
EAAOP2 2009

Electrochemical incineration of organic pollutants: effect of the nature of the pollutants and of the temperature

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Abstract

The electrochemical oxidation of some organic pollutants, including three carboxylic acids (oxalic, formic and maleic), at boron doped diamond (BDD) and DSA anodes, using galvanostatic alimentations, was investigated in order to study the effect of the temperature and of the nature of the pollutants on the process. In incineration electrolyses, the performances of the process in terms of carboxylic acid conversion and current efficiency dramatically depend on the adopted operative conditions. The abatement of the organic pollutant depends on the nature of the carboxylic acid. Quite interestingly, the opposite effect of the nature of the substrate on the performances of the process was observed at BDD and DSA anodes.

Key Words : Electrochemical incineration, influence of Temperature, BDD, DSA, Oxidation of organics

1 Introduction

Recent researches have demonstrated that electrochemical methods offer an attractive alternative to traditional routes for treating wastewaters containing toxic or/and refractory organic pollutants. [1,2]

Electrochemical incineration is the electrochemical oxidation of organics in water to carbon dioxide (see Eq. (1) for the case of oxalic acid). In particular, the incineration can involve both a direct, if the oxidation of organic substances is performed at the anode, and/or an indirect processes, if the oxidation of organic substances is performed by oxidants generated at the electrodes.



Electrochemical oxidation studies are mainly applied to the destruction of aromatic and halogenated compounds contained in industrial wastewaters. In the oxidation process, phenol derivatives are transformed into carbon dioxide through several steps that involve the formation of intermediate products such as quinones and carboxylic acids, that are generally more resistant to the anodic oxidation of starting compounds. Hence, the investigation of the electrochemical incineration of this compounds is of a certain relevance [3].

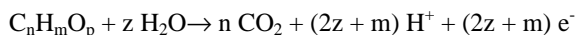
Generally, the effectiveness of the electrochemical oxidation of organics depends on many factors including the electrodic material, the current density, the flow dynamic regime and the pH. In particular, the performances of the process strongly depend also on the nature of the organic pollutant. Hence, we are currently carrying out a wide study aimed to determine the influence of the nature of the substrate on the process of electrochemical incineration of organics. In this work, in particular we focused on the oxidation of some carboxylic acids, including maleic (MA), oxalic (OA) and formic (FA), since these substances are generally quite resistant to the electrochemical oxidation. Furthermore, the effect of some operative parameters, including the temperature, was investigated in detail. Two very different anodes

were used: the Ti/IrO₂-Ta₂O₅ which presents a quite low oxygen overpotential and boron doped diamond (BDD) which is probably one of the more promising materials for the electrochemical incineration [4,5].

2 Materials and methods

Electrolyses were performed in two different systems: system **I** was constituted of a bench-scale batch divided (through a cation-exchange membrane Nafion 324) or undivided glass cell, equipped with a SCE reference electrode, a Ti/IrO₂-Ta₂O₅ or BDD anode (wet surface area 6,28 cm²) and a nichel or stainless steel cathode. Electrolytic solution was stirred by magnetic stir bar. The volume was generally of 80 ml in the anodic compartment and of 50 ml in the cathodic one. System **II** was constituted of a continuous batch recirculation reaction system equipped with a filter press undivided micro flow cell ElectroCell AB. The cell was equipped with a BDD or Ti/IrO₂-Ta₂O₅ thin sheet anode of surface area 9.14 cm² and one nickel cathode (distance between cathode and anode lower than 5 mm). The electrolytic solution (250 mL) is continuously fed with a continuous stream of nitrogen dispersed in the liquid phase by a diffuser in a jacketed solution reservoir. The circulation of the solution was provided by a centrifugal pump. Temperature was controlled using a cryostat bath Julabo F30-Ultratemp 2000 with an aqueous solution of ethylene glycol. Amel 2053 was used for all 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. Carboxylic Acids concentration was evaluated by liquid chromatographic analyses performed with a Alltech Platinum EPS C18 column using HP 1100 HPLC equipped with UV-Vis detector (adopted $\lambda=210$ nm). A buffer solution containing KH₂PO₄ and H₃PO₄ at pH = 2.5 was used as mobile phase. The current efficiency of the process was estimated by considering the following oxidation reaction:



Bi-hydrate Oxalic acid 99% from Aldrich, Maleic acid 99% from Fluka and Formic acid 98% from J.T.Baker, were used as substrates. The supporting electrolyte was composed by 0.035 M Na₂SO₄ (Janssen Chimica) and H₂SO₄ (Sigma Aldrich).

3 Result and Discussion

3.1 Effect of the nature of organic substrate

A first set of electrolyses was performed in system **II** (flow rate of 0.2 l/min) for oxalic and formic acids, and in system **I** for maleic acid at DSA and BDD anodes, with a current density of 39 mA/cm², pH = 2 and T = 25 °C. The electrolyses were stopped when the charge passed was 7000 C = 1.45 Q_{th} for system **II** and 6000 C = 5.23 Q_{th} for system **I**, where Q_{th} = charge necessary for a total conversion of the carboxylic acid with a CE = 100%.

A comparison of the performances of electrolyses conducted on the three carboxylic acids at Iridium oxide anode is shown in Figure 1.

Interestingly, at BDD similar conversions were obtained for all the investigated acids under adopted operative conditions. In particular the abatement of the organic increases with the order oxalic < formic < maleic. Quite interestingly, the opposite situation is encountered at DSA anode. In particular, in this case a very low abatement of maleic acid arises.

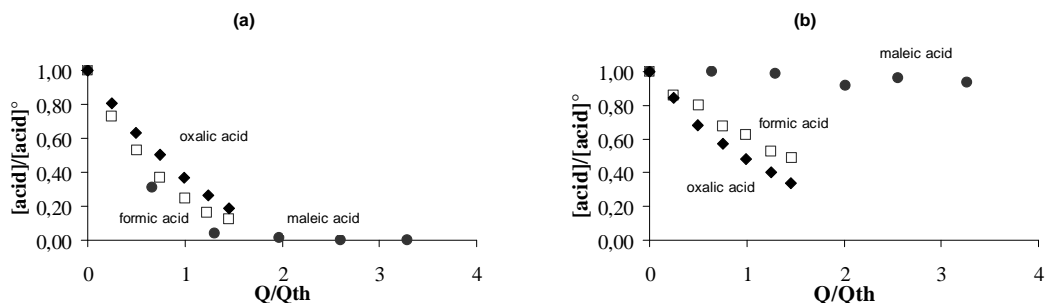


Figure 1. Profile of acid concentration vs. Q/Q_{th} for electrolysis performed with galvanostatic alimentation at BDD (a) and Iridium oxide (b) anodes. Experimental conditions: 39 mA/cm^2 . $\text{pH} = 2$. System solvent supporting electrolyte (SSE): Water, Na_2SO_4 , H_2SO_4 . Initial formic and oxalic acid concentration: 100 mM . Initial maleic acid concentration: 20 mM . $T = 25^\circ\text{C}$.

3.2 Effect of the electrodic material at room temperature

The nature of electrodic material can affect dramatically the performances of the electrochemical incineration process.

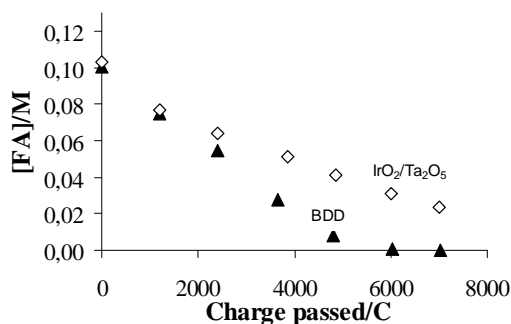


Figure 2. Profile of formic acid concentration vs. charge passed for electrolyses performed with galvanostatic alimentation. Experimental conditions: 17 mA/cm^2 and 1.2 l/min . $\text{pH} = 2$. System solvent supporting electrolyte (SSE): Water, Na_2SO_4 , H_2SO_4 . Initial formic acid concentration: 100 mM . $T = 25^\circ\text{C}$. Electrolyses were stopped when the charge passed was $7000 \text{ C} = 1.45 Q_{th}$, where Q_{th} = charge necessary for a total conversion of the formic acid with a $\text{CE} = 100\%$.

As shown in Figure 2, in the case of formic acid, a conversion of about 78% with a current efficiency slightly lower than 60% was achieved using $\text{Ti/IrO}_2\text{-Ta}_2\text{O}_5$ anode, while a conversion higher than 99% (current efficiency of about 70%) was obtained in the case of BDD. Similar results were also obtained using oxalic acid and maleic acids as substrates. In particular, this effect seems to be more evident for the electrochemical oxidation of maleic acid. Thus, for this acid, under the same operative conditions, conversions of 20% and 100% were obtained at $\text{IrO}_2\text{-Ta}_2\text{O}_5$ and BDD, respectively.

3.3 Effect of the flow rate and current density

Experiments were carried out at different values of flow rate and current density, since, according to literature, these parameters are expected to affect the performances of the electrochemical incineration. In particular, for what concern the abatement of OA, Martinez et al. [4] have found that at IrO₂-Ta₂O₅, higher current densities give rise to lower abatement of this organic compound. Furthermore, we have recently shown for the incineration of OA at BDD anodes [7] that the current density and the flow rate effects depend on each other. Hence, in order to evaluate the effect of the current density and the flow rate on the performances of the process, some experiments were carried out at pH of 2 by changing both the flow rate (from 0.2 to 1.2 l/min) and the current density (from 17 to 39 mA/cm²).

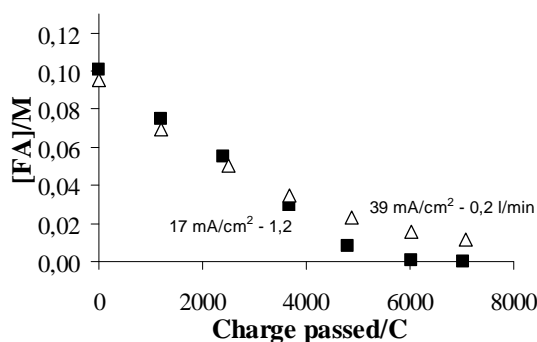


Figure 3. Profile of formic acid concentration vs. charge passed for electrolysis performed with amperostatic alimentation, at BDD. System solvent supporting electrolyte (SSE): Water, Na₂SO₄, H₂SO₄. Initial formic acid concentration: 100 mM. pH = 2. T = 25°C. Electrolyses were stopped when the charge passed was 7000 C = 1.45 Q_{th}, where Q_{th} = charge necessary for a total conversion of the formic acid with a CE = 100%.

As shown in Figure 3 for the electrochemical oxidation of formic acid on BDD anodes, higher abatements were obtained at 17 mA/cm² and 1.2 l/min, since under these conditions, mass transfer control arises for a smaller part of the process.

Analogous results were obtained for the electrochemical oxidation of oxalic.

3.4 Effect of the temperature

The effect of the temperature on the electrochemical incineration of some organic compounds has been investigated at different anodic materials. Interestingly, according to literature data referring to oxalic acid [3,4,6], the effect of the temperature on the performances of the process strongly depends on the nature of the anodic material. In fact, an increase of the temperature gives rise to a slight decrease of the OA abatement at BDD [3] and to a drastic increase at IrO₂ based anodes [4]. In order to evaluate the effect of the temperature on the process, we have performed a set of experiments at different temperatures at different operative conditions for different organic substrates.

Table 1. Influence of Temperature on the Incineration of Carboxylic Acids^a

Entry	[Carboxylic acid] (M)	Electrode material	T (°C)	I/A (mA/cm ²)	Flow rate (l/min)	Current Efficiency (%)	Conversion (%)	Time Passed (min)	(Q/Q _{th}) ^b
1	[Oxalic acid] 0,1	IrO ₂ /Ta ₂ O ₅	25	39	0.2	45 – 49	66 – 70	333	1.45
2	[Oxalic acid] 0,1	IrO ₂ /Ta ₂ O ₅	50	39	0.2	59 – 63	90 – 94	333	1.45
3	[Oxalic acid] 0,1	IrO ₂ /Ta ₂ O ₅	70	39	0.2	45 – 49	96 – 100	455	2.06
4	[Formic acid] 0,1	IrO ₂ /Ta ₂ O ₅	25	17	1.2	54 – 58	76 – 80	777	1.45
5	[Formic acid] 0,1	IrO ₂ /Ta ₂ O ₅	50	17	1.2	57 – 61	98 – 100	777	1.45
6	[Formic acid] 0,1	BDD	25	17	1.2	67 – 71	> 99%	777	1.45
7	[Formic acid] 0,1	BDD	50	17	1.2	64 – 68	> 99%	777	1.45
8	[Maleic acid] 0,02	IrO ₂ /Ta ₂ O ₅	25	39	/	4 – 8	18 – 22	409	5.2
9	[Maleic acid] 0,02	IrO ₂ /Ta ₂ O ₅	50	39	/	1 – 5	11 – 15	409	5.2

^a Amperostatic electrolyses. $i = 39 \text{ mA/cm}^2$. System solvent supporting electrolyte (SSE): Water, Na₂SO₄, H₂SO₄. pH = 2.

For oxalic and formic acid: continuous batch recirculation reaction system. V = 250 ml.

For maleic acid: bench-scale batch divided cell. V = 80 ml.

^b Q_{th} = charge necessary for a total conversion of the oxalic acid with a CE = 100%.

As shown in Table 1, an increase of the temperature gave rise to a drastic increase of the abatement of the acid for OA and FA at IrO₂-Ta₂O₅ anodes (entries 1-3, 4-5) while no a significant effect was detected in the case of BDD (entries 6-7).

At the DSA electrode, a conversion of about 99% was obtained at T = 70 °C, in the case of oxalic acid and at T = 50 °C, in the case of formic acid, after a circulated charge of 2 and 1.45 times Q_{th}, respectively. Then, incineration of these carboxylic acids can be carried out successfully at IrO₂-Ta₂O₅ anodes with very high conversions and CE which are at least comparable to that obtained at BDD at room temperature.

On the other hand, the increase of the temperature presents a slightly negative effect in the case of maleic acid (entries 8-9).

4 References

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