between the targeted reactive path and side unwanted reactions and the design of new materials/apparatuses that can favour the selective occurrence of the desired route. The experimental validation of mathematical models can, furthermore, provide precious indications for scale-up stages and confirm the assumptions on which the model is based allowing a reliable description of the process. As far as the electrochemical abatement of organic pollutants in wastewater is concerned, unwanted reactions should be severely minimized in order to avoid the formation of secondary pollutants and/or an increase of energetic costs. Hence, the modeling of these processes has attracted in the last years the interest of numerous researchers [8–23,40]. Particular attention was devoted to processes performed at BDD, due to the extreme efficacy of this electrode toward the oxidation of numerous pollutants. Oxidation by electron transfer at the anode surface and oxidation by means of hydroxyl radicals, whose main stages occur at the electrode surface, were in literature often classified as “direct processes” while oxidation by means of other electrogenerated oxidants, that generally take place in homogeneous phase, are called “indirect processes” [4]. The modeling of both “direct” and “indirect processes” was attempted by various authors as recently reviewed

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[17]. Comninellis and co-authors proposed a very simple theoretical kinetic model with no adjustable parameters for the oxidation of organics in batch systems with galvanostatic alimentation. Authors assumed that the electrochemical oxidation of the organic compound at BDD at high anodic potentials, close to oxygen evolution, is a fast reaction and it is controlled by mass transport toward the anode [13,14]. As a consequence, this model allows to fit with accuracy experimental data when the current efficiency in the absence of mass transfer limitations is close to 100% and it does not allow to predict the evolution of the concentrations of different specie present in the system. On the other hand, this simple model presented a very good agreement with experimental data for several organic compounds and various operative conditions for what concern the evolution of COD with the time or the charge passed.

Polcaro and co-authors reported a more complex model with the aim of evaluating the trends of the concentrations of the starting pollutant and intermediate products in the stagnant layer and in the bulk [18]. A diffusion-reaction model was, in particular, used for the diffusion layer while the bulk of the solution was represented by a stirred-tank reactor. By a numerical solution of pertaining equations (mass balance equations in the bulk and in the stagnant layer for the starting pollutant and intermediates and in the diffusion layer for hydroxyl radicals), authors were able to predict the temporal drift of the concentration of different compounds present in the bulk of the solution during the electrolyses, as well as the evolution of the space profile of the species. Furthermore, the model applied also to the case of an oxidation process that gives rise to a current efficiency lower than 100% in the absence of mass transfer limitations.

In order to reduce the mathematical complexity of theoretical models aimed to describe the concentrations of compounds involved in the oxidation process, Rodrigo and co-authors considered some simplifying assumptions. Their models divide the electrochemical reactor into three zones: two close to the electrodes (electrochemical zones) and a third corresponding to the bulk of the solution (chemical zone) that were considered as consecutive stirred-tank reactors [19–21]. Hence, in each zone, the concentration was assumed to depend on the time passed but not on the position.

We have recently modeled the direct oxidation of oxalic acid at both metal oxide electrodes [11] and at BDD [22]. Later also the indirect oxidation by means of active chlorine generated by the oxidation of NaCl was studied in detail [23].

The proposed model, developed as an extension of the model of Comninellis et al. [13–14], was very simple and allowed to describe the effect of several parameters on the oxidation of oxalic acid [22]. On the other hand oxalic acid is known to present a very single behaviour in comparison with other organics, including other carboxylic acids [22,35]. In particular, oxalic acid is likely to be oxidized by direct electron transfer at the BDD surface in contrast with most of organics that are expected to be oxidized by means of electrogenerated hydroxyl radicals [29,35]. Thus, in this paper we have tested the possibility of using this model for the oxidation at BDD of numerous organics presenting very different characteristics (namely, oxalic, formic and maleic acid, 1,2-dichloroethane and 1,1,2,2-tetrachloroethane). Moreover, the model was extended to take in account the possible presence of more organics in the same solution. Theoretical predictions were compared with experimental data and allowed, without a significant computational effort, a proper description of the effect of numerous operative parameters (such as the current density, the flowdynamic regime and the pollutants concentration) on the performances of the process and the prediction of the concentration profiles of the main specie present in the system for electrolyses performed in the presence of more organics.

2. Experimental

Electrolyses were performed in different systems: systems **Ia** and **Ib** were constituted of a bench-scale batch undivided or divided (through a cation-exchange membrane Nafion 324) glass cell, respectively, equipped with a SCE reference electrode, a BDD-Nb thin sheet anode (wet surface area in most cases 4.5 cm^2) and a nickel cathode. Anodic solution was stirred by magnetic stir bar. The volume of each compartment was usually of about 60 mL. System **II** was constituted of a batch reaction system with continuous recirculation of 250 mL of electrolytic solution, previously described in detail [22]. The cell was undivided and equipped with a BDD-Nb thin sheet anode (surface area 9.14 cm^2) and one nickel cathode. Amel 2055 potentiostat was used for electrolyses. Samples of the electrolytic solution were periodically taken and analyzed during the electrolyses to evaluate the performances of the process in terms of conversion of the acid during the different stages of the experiments. The electrochemical oxidation of maleic acid was performed in the divided cell **Ib** to avoid the cathodic reduction to the succinic acid [29] while that of the aliphatic chlorides in a simple sealed undivided cell **Ia** with a low free volume, to avoid the release of these volatile compounds. The electrochemical oxidation of formic and oxalic acid, was, otherwise, carried out in system **II** to evaluate also the effect of flowdynamic on the performances of the process. Carboxylic acid and aliphatic chlorides concentrations were evaluated by liquid and gas chromatographic analyses respectively, as previously reported [22,24]. For some experiments, the trend of the oxidative process was monitored by measuring the chemical oxygen demand (COD); for this kind of analyses an Ocean Optic UV-Vis Spectrophotometer (DH-2000) was used. The supporting electrolyte was composed by Na_2SO_4 (about 0.035 M) (Janssen Chimica) and H_2SO_4 (Sigma-Aldrich). All these chemicals were analytical grade. BDD anodes were supplied by Condias. The thickness of the stagnant layer for the adopted experimental conditions was estimated through a typical limiting-current essay as previously reported [22]. The diffusion coefficient D was estimated, according to the literature, to be $10^{-5}\text{ cm}^2\text{ s}^{-1}$ for 1,2-dichloroethane and 1,1,2,2-tetrachloroethane [36] and $1.1 \times 10^{-5}\text{ cm}^2\text{ s}^{-1}$ for oxalic acid [22,37]. In the case of maleic acid, the diffusion coefficient was considered similar to that of the succinic one ($0.9 \times 10^{-5}\text{ cm}^2\text{ s}^{-1}$ [38]). In the case of formic acid, higher values of D are usually reported for water solutions of about $1.3 \times 10^{-5}\text{ cm}^2\text{ s}^{-1}$ [38]. On the other hand, in a previous paper on the electrochemical oxidation of formic acid in micro reactors at BDD anode, the mass transfer to the anode was successfully modeled considering a value of D of $10^{-5}\text{ cm}^2\text{ s}^{-1}$ [39]. Since the concentrations profile of formic acid for a process under mass transfer control was quite similar to that of oxalic acid (see Section 4.1 and Fig. 1a), the same value of D of $1.1 \times 10^{-5}\text{ cm}^2\text{ s}^{-1}$ was considered for both acids.

3. Theoretical considerations and mathematical model

3.1. Reaction mechanism and main hypotheses of the model

The electrochemical oxidation of water at BDD has been extensively investigated by various authors [6,17]. Oxygen evolution at BDD starts at about 2.3 V vs. SCE by oxidation of water and formation of hydroxyl radicals [17,25,26]. Many authors have supposed, on the bases of the poor adsorption ability of the BDD surface, that hydroxyl radicals generated by water oxidation at BDD are quasi free or very weakly adsorbed on the electrode surface [5]. In the presence of organics, hydroxyl radicals can be involved competitively in their oxidation as proposed by Johnson et al. [27] and in

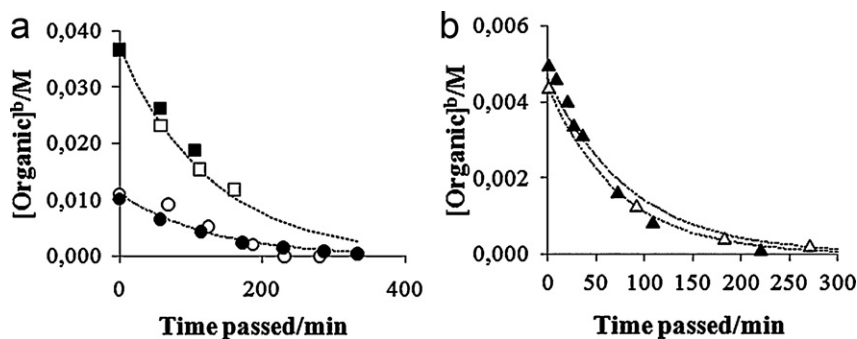


Fig. 1. Anodic oxidation of formic, oxalic and maleic acid and 1,2-dichloroethane performed at BDD under mass transfer kinetic control. (a) Reports the profiles of oxalic (operative conditions reported in Table 3, entries 1 (○) and 2 (□), respectively) and formic acid (operative conditions reported in Table 3, entries 3 (●) and 4 (■), respectively). (b) Reports the profiles of maleic acid (▲) (operative conditions reported in Table 3, entry 5) and 1,2-dichloroethane (△) (operative conditions reported in Table 3, entry 6). Theoretical curves (---) obtained by Eq. (9).

the oxygen evolution. Furthermore, organics can be oxidized by direct anodic electron transfer or by means of other electrogenerated reagents such as active chlorine, O_3 , H_2O_2 , $H_2S_2O_8$, etc. [4]. To rationalize chronoamperometric measurements performed with numerous carboxylic acids at BDD, it has been recently proposed that, in the range of potential of oxygen evolution, the oxidation of organics at diamond films involves a very fast reaction between weakly adsorbed hydroxyl radicals and organics which occurs in competition with oxygen evolution, adsorption and direct anodic oxidation of the organics [28]. As above mentioned, oxidation of free or adsorbed organics by electron transfer exchange and oxidation by means of hydroxyl radicals, that take place in the proximity of the anode, were in literature often classified as “direct processes”

while oxidation by means of other electrogenerated oxidants, that usually take place in homogeneous phase, are called “indirect processes” [4].

In the frame of this work, as above mentioned, a simple theoretical model previously tested for the anodic oxidation of oxalic acid will be, in particular, used to predict the oxidation of organics at BDD anodes by “direct processes”. Hence, this model will be synthetically described in the following and in the Section 3.2 by focusing on more relevant aspects that concern the extension to BDD anodes and reporting the more relevant theoretical equations in Table 1. In the Section 3.3 an original extension of the model to take in account the possible presence of more organics in the same solution will be presented.

Table 1
Theoretical expressions for the instantaneous current efficiency ICE and pollutant conversion X for the anodic oxidation of one organic at BDD as deduced by reference [11].

Rate determining step	ICE	X
Mixed kinetic regime	$ICE = \frac{1}{1+2[RH]^* / ([RH] + ([RH]^2 + 4[RH]^* [RH]^b)^{0.5})}$ (5)	X is obtained by numerical integration of Eq. (7): $d[X] = \frac{ICE}{nFV} dQ = \frac{dQ/(nFV)}{1+2[RH]^* / ([RH] + ([RH]^2 + 4[RH]^* [RH]^b)^{0.5})}$ (7)
Oxidation reaction $i_{lim} = nFk_m [RH]^b \gg i_{app} ICE^{OC}$ (i.e., if $[RH]^b \gg C^* ICE^{OC}$)	$ICE^{OC} = \frac{1}{1+([RH]^* / [RH]^b)}$ (6)	X is obtained by Eq. (6b) or by Eq. (6c) $[RH]^{b,Q=0} X - [RH]^* \ln(1-X) = Q/(nFV)$ (6b)
Mass transfer control $i_{lim} \ll i_{app} ICE^{OC}$ (i.e., $[RH]^b \ll C^* ICE^{OC} < C^*$)	$ICE^{MT} \approx \frac{[RH]^b}{C^*} = \frac{nFk_m [RH]^b}{i_{app}}$ (8)	$d[X] = \frac{dQ/(nFV)}{1+([RH]^* / [RH]^b)}$ (6c) $X = 1 - \exp\left[\frac{-Q}{(nFV C^*)}\right] = 1 - \exp\left[-\left(\frac{A k_m}{V} t\right)\right]$ (9)

Where X is the conversion $= ([RH]^{b,t=0} - [RH]^{b,t}) / [RH]^{b,t=0}$, $[RH]^* = [RH]^b - [RH]^* - C^*$, $C^* = i_{app} / (nFk_m)$, n is the number of electrons exchanged for the anodic oxidation of RH to carbon dioxide or to a stable product, F the Faraday constant (96487 C mol^{-1}), V the volume, Q the charge passed, k_m the mass transfer coefficient of the organic RH , ICE^{OC} and ICE^{MT} are the instantaneous current efficiency for a process under the kinetic control of the oxidation reaction and mass transfer of the pollutant, respectively.

Table 2
Electrochemical oxidation at BDD under oxidation reaction control. Fitting parameters and kinetic constants for the reaction between hydroxyl radicals and investigated organics.^a

Substrate	$[RH]^*$ (mM) ^b	p_1 ^c	p_2 ^c	k_{OH} ($\text{L mol}^{-1} \text{ s}^{-1}$) ^d
Oxalic acid	13			9.2×10^6
Formic acid	2			$0.5\text{--}1.6 \times 10^8$
Maleic acid	0.3	$0.1^e\text{--}0.45^f$	$0.55^e\text{--}0.55^f$	4.6×10^8
1,2-Dichloroethane	6			2.2×10^8
1,1,2,2-Tetrachloroethane	3			n.d.

^a System solvent supporting electrolyte (SSE): water, $\text{Na}_2\text{SO}_4/\text{H}_2\text{SO}_4$. $T = 25$ and 10°C for experiments performed in the presence of carboxylic acids and aliphatic chlorides, respectively.

^b $[RH]^*$ were estimated as fitting parameters for electrolyses performed in the presence of only one organic for a process under the kinetic control of the oxidation reaction.

^c $p_1 = r_{OA}/r_{MA}$ and $p_2 = r_{FA}/r_{MA}$ were obtained (with $[RH]^*$) as fitting parameters for the profile concentrations of oxalic, formic and maleic acids recorded during an electrolysis performed with maleic acid.

^d Rate constant for the reaction between hydroxyl radicals and investigated organics [30,31].

^e p_1 and p_2 were estimated assuming that the oxidation of maleic, formic and oxalic acid takes place by the same oxidation reaction mechanism.

^f p_1 and p_2 were estimated assuming that the oxidation of oxalic acid takes place by direct electron transfer while that of maleic and formic by means of reaction with hydroxyl radicals.

^g p_1 and p_2 were estimated assuming that the oxidation of oxalic acid takes place by direct electron transfer while that of maleic and formic by means of reaction with hydroxyl radicals.

The following assumptions were in particular made for the sake of simplicity [11]:

- Constant current electrolyses are considered since the galvanostatic mode is general preferred from an applicative point of view.
- Oxidation of organics in the range of potential of oxygen evolution is considered. Indeed, oxidation of organic pollutants is usually performed in these conditions to avoid the fouling of the electrodes.
- The oxidation of the organics is considered as a surface or a pseudo-surface processes [18] that can take place under oxidation reaction control, mass transfer control or under mixed kinetic regimes depending on the rate of mass transfer of the pollutant toward the anodic surface in comparison with the oxidation rate. Thus, as above mentioned, hydroxyl radicals generated at BDD are expected to exist as weakly physical adsorbed on the anodic surface or as free molecules that can diffuse for a very thin portion of the diffusion layer due to their very high reactivity.
- The chemi-adsorption of the organic pollutant RH and of its oxidation products is considered to be negligible or, anyway, not affecting significantly the oxidation rates of water and of the organic itself.

3.2. Oxidation of one organic

As a consequence of above mentioned assumptions, the instantaneous current efficiency ICE for the treatment of waste waters contaminated by one organic pollutant can be given by the following expression [11]:

$$ICE = \frac{i_{RH}}{i_{app}} = \frac{i_{RH}}{i_{RH} + i_{O_2}} = \frac{1}{1 + (i_{O_2}/i_{RH})} = \frac{1}{1 + ([RH]^* / [RH]^{y=0})} \quad (1)$$

where i_{RH} and i_{O_2} are the current densities involved in the oxidation of the organic and in the oxygen evolution process, respectively, i_{app} is the applied current density, $[RH]^{y=0}$ is the concentration of the organic RH at the anodic surface and the term $[RH]^*$ is the value of $[RH]^{y=0}$ which gives a current density for the RH oxidation equal to the current density involved for the oxygen evolution reaction, e.g. the value of $[RH]^{y=0}$ that gives a current efficiency of 50% [11].

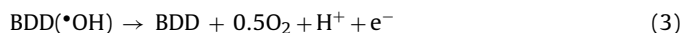
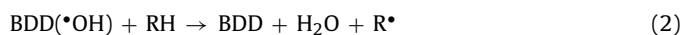
If the oxidation of the organic takes place by direct anodic oxidation with n electrons exchanged per each molecule, $[RH]^*$ is given by $[RH]^*_{dir} = 2r(E)/nk(E)$ where $k(E)$ is the heterogeneous rate constant for the oxidation of RH and $r(E)$ is the rate of the solvent oxidation. In particular, if the transfer coefficient α assumes similar values for the oxidation of water and the organic, $[RH]^*_{dir}$ is given by the following expression and does not depend on the working potential and the current density [11]:

$$[RH]^*_{dir} = \left(\frac{k'}{k_{RH}} \right) \exp \left[(1 - \alpha)F \left(\frac{E^{\circ}_{RH} - E^{\circ}_W}{RT} \right) \right]$$

where k' is given by the product of the standard rate constant for the oxidation of the solvent and the solvent concentration and E°_W is the standard potential for the oxidation of the water. As a consequence $[RH]^*_{dir}$ is expected to be dependent only on the nature of the organic and on the temperature.

On the other hand, if the oxidation takes place by means of hydroxyl radicals, the physical meaning of $[RH]^* = [RH]^*_{HO}$ for BDD anode is more difficult to be assessed. Thus, according to the pertaining literature, it is not clear if hydroxyl radicals reacting with organics (Eq. (2)) are free or physically adsorbed to the anode surface and different mechanism were proposed for the oxygen evolution at BDD [17]. In particular, two probable mechanisms involve the anodic oxidation of the hydroxyl radical (Eq. (3)) or the coupling of two HO^{\bullet} . Note that coupling of HO^{\bullet} can proceed

toward the formation of hydrogen peroxide which can at its turn be oxidized to oxygen [11].



In all cases, the value of $[RH]^*_{HO}$ must depend on the nature of the organic while different relationships between $[RH]^*_{HO}$ and i are expected depending on the proposed reaction mechanism. Thus, the effect of the current density on $[RH]^*$ has to be assessed by experimental tests. In this perspective, the effect of i on ICE for experiments performed under the kinetic control of the oxidation reaction (e.g., high organic concentrations and low current densities) has to be evaluated. A large series of data was reported in the literature concerning these operative conditions and no effect of the current density is usually reported (see as an example reference [29]). On the other hand, under usually adopted operative conditions, the oxidation of organics usually proceeds at BDD with very high current efficiencies close to 100% so that the effect of the current density is not easy to be evaluated. Thus, in this work we have performed some experiments under the kinetic control of the oxidation reaction by working at quite low values of both current density and organic concentration in order to have $ICE < 100\%$. Experiments were performed in the presence of formic acid (initial concentration 10 mM) that, according to the literature, is expected to be oxidized at BDD anodes by means of hydroxyl radicals, at 1 and 2 mA/cm². Quite interestingly, as discussed more in detail in the Section 4.2, no an appreciable effect of the current density was observed under adopted conditions (Fig. 5a and Table 3, entries 7 and 17) in spite of the fact that ICE values lower than 80% were recorded. Quite interestingly, no effect of the current density on ICE was observed for a process under the kinetic control of the oxidation reaction also for oxalic acid, which is likely to be involved in a oxidation by direct anodic electron transfer [22]. Hence, $[RH]^*$ was here assumed, in a first approximation approach, not to depend on the current density for both oxidations performed by anodic electron transfer or reaction with hydroxyl radicals. Please note that according to above mentioned considerations, $[RH]^*$ is not easy to be obtained by theoretical estimations. On the other hand, for a given substrate $[RH]^*$ can be easily obtained by fitting experimental data by Eq. (6) for a process under the kinetic control of the oxidation reaction.

Under pseudo-steady state conditions, prevailing during an electrolysis carried out with amperostatic alimentation, the following expression should apply:

$$k_m([RH]^b - [RH]^{y=0}) = \frac{i_{app} ICE}{nF} \quad (4)$$

where k_m is the mass transfer constant and $[RH]^b$ is the concentration of the organic in the bulk of the aqueous phase. Hence, by combination of Eqs. (1) and (4) and elimination of the term $[RH]^{y=0}$, one can obtain, as previously reported in literature [11], the expression for the ICE reported in Eq. (5) in Table 1. In the limiting cases of an organic concentration, respectively, strongly higher and strongly lower than $C^* = i_{app}/(nFk_m)$ the expressions reported in Table 1 can be furthermore considered [11,22].

3.3. Oxidation of a multi component polluting mixture

If more organics are present in the system since the beginning of the electrolysis or as a result of the formation of intermediates, Eq. (1) has to be properly modified. As an example in the case of the presence of two organics named, respectively, $RH(I)$ and $RH(II)$,

Table 3
Experimental conditions adopted during the experiments performed with the initial presence of one organic.^a

Entry	Cell	Pollutant	C ⁰ (mM)	<i>i</i> _{app} (mA cm ⁻²)	Φ _v (mL min ⁻¹)	<i>K</i> _m (cm s ⁻¹)
1	II	OA	10	39	0.2	0.0039
2	II	OA	37	39	0.2	0.0039
3	II	FA	10	39	0.2	0.0039
4	II	FA	37	39	0.2	0.0039
5	Ib	MA	4.6	25		0.0018
6	Ia	DCA	4.4	15		0.0023
7	II	FA	10	1	1.2	0.0086
8	II	OA	50	17	1.2	0.0086
9	Ia	DCE	15	15		0.0023
10	II	FA	10	20	1.2	0.0086
11	Ia	DCE	4	15		0.0023
12	II	FA	100	17	1.2	0.0086
13	II	FA	100	39	0.2	0.0039
14	II	OA	100	17	1.2	0.0086
15	II	OA	100	39	0.2	0.0039
16	II	OA	100	39	1.2	0.0086
17	II	FA	10	2	1.2	0.0086
18	II	FA	10	5	1.2	0.0086
19	II	FA	10	20	1.2	0.0086
20	Ib	MA	22	6		0.0018
21	Ib	MA	22	12.5		0.0018
22	Ib	MA	22	20		0.0018
23	Ia	TCE	4	20		0.0023
24	Ia	TCE	4	4.5		0.0023
25	Ib	MA	83	25		0.0018
26	Ib	MA	42	25		0.0018
27	Ib	MA	20	25		0.0018
28	Ia	DCE	15	15		0.0023
29	Ia	DCE	13	15		0.0023

^a Amperostatic electrolyses of water solutions of oxalic acid (OA), formic acid (FA), maleic acid (MA), 1,2-dichloroethane (DCE) and 1,1,2,2-tetrachloroethane (TCE). Experiments performed with carboxylic acids and aliphatic chlorides at room temperature and 10 °C, respectively. Electrolytic solution: Water, Na₂SO₄, H₂SO₄ (pH 2).

oxidized by the same route, the following equation can be applied:

$$k_{m(i)}([RH(i)]^b - [RH(i)]^0) = i_{app} ICE(i)/nF \quad i = 1, 2, \dots, m \quad (14b)$$

Please, consider that all the equations above presented can be readily used for the prediction of the abatement of the organics contained in the mixture and the current efficiency since all the involved parameters can be easily determined or estimated *a priori*. Thus the mass transfer coefficients can be readily obtained from equation $k_m = D/\delta$. The diffusion coefficient D can be often found in literature, computed by electroanalytical experiments or by the Wilke-Chang expression, the thickness of the stagnant layer δ can be estimated through a typical limiting-current essay [22] while the value of $[RH]^*$ for a given organic can be estimated by electrolyses performed under the kinetic control of the oxidation reaction and fitting the data through Eq. (6).

4. Results and discussions

4.1. Comparison between experimental data and theoretical model for the electrochemical abatement of a single organic substance

A comparison between the theoretical model above discussed and experimental data relative to the electrochemical oxidation of three carboxylic acids (namely, oxalic, formic and maleic acid) and two aliphatic chlorides (1,2-Dichloroethane and 1,1,2,2-Tetrachloroethane) at BDD was carried out. These substances were chosen as model compounds for several reasons. Carboxylic acids are common intermediates of the chemical and electrochemical oxidation of several compounds. They are rather stable and are often mineralized at longer times with respect to the starting substrates. Thus, in advanced oxidation processes (AOPs), including electrochemical processes, various carboxylic acids (usually oxalic, formic, acetic and maleic) are usually formed and their slow mineralization by means of hydroxyl radicals prolongs the processing time with consequently higher costs of the treatment [33,34].

$$ICE(I) = \frac{i_{RH(I)}}{i_{app}} = \frac{i_{RH(I)}}{i_{RH(I)} + i_{RH(II)} + i_{O_2}}$$

$$= \frac{1}{1 + (i_{O_2}/i_{RH(I)}) + (i_{RH(II)}/i_{RH(I)})}$$

Hence, by assuming that the competition between the oxidation of the organic $RH(i)$ and the oxygen evolution is not affected by the presence of other organics the current efficiencies for the oxidation of $RH(I)$ and $RH(II)$ can be simply given by the following equations:

$$ICE(I) = \frac{1}{1 + ([RH(I)]^*/[RH(I)]^{y=0})(1 + ([RH(II)]^{y=0}/[RH(II)]^*))} \quad (10)$$

$$ICE(II) = \frac{1}{1 + ([RH(II)]^*/[RH(II)]^{y=0})(1 + ([RH(I)]^{y=0}/[RH(I)]^*))} \quad (11)$$

$$k_{m(I)}([RH(I)]^b - [RH(I)]^0) = \frac{i_{app} ICE(I)}{nF} \quad (12)$$

$$k_{m(II)}([RH(II)]^b - [RH(II)]^0) = \frac{i_{app} ICE(II)}{nF} \quad (13)$$

where $[RH(i)]^*$ is the $[RH]^*$ value for a solution contained only the organic pollutant denoted $RH(i)$.

If $k_{m(i)}$ and $[RH(i)]^*$ are estimated by proper experiments, one have a system of 4 equations (Eqs. (10)–(13)) and 4 variables that can be easily computationally solved. Of course, a simple extension of this approach is necessary in the presence of more organic pollutants in the system (see Eqs. (14) and (14b) for a system composed by m pollutants):

$$ICE(i) = \frac{1}{1 + ([RH(i)]^*/[RH(i)]^0) \left(1 + \sum_{j \neq i} ([RH(j)]^0/[RH(j)]^*) \right)} \quad i = 1, 2, \dots, m \quad (14)$$

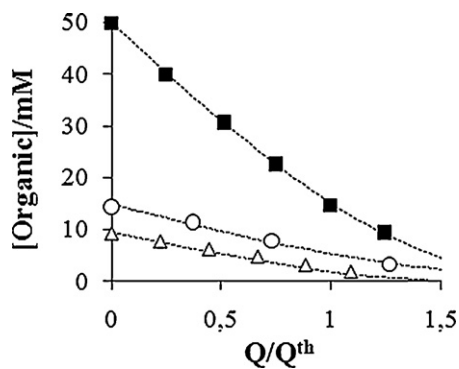


Fig. 2. Anodic oxidation of formic (Δ), oxalic (\blacksquare) and 1,2-dichloroethane (\circ) performed at BDD under oxidation reaction kinetic control. Experimental conditions reported in Table 3, entries 7–9. Theoretical curves (---) obtained by Eq. (6b) with the values of $[RH]^*$ listed in Table 2. Q^{th} theoretical charge necessary for complete oxidation of the organic with a process with a current efficiency of 100%.

Aliphatic chlorides are very important pollutants that, according to the recent literature, in spite of their quite high resistance to conventional oxidation processes, can be completely converted in chloride ions and carbon dioxide by electrochemical oxidation at BDD anodes in water [7,24]. The electrochemical abatement at BDD of oxalic and formic acid and 1,2-dichloroethane and 1,1,2,2-tetrachloroethane proceed without the formation of appreciable amounts of by-products while the treatment of maleic acid gives rise to the formation of formic and oxalic acids as main by-products [24,29].

Let us focus our attention first on a process kinetically controlled by mass transfer. This was realised by a series of electrolyses performed with an amperostatic alimantation, a high current density and an initial organic concentration lower than $C^* = i_{\text{app}}/(nFk_m)$. As shown in Fig. 1, experimental results are in good agreement with the theoretical predictions for all the tested substrates and at all investigated initial organic concentrations in spite of the fact that no adjustable parameters were used. The anodic treatment of water solutions of maleic acid results in the formation of some carboxylic acids as by-products, the more relevant being formic and oxalic acids [29]. On the other hand, for the experiments performed under mass transfer kinetic control very small concentrations of these products were formed. This result can be tentatively explained considering that under mass transfer control, an excess of hydroxyl radicals is generated with respect to the amount necessary for the abatement of the maleic acid coming to the electrode, thus preventing the formation of significant concentration of intermediates.

Let us consider now a process kinetically controlled by the oxidation reactions. This situation arises if one performs electrolyses with low applied current density and an initial organic concentrations dramatically higher than C^* so that the process takes place under the kinetic control of the oxidation reaction for a large part of the electrolysis up to high conversions. Experimental data were in good agreement with theoretical predictions for all the investigated organics when the parameters $[RH]^*$ (determined as adjustable parameters) reported in Table 2 were used (as shown in Fig. 2 for oxalic and formic acids and 1,1,2,2-dichloroethane).

The oxidation of formic and maleic acids proceeded with very high current efficiencies close to 100% up to low values of the concentrations of the acid so that it was necessary to perform some electrolyses with quite low values of both the initial concentration (5–10 mM) and of the current density (1–6 mA cm⁻²) to estimate the value of $[RH]^*$ for these compounds.

The different $[RH]^*$ observed for the investigated carboxylic acids correspond to different oxidation rates at BDD. In this perspective one can consider that, as shown in Table 2, the rate constant for the reaction between hydroxyl radicals and

investigated carboxylic acids k_{OH} decreases with the same order as $1/[RH]^*$. According to the literature the oxidation of oxalic acid, which presents a relatively small value of k_{OH} , is likely to take place by an anodic direct electron transfer [22,29]. The oxidation of other carboxylic acids probably involves the oxidation by means of hydroxyl radicals for a process under mass transport kinetic control [29].

Let us now discuss the general case of a process whose rate determining step during the electrolysis changes from an oxidation reaction control in the first stage to mass transfer control in the last part with a mixed regime between them. In this case a general expression for the instantaneous current efficiency has to be adopted (see Eq. (5)) and the profiles of the organic concentration during the electrolysis as a function of charge or time passed can be numerically computed by Eq. (7), that is a function of the parameters $[RH]^*$ and C^* . Indeed, all the performed experiments gave a profile of ICE vs. $[RH]^b$ and of $[RH]^b$ vs. charge passed in good agreement with theoretical predictions when the parameters $[RH]^*$ reported in Table 2 were used (see Figs. 3–6). As an example, Fig. 3 reports two experiments performed with formic acid and 1,2-dichloroethane with a value of the initial concentration of the organic close to C^* in order to have a process under a mixed kinetic regime at least for the first stages of the electrolyses. In both cases, theoretical predictions based on an oxidation or a mass transport kinetic control were not in good agreement with the experimental data while the equations based on a mixed kinetic regime predicted quite well the evolution of the concentrations of the organics with the passed charge.

The oxidation of maleic acid (MA) at BDD proceeds according to the literature with the formation of three different main products: carbon dioxide, formic acid (FA) and oxalic acid (OA), the last two products evolving by oxidation to CO₂ [29]. The competition between these routes was here described by two competition kinetic parameters named $p_1 = r_{\text{OA}}/r_{\text{MA}}$ and $p_2 = r_{\text{FA}}/r_{\text{MA}}$ (where r_{MA} is the total oxidation rate of maleic acid and r_{OA} and r_{FA} the oxidation rate of maleic acid to oxalic and formic acids, respectively). These parameters were obtained as fitting parameters together with $[RH]^*$ (see Table 2) by comparing theoretical predictions with the experimental trends of the concentration of maleic, formic and oxalic acid with the charge passed. The ICE were first computed by Eq. (14) with mass balance equations reported in Eqs. (15)–(16), by assuming that the three acids are oxidized by the same reaction path.

$$k_{m(\text{MA})}([MA]^b - [MA]^{y=0}) = \frac{i_{\text{app}} ICE(\text{MA})}{nF} \quad (15)$$

$$k_{m(\text{FA})}([FA]^b - [FA]^{y=0}) + k_{m(\text{MA})}([MA]^b - [MA]^{y=0})p_2 = \frac{i_{\text{app}} ICE(\text{FA})}{nF} \quad (16a)$$

$$k_{m(\text{OA})}([OA]^b - [OA]^{y=0}) + k_{m(\text{MA})}([MA]^b - [MA]^{y=0})p_1 = \frac{i_{\text{app}} ICE(\text{OA})}{nF} \quad (16b)$$

Quite interestingly, the sum of the competition parameters p_1 and p_2 was lower than one (see Table 2). This could indicate that a part of the maleic acid is oxidized to carbon dioxide without the intermediate formation of these compounds. In this perspective, it seems useful to observe that the formation of minor concentrations of other intermediates was observed, including malonic and fumaric acids.

It has been observed that OA is likely to be oxidized by direct electron transfer at the anode surface while FA and MA are expected

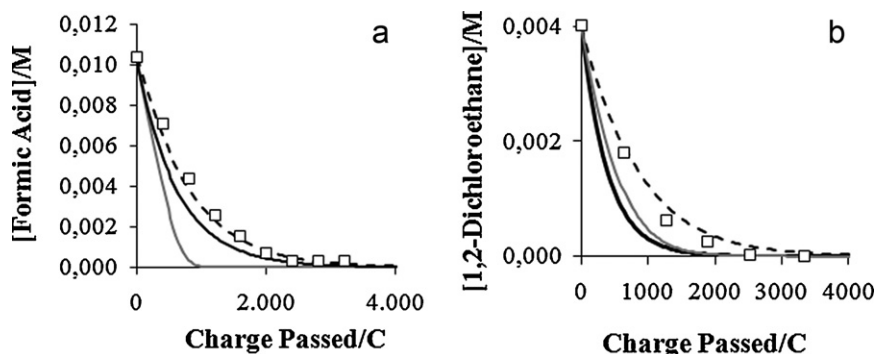


Fig. 3. Anodic oxidation of formic (a, experimental conditions reported in Table 3, entry 10, $C^* = 0.013$ M) and 1,2-dichloroethane (b, experimental conditions reported in Table 3, entry 11, $C^* = 0.006$ M) performed at BDD under mixed kinetic regime. Theoretical curves obtained for a mass transport control (Eq. (9)) (—), an oxidation reaction control (Eq. (6c)) (---) and a mixed kinetic regime (Eq. (7)) (· · ·) with the values of $[RH]^*$ listed in Table 2.

to be oxidized by means of hydroxyl radicals. In this perspective the *ICE* for the oxidation of oxalic acid can be given by Eq. (1) and that for the oxidation of the other two acids by the following equations:

$$ICE(MA) = \frac{1 - ICE(OA)}{1 + ([MA]^*/[MA]^{y=0})(1 + ([FA]^{y=0}/[FA]^*))} \quad (17)$$

$$ICE(FA) = \frac{1 - ICE(OA)}{1 + ([FA]^*/[FA]^{y=0})(1 + ([MA]^{y=0}/[MA]^*))} \quad (18)$$

In this case, experimental data could be fitted by a theoretical model based on Eqs. (1), (15)–(18) by using values of p_1 and p_2 or 0.45 and 0.55 respectively (see Fig. 5c and Table 2).

It was observed that FA presented a higher and lower concentration of the oxalic acid in the initial and final stages of the electrolyses, respectively. This is probably due to the fact that MA is preferentially converted to FA than to the OA ($p_2 > p_1$). On the other hand, oxalic acid is less easily oxidized at BDD than the formic acid, at least when it is present in low concentrations, and, as a consequence, tends to accumulate in the system.

4.2. Effect of current density, flow rate and organic concentration on the process

Let us consider now the effect of some operative parameters such as the flow rate, the current density and the initial concentration of the organic on the abatement of investigated pollutants. According to the theoretical model presented in the Section 3.2, an effect of the flow rate and of the current density is not expected for a process under oxidation reaction control (see Eq. (6)). On the other hand, *ICE* is expected to decrease linearly with i_{app} and to increase with the flow rate through its effect on the mass transfer coefficient

for a process under mass transfer control (see Eq. (8)). As shown in Fig. 4, the theoretical model well simulates the combined effect of flow rate and current density on the abatement of formic and oxalic acid. A drastic increase of the abatement occurred by increasing the flow rate from 0.2 to 1.2 L min⁻¹ and decreasing the current density from 39 to 17 mA cm⁻² for the electrolyses performed with an initial concentration of the acids of 0.1 M. Indeed, for the electrolyses performed at 39 mA cm⁻² and a flow rate of 1.2 L min⁻¹, a quite high value of C^* of 0.044 M occurs so that the process takes place for a large part of the electrolyses under mass transfer kinetic control and the combined increase of the flow rate and decrease of the current density results in a more effective mass transfer. On the other hand, no significant effect was observed increasing the current density from 17 to 39 mA cm⁻² when a flow rate of 1.2 L min⁻¹ was imposed (Fig. 4b). This is due to the fact that under these conditions, C^* assumes quite low values (lower than 0.016 M) so that the process occurs for a large part of the experiments under oxidation reaction control.

A detailed analysis of the effect of the current density on the abatement of FA and MA and 1,1,2,2-tetrachloroethane is reported in Fig. 5. For all the investigated organics a good agreement between theoretical predictions and experimental data was observed. As shown in Fig. 5a and b, an increase of the current density results in higher residual concentrations of formic acid for the same passed charge (e.g., in lower current efficiencies) but in a faster abatement (e.g., in higher productivity of the electrochemical cell). On the other hand, when one carries out the process under an oxidation reaction kinetic control by working at sufficiently low current density, a further decrease of the current does not affect the current efficiency but results in lower productivity of the cell. Correspondingly, at high current density, the process is prevalently under the

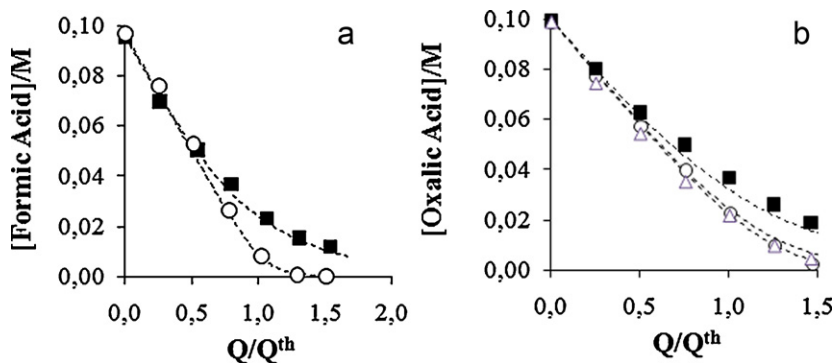


Fig. 4. Effect of flow rate and current density on the anodic oxidation of formic (a) and oxalic (b) acid at BDD. Electrolyses performed in system II at 1.2 L min⁻¹ and 17 mA cm⁻² (○, Table 3, entries 12 and 14 for formic and oxalic acid, respectively), 0.2 L min⁻¹ and 39 mA cm⁻² (■, Table 3, entries 13 and 15 for formic and oxalic acid, respectively) and 1.2 L min⁻¹ and 39 mA cm⁻² (△, Table 3 entry 16). Theoretical curves (---) obtained by Eq. (7) with the values of $[RH]^*$ listed in Table 2.

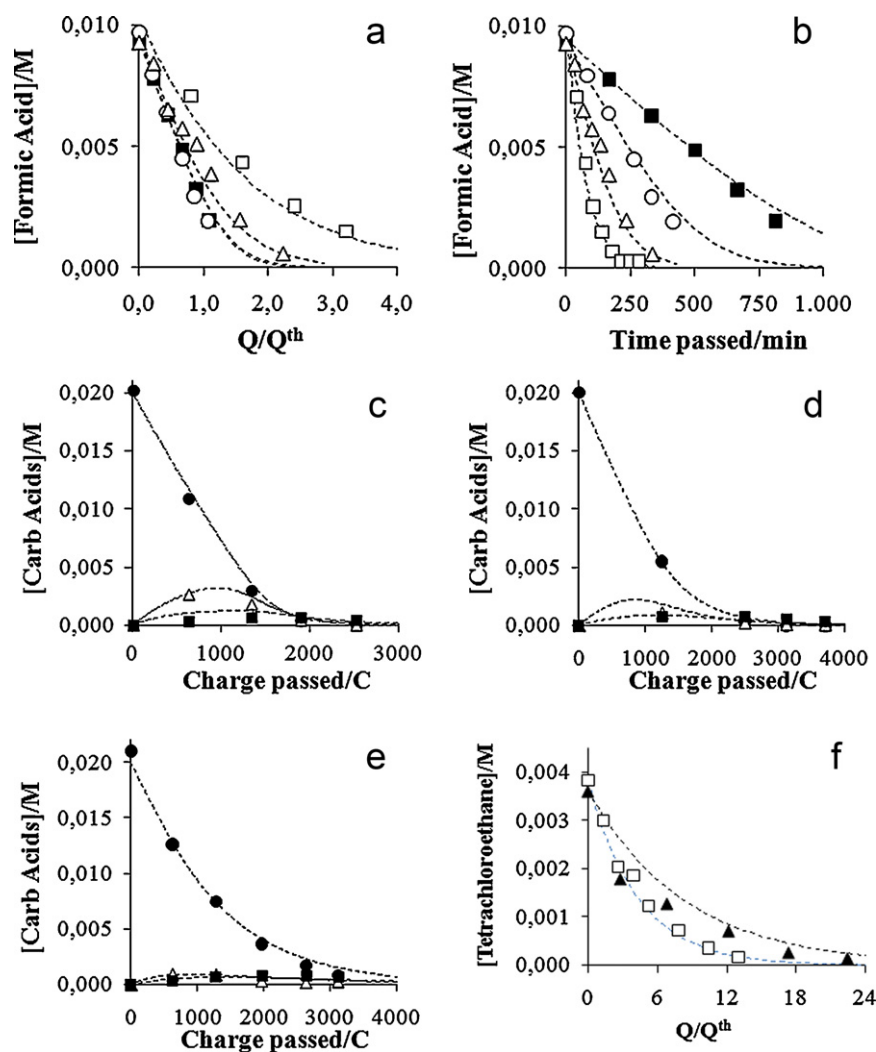


Fig. 5. Effect of current density on the anodic oxidation of formic (a and b) and maleic (c, d and e) acid and 1,1,2,2-tetrachloroethane (f) at BDD. Anodic oxidation of formic acid (initial concentration 10 mM) performed at 1 (■, Table 3, entry 7), 2 (○, Table 3, entry 17), 5 (△, Table 3, entry 18) and 20 (□, Table 3, entry 19) mA cm^{-2} . Anodic oxidation of maleic acid performed at 6 (c, Table 3, entry 20), 12.5 (d, Table 3, entry 21) and 20 mA cm^{-2} (e, Table 3, entry 22). Anodic oxidation of 1,1,2,2-tetrachloroethane performed at 20 (□, Table 3, entry 23) and 42.5 (▲, Table 3, entry 24) mA cm^{-2} . For the electrolyses performed in the presence of maleic acid, the profile concentrations of maleic (●), formic (△) and oxalic (■) acids were reported. Theoretical curves for formic acid and 1,1,2,2-tetrachloroethane (---) obtained by Eq. (7) with the values of $[RH]^*$ listed in Table 2. Theoretical curves for electrolyses of solutions of maleic acid (---) obtained by Eqs. (1), (15)–(18) with the values of $[RH]^*$, p_1 and p_2 listed in Table 2.

mass transfer control, and a further increase of the current density results in similar times of treatment but lower current efficiencies. As a consequence of these considerations, an intermediate value of the current density is likely to be a good candidate to optimize the process. A more accurate selection of the current density value needs to be based on economic quantitative considerations from one side and on accurate data on the effect of the current density on the abatement on the other side, that can be efficiently provided by the proposed theoretical model.

As shown in Fig. 5c–e, higher current densities resulted for the same amount of the passed charge, from one hand, in lower abatements of the maleic acid for the same amount of charge passed but, on the other hand, in lower concentrations of the intermediate products. Quite interestingly, the effect of current density on the concentration profiles of by-products was well captured by the model, thus showing its efficacy also in the presence of more organics in the electrochemical cell.

It is well known that the concentration of the organic affects drastically the performances of the process. In fact, both oxidation reactions and mass transfer rates are expected to decrease linearly with the organic concentration. The effect of the

initial concentration of the organic C^0 was studied by performing some series of electrolyses in the presence of maleic acid or 1,2-dichloroethane with various C^0 . As shown in Fig. 6, also in this case predictions of the model were in good agreement with experimental data. In the case of the electrolyses of solutions of maleic acid, the reduction of C^0 resulted in a dramatic decrease of the concentration of the formic acid (Fig. 6b). This is due to the fact that the reduction of C^0 results in a shift of the kinetic control from the oxidation reaction to the mass transfer one. Conversely, a less drastic reduction of the OA concentration arised (Fig. 6c). This result is effectively predicted by the model and it can be attributed to the lower oxidant ability of BDD for the oxalic acid that, as a consequence, survives in the aqueous medium for longer times also in the presence of an excess of hydroxyl radicals (computed with respect to all the organics present in the system).

4.3. Electrolyses performed in the presence of a multi component polluting mixture

In many cases of applicative interest, many organics are present from the beginning in the waste waters. In these conditions, it

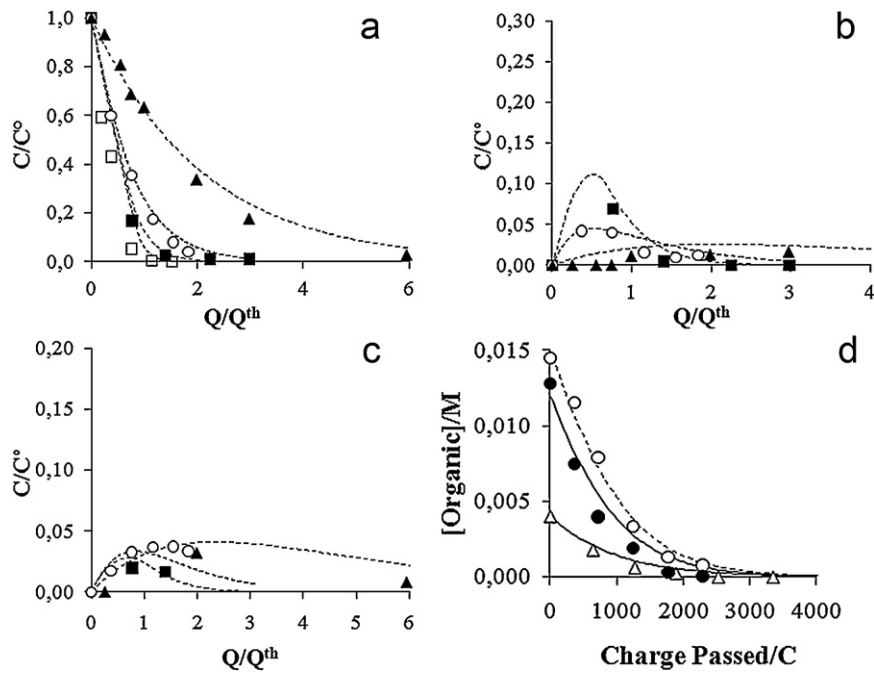


Fig. 6. Effect of the initial concentration C^0 on the anodic oxidation of maleic acid (a–c) and 1,2-Dichloroethane (d) at BDD. (a–c) Report the profile concentrations of maleic, formic and oxalic acid, respectively, for the oxidation of maleic acid. Anodic oxidation of maleic acid performed with $C^0 = 83$ (\square , Table 3, entry 25), 42 (\blacksquare , Table 3, entry 26), 20 (\circ , Table 3, entry 27) and 5 (\blacktriangle , Table 3, entry 5) mM. Anodic oxidation of 1,2-dichloroethane performed with $C^0 = 15$ (\triangle , Table 3, entry 28), 13 (\bullet , Table 3, entry 29) and 4 (\circ , Table 3, entry 11) mM. Theoretical curves for 1,2-dichloroethane (---) obtained by Eq. (7) with the value of $[RH]^*$ listed in Table 2. Theoretical curves for electrolyses of solutions of maleic acid (---) obtained by Eqs. (1), (15)–(18) with the values of $[RH]^*$, p_1 and p_2 listed in Table 2.

would be important to predict the evolution of the various species present in the system. In order to study this important case, some electrolyses were performed in the presence of mixtures of carboxylic acids. A first experiment was performed in the presence of formic and maleic acids, both the compounds presenting an initial

concentration of about 10 mM. As shown in Fig. 7a, a good agreement between experimental data and theoretical predictions arose when the values of $[RH]^*$ of Table 2 were used. A study on the electrochemical oxidation at BDD of mixtures of carboxylic acids was carried out also by Weiss and co-authors [32]. Experimental data

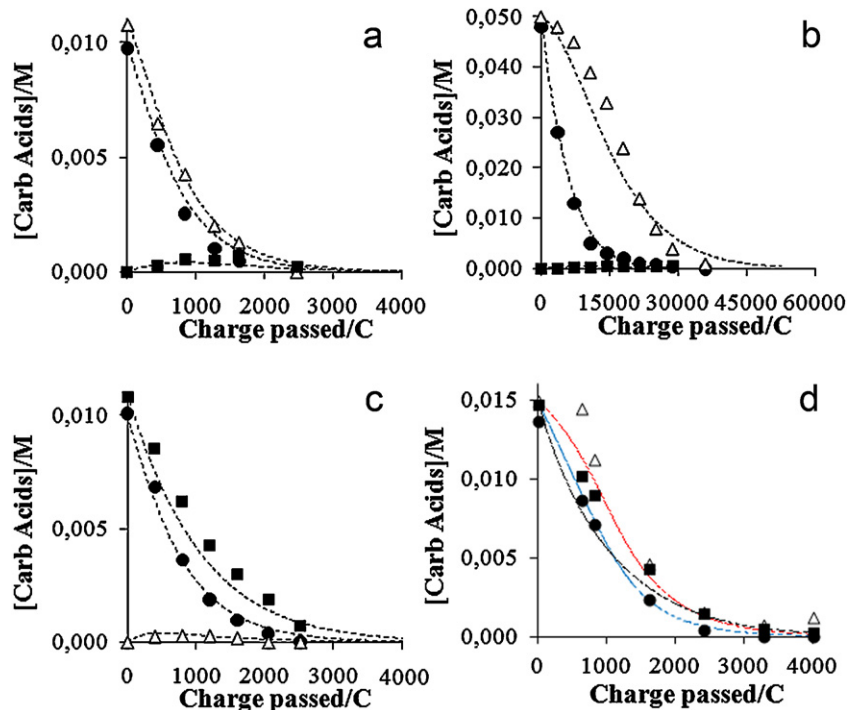


Fig. 7. Profile concentrations of maleic (\bullet), formic (\triangle) and oxalic (\blacksquare) acids for electrolyses performed in the presence of FA (10 mM) and MA (10 mM) (a), OA (10 mM) and MA (10 mM) (Fig. 7c), FA (15 mM) (Fig. 7b), FA (15 mM), OA (15 mM) and MA (15 mM) (d). Experiments performed in system Ib. System solvent supporting electrolyte (SSE): Water, Na_2SO_4 , H_2SO_4 (pH 2). (b) reports experimental data published by Weiss and co-workers [33] for the electrolysis of a solution of both FA (50 mM) and MA (50 mM) performed in an undivided cell. Theoretical curves for maleic (---), formic (---) and oxalic acid (---) obtained by Eqs. (1), (15)–(18) with the values of $[RH]^*$, p_1 and p_2 listed in Table 2.

found by these authors for the abatement of a mixture of formic and maleic acids (initial concentrations of about 50 mM for each acid) were reported in Fig. 7b. To rationalize the very high abatements observed for maleic acid, we have to focus to the fact that experiments were performed in an undivided cell [32]. Thus, the cathode reduction of maleic acid to the succinic one is expected to take place [29]. Hence, to model the process, we have assumed that the profile concentration of maleic acid resulted both from the anodic oxidation at BDD and from the cathode reduction to the succinic acid. The last process was assumed to take place under mass transfer control while the same value of $[RH]^*$ was considered, in a first approximation approach, for both formic and succinic acids. As shown in Fig. 7b, also in this case an acceptable agreement between theoretical predictions and experimental data was observed in spite of the considered approximations.

Fig. 7c reports the concentration profiles of maleic, formic and oxalic acids recorded during an electrolysis performed with an initial concentration of maleic and oxalic acid of about 10 mM. Quite interestingly, also in this case the model was able to predict the comparative rates of degradation of the two acids. As shown in Fig. 7d, when the electrolyses were performed with an initial concentration of about 15 mM of all the investigated three acids, a slower degradation of FA took place with respect to both MA and OA. Similar results were found also by Weiss and co-authors [32]. These authors performed one experiment in the presence of MA, FA and OA, all presenting a concentration of about 50 mM. Similar abatements were observed for MA e OA while FA presented drastically higher residual concentrations for the same amount of the passed charge. These results seem in contradiction with the lower values of $[RH]^*$ and the higher k_{OH} presented by the formic acid with respect to the oxalic one and they are very difficult to explain by assuming that all the investigated acids are oxidized by the same reaction path. On the other hand, as shown in Fig. 7d, experimental data are in good agreement with theoretical predictions if oxalic acid is assumed to be oxidized by direct electron transfer exchange while the other two acids by reaction with hydroxyl radicals. Thus, according to this reaction scheme, the oxidation of oxalic acid takes place in competition with the oxidation of water to hydroxyl radicals and as a consequence makes more difficult also the oxidation of maleic and formic acids. These two acids are involved in a competitive reaction with hydroxyl radicals and the formic acid, which has the higher value of $[RH]^*$, presents the lower abatement.

5. Conclusions

A simple and easily manageable theoretical model, previously developed for the oxidation of oxalic acid at metal oxide, was here extended to the oxidation of different organics at BDD anodes also in multicomponent systems. A good agreement between theoretical predictions and experimental data was obtained for all the investigated organics (namely, oxalic, formic and maleic acids, 1,1-dichloroethane and 1,1,2,2-tetrachloroethane) under different kinetic regimes i.e. in the cases of mass transfer control, oxidation control and mixed kinetic control. The effect of current density, flow rate and organic initial concentration on the performances of the process (measured in terms of current efficiency and organic abatement) were well predicted too. Interestingly, the proposed model was able to describe the concentration profiles of the species present in the system also when more organics were loaded in the electrolytic solution since the beginning of the experiments. Collected results clearly indicate that such a simple model can be used to describe properly the direct oxidation of organics at BDD. Furthermore, the comparison between the theoretical model and the experimental data strongly sustain the hypothesis that oxalic acid

is oxidized by anodic electron transfer exchange while formic and maleic acids by reaction with hydroxyl radicals.

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