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Kinetics of the oxidation of formaldehyde in a flow electrochemical reactor with TiO_2/RuO_2 anode

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Abstract

This paper reports the electrochemical degradation of solutions containing formaldehyde by means of an electrochemical tubular flow reactor with a titanium anode coated with metal oxides ($Ti/Ru_{0.3}Ti_{0.7}O_2$). Due to the simplicity and low molecular weight of the compound it was possible to achieve high mineralization rates; the oxidation reaction of formaldehyde as well as TOC and COD removal were controlled by mass transfer. For solutions with $0.4\,g\,L^{-1}$ of formaldehyde, electrodegradation followed a pseudo first-order kinetics, and the mass transport coefficients were calculated. After the experiments, a 97% reduction of TOC was observed, and the final formaldehyde and COD concentrations were below the detection limit threshold. For solutions with $12\,g\,L^{-1}$ of formaldehyde processed at $100\,mA\,cm^{-2}$, a transition from a zero-order kinetics to a first-order kinetics started at the concentration for which the current density corresponded to the value of the limiting current.
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1. Introduction

Electrochemical technology has been considered as a tool for controlling formaldehyde (FA) concentration in aqueous media [1–4]. The performance of DSA type oxide anodes has been tested for the electrooxidation of organic pollutants in aqueous media, markedly in the potential region in which oxygen evolution occurs as a simultaneous process [5,6]. TiO_2 based RuO_2 or IrO_2 electrodes have been used for the electrooxidation of FA and a $(TiO_2)_{0.7}(RuO_2)_{0.3}$ anode composition has exhibited higher FA and formic acid oxidation rates when compared to an IrO_2 containing electrode [1,2]. Low electrochemical activity of IrO_2 electrodes for FA oxidation has also been observed during cyclic voltammetry and electrochemical impedance spectroscopy experiments [3]. As it is known, IrO_2 containing oxide anodes present lower overpotential for the oxygen evolution, which is a preferential reaction over organics oxidation [5,6]. In an attempt to increase the overpotential for oxygen evolution, and to improve the electrode performance towards eletrooxidation of organic molecules, doping of oxide surfaces with Sn and Pb may be an efficient strategy. SnO_2 supported on Ti has been used as electrode for the oxidation of FA with a significant electro-catalytic activity [4]. By adding PbO_2 to TiO_2/RuO_2 oxide anodes, combustion reaction of organics is favored [1]. Combustion reaction of organics is more likely to occur on SnO_2 and PbO_2, while on RuO_2 or IrO_2 based anodes a selective oxidation process takes place [5,6]. After the anodic discharge of water, the following step is the formation of hydroxyl radicals, which either oxidize the organics or else react to form molecular oxygen. During this process, hydroxyl radicals ($OH^{\bullet}$) remain physically or chemically adsorbed on the anode surface, depending on the anode material. Physically adsorbed $OH^{\bullet}$ is responsible for the oxidation of organics directly to carbon dioxide in a reaction known as combustion. On TiO_2 based RuO_2 or IrO_2 electrodes, $OH^{\bullet}$ is chemically adsorbed in the oxygen vacancies of the oxide as MO_{x+1}, where MO_x represents a metallic oxide coating. Following that, it promotes a selective oxidation resulting in lower molecular weight species that undergo further oxidation [5]. As it will be reported in this paper, it is possible to operate an electrochemical oxidation of small organic molecules under full mass transport control in which combustion reaction follows a pseudo-first-order kinetics.

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Formaldehyde was chosen for this work because this organic molecule has been used as a model compound for the electrochemical oxidation of small organic molecules [1–4]. FA enters waterways via waste streams from hospitals and mortuaries. Formalin, an aqueous solution containing 37% of FA and 10% of methanol, is used as an embalming solution, and for preserving biological samples and corpses. Traditionally, the degradation of this wastewater is provided by biological digestion. However, the aerobic oxidation process is sensitive to pollutant concentration fluctuations and to flow rate. For this reason, direct discharge to a biological wastewater treatment plant often inactivates the microorganisms responsible for the digestion, resulting in the failure of such a treatment system [7–9].

Previous works on FA electrooxidation were either on a laboratory scale [1,2] or with analytical purposes [3,4]. The present work, in contrast, reports a pilot scale experimental unit for the electrochemical treatment of aqueous effluents containing formaldehyde. A titanium electrode coated with $(TiO_2)_{0.7}(RuO_2)_{0.3}$ was used. Performance of the electrochemical reactor in reducing formaldehyde, TOC and COD concentration was optimized as a function of current density. Concentration profiles observed during electrolysis allowed a kinetic analysis, and degradation apparent rate constants were calculated.

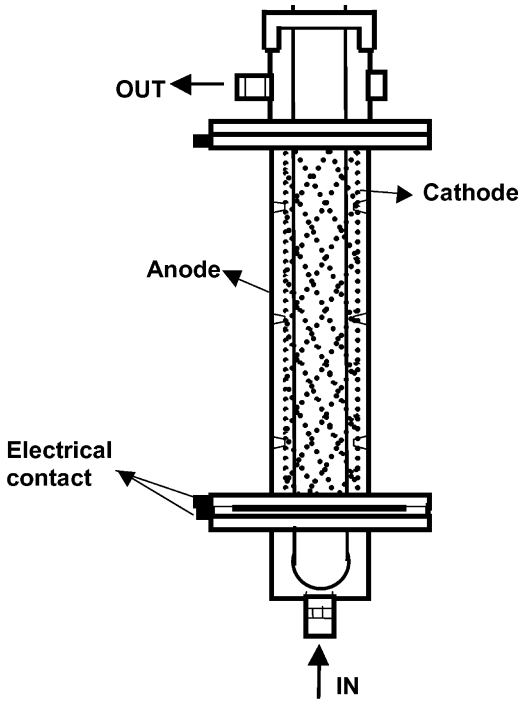

Fig. 1. Schematic diagram of the electrochemical reactor.

2. Experimental

2.1. Apparatus

The experimental apparatus consisted of an electrochemical reactor, a hydraulic pump to recirculate the solution, a flow meter and a reservoir (25 L); this configuration is similar to the one previously used for landfill leachate degradation [10]. The electrochemical reactor, shown in Fig. 1, was a single compartment tubular flow reactor comprising a 0.07 m internal diameter, 1.0 m long titanium tube (wall 0.5 mm thick) with its inner surface (area = 0.18 m^2)m coated with an oxide layer composed of $(TiO_2)_{0.7}(RuO_2)_{0.3}$. The coated titanium tube was supplied by De Nora do Brasil Ltda. and used as the cell anode. Concentric to this tube, the cathode consisted of a 0.055 m diameter titanium tube to which an expanded Ti plate screen (mesh diagonals of 5 mm × 2 mm) was welded to increase the area and promote turbulence. The anode/cathode gap was 3 mm.

The experimental set up was operated in batch recirculation mode, with the flow rate adjusted to 3000 L h^{-1}. Electrical current and continuous solution pumping causes the temperature to rise; therefore, a refrigerating system was inserted into the reservoir to prevent temperature variations. This system consisted of a stainless steel coil with recirculating water kept at a temperature of 20 ± 1 °C. All the experimental runs were carried out using 22 L of solution, a volume that sufficed to fill the reservoir and connecting pipes.

Five-hour experiments were carried out with a 0.4 g L^{-1} formaldehyde solution. For controlled current electrolyses, FA was added to a supporting electrolyte containing 0.1 mol L^{-1} of K_2SO_4. The experimental set up was connected to a power supply, and six current densities were applied: 25, 50, 75, 100, 125 150 mA cm^{-2}. Experiments were also carried out with a FA concentration of 12 g L^{-1} and a current density of 100 mA cm^{-2} was applied. In all runs, samples were taken at predetermined time intervals for subsequent analytical characterization.

2.2. Analyses

Formaldehyde concentration analyses followed EPA method 8315A, in which free carbonyl compounds were determined by reaction with 2,4-dinitrophenylhydrazine (DNPH) by means of High Performance Liquid Chromatography (HPLC, Shimadzu Class vp) with an ultraviolet detector of 365 nm wavelength and a Supelco LC-18 column. The mobile phase was composed of 34%A/66%B, where eluent A is acetonitrile and eluent B a 1:1 mixture of methanol and water. Isocratic elution at a flow of 0.8 mL min^{-1} was used.

Two other analyses were done: total organic carbon (TOC) in a TOC 5000A Shimadzu equipment, and chemical oxygen demand (COD) in a HACH DR/2010 system. For the solution containing 400 mg L^{-1} of FA, initial values of TOC and COD were 170 mg L^{-1} and 510 mg O_2 L^{-1}, respectively. The solution with 12 g L^{-1} of FA had an initial COD value of 16.45 g O_2 L^{-1}.

3. Results and discussion

3.1. Electrolysis of low concentration FA solution

Initial experiments were done in the experimental unit with current densities of 25, 50, 75, 100, 125 and 150 mA cm^{-2}, for a period of 5 h. Fig. 2A–C present plots of formaldehyde, TOC and COD concentrations as a function of electrolysis time. To facilitate comparison, concentration values were normal-

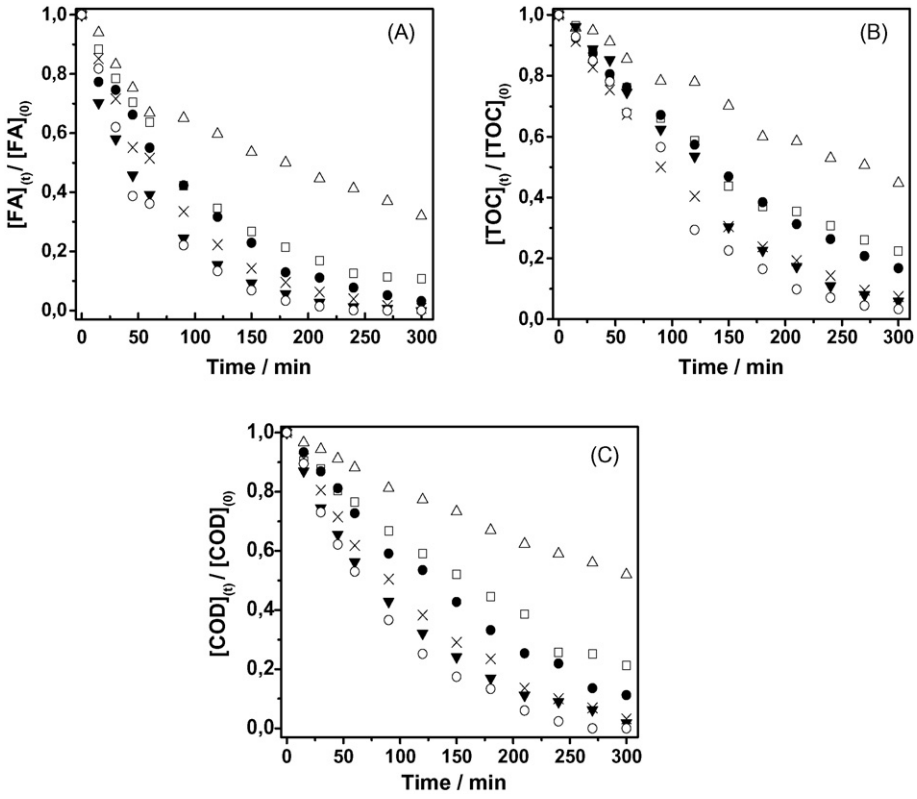

Fig. 2. Normalized concentration profiles of FA, TOC and COD as a function of electrolysis time in different current densities: (△) 25 mA cm^{-2}, (□) 50 mA cm^{-2}; (●) 75 mA cm^{-2}; (×) 100 mA cm^{-2}; (▼) 125 mA cm^{-2}; (◯) 150 mA cm^{-2}. $\Phi = 3000\,L\,h^{-1}$ and $C(0) = 400\,mg\,L^{-1}$.

ized respective to initial concentrations. The plots reveal that formaldehyde, TOC and COD have similar exponential-like decaying curves. Initial concentrations of the organic compound, TOC and COD diminish as electrolysis proceeds, and there is a positive effect caused by the increase of current density: the higher the current density, the faster the three parameters under study decrease. Table 1 shows the percentages of concentration reduction for formaldehyde, TOC and COD. As can be seen in Table 1, after 5 h of electrolysis formaldehyde concentration drops to less than 10% for most current densities. This performance was also observed for TOC and COD for current densities of 100 mA cm^{-2} and higher. High percentages of COD and TOC removal mean complete oxidation and combustion of organic substrates, respectively. Final values of TOC and COD are significant in view of the electrode type used in the experiments. As already mentioned, oxides such TiO_2/RuO_2 are not the most indicated for combustion of organics. However, results showed that the chosen electrode is behaving as suitable for the combustion reaction. The considerable reduction in TOC and COD values, decaying according to a kinetics similar to FA decay, confirms this observation. This behavior is probably due to the simplicity and low molecular weight of the compound chosen for this work; the only possible intermediate before it is transformed into carbon dioxide is formic acid. Furthermore, initial concentrations of FA, COD and TOC are sufficiently low for the reaction rate to be controlled by mass transport, as discussed below. For that reason, Fig. 2 shows high removal rates for COD and TOC, and an exponential-like decay.

Table 1
Concentration reduction percentages for formaldehyde, TOC and COD obtained in the electrochemical process, under different current densities, after treating the aqueous solution for 5 h

i (mA cm^{-2})	Formaldehyde (%)	TOC (%)	COD (%)
50	89.3	77.6	78.8
75	96.8	83.2	88.8
100	99.2	92.6	96.8
125	ND	94.0	98.1
150	ND	96.7	ND

$[FA]_{(0)} = 400\,mg\,L^{-1}$. ND: non detectable.

For a combustion reaction to follow a first-order kinetics relative to FA, there must be a low concentration of the compound and an excess of hydroxyl radicals; the latter is achieved by using high current densities. Hydroxyl radicals are formed according to Eq. (1):

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

Then, FA combustion reaction takes place:

$$CH_2O + OH^{\bullet} \rightarrow CO_2 + 3H^+ + 3e^- \quad (2)$$

and the global reaction is:

$$CH_2O + H_2O \rightarrow CO_2 + 4H^+ + 4e^- \quad (3)$$

Assuming that the reaction of Eq. (1) is fast, an excess of $OH^{\bullet}$ makes the CH_2O diffusion the controlling step of the reaction represented by Eq. (3).

For high current density values and low initial concentration values it can be assumed that the anodic combustion of FA is a diffusion controlled reaction. However, under such conditions, only part of the applied current, which is equal to the limiting current, is used for the combustion reaction. The remainder is responsible for the secondary reaction of oxygen evolution, according to the following equation:

$$OH^{\bullet} \rightarrow 1/2O_2 + H^+ + e^- \quad (4)$$

3.2. Kinetics of the FA electrooxidation process

Taking into account that four electrons are exchanged in the reaction of Eq. (3), the limiting current density for a given instant t in FA combustion is:

$$i_L(t) = 4F\, k_m\, [FA] \quad (5)$$

where $i_L(t)$ is the limiting current density at the instant t, F the Faraday constant, k_m the average mass transport coefficient, and [FA] is the formaldehyde concentration at the instant t. Then, the FA removal rate (r) can be written as:

$$r = \frac{i_L}{4F} = k_m[FA] \quad (6)$$

From the mass balance of the whole system operating in a batch recirculation mode, we get:

$$\frac{d[FA]}{dt} = -\frac{A}{V}r \quad (7)$$

where A is the electrode area and V is the total volume of the solution being processed. Integration between the appropriate limits results in:

$$\frac{[FA]_{(t)}}{[FA]_{(0)}} = \exp\left(-\frac{Ak_m}{V}t\right) \quad (8)$$

Behavior of COD removal can be analyzed in the same way. The limiting current density for FA combustion can also be related to the COD during electrolysis. FA concentration in the solution can be related to COD by:

$$[FA] = \frac{COD}{n} \quad (9)$$

where n is the number of mols of oxygen needed for the complete oxidation of FA. The stoichiometry of the FA combustion indicates that just 1 mol of O_2 is needed for the oxidation of the organic compound to CO_2 and H_2O:

$$CH_2O + O_2 \rightarrow CO_2 + H_2O \quad (10)$$

Therefore, the limiting current density for FA combustion can be related to COD in a way similar to Eq. (5):

$$i_L(t) = 4Fk_m\, COD \quad (11)$$

By a similar reasoning, integration of the equation resulting from the mass balance is similar to Eq. (8):

$$\frac{COD_{(t)}}{COD_{(0)}} = \exp\left(-\frac{Ak_m}{V}t\right) \quad (12)$$

Taking into account the exponential form of Eqs. (8) and (12), FA, COD and TOC decay data exhibited in Fig. 2 have been linearized as shown in the plots of Fig. 3(A–C). The slopes (s) of the curves are directly related to the average mass transport coefficient of the FA combustion reaction:

$$s = -\frac{k_m A}{V} \quad (13)$$

Values of k_m as a function of applied current densities are presented in Table 2. Assuming for the mass transport coefficient average values of 2.5×10^{-5} m s^{-1} for FA and 1.6×10^{-5} m s^{-1} for COD, and for the initial concentrations of FA and COD presented in the experimental section the values of 13.3 mol m^{-3} and 15.9 mol O_2 m^{-3}, respectively, it is possible to calculate the initial limiting current densities for the electrodegradation of FA and COD using Eqs. (5) and (11). This leads to the limiting current density values of 12.8 mA cm^{-2} and 9.8 mA cm^{-2}, respectively. However, current densities applied were in the range of 25–150 mA cm^{-2}. Some of the experiments were done with current densities between 10 and 20 mA cm^{-2}, but it was observed that degraded FA fractions were insignificant when compared to those obtained with higher current densities, and there was no appreciable COD or TOC concentration reduction.

Earlier experiments reported in the literature have shown that, for the same type of electrode, the mineralized fraction of FA at 40 mA cm^{-2} was small, and formic acid was formed as an intermediate [2]. Due to the characteristics of the electrode, in order to achieve a reasonable performance in the oxidation process followed by mineralization of organic compounds, it is necessary to operate at high potential values within the region of anodic discharge of the water. This assures a high availability of hydroxyl radicals for the combustion reaction.

3.3. Electrolysis of higher concentration FA solution

In a new experiment, a FA solution of a higher concentration was subjected to electrolysis at 100 mA cm^{-2} under the same hydrodynamic condition, and using the same supporting electrolyte. Initial FA concentration was 12 g L^{-1}(400 mol m^{-3}), which resulted in a COD value of 16.45 g O_2 L^{-1} (514 mol O_2 m^{-3}). According to Eqs. (5) and (11), limiting current densities for FA combustion would be 386.0 mA cm^{-2} and 317.4 mA cm^{-2} for FA and COD, respectively. This means that the value of 100 mA cm^{-2} used as the applied current density is three times smaller than limiting currents. For such a situation it is to be expected that concentration reductions of FA and COD over time is linear, and the characteristic of a mass transport controlled reaction is lost. Concentration will drop linearly following a pseudo-zero-order kinetics until the applied current density of 100 mA cm^{-2} becomes the limiting current for the decreasing concentration. Using once more Eqs. (5) and (11), this should happen when concentrations reach the approximate values of 3 g L^{-1} of FA and 5 g L^{-1} of COD. Beyond these values, the electrochemical degradation process once more assumes a pseudo-first-order kinetics, and the combustion reaction is controlled by mass transport.

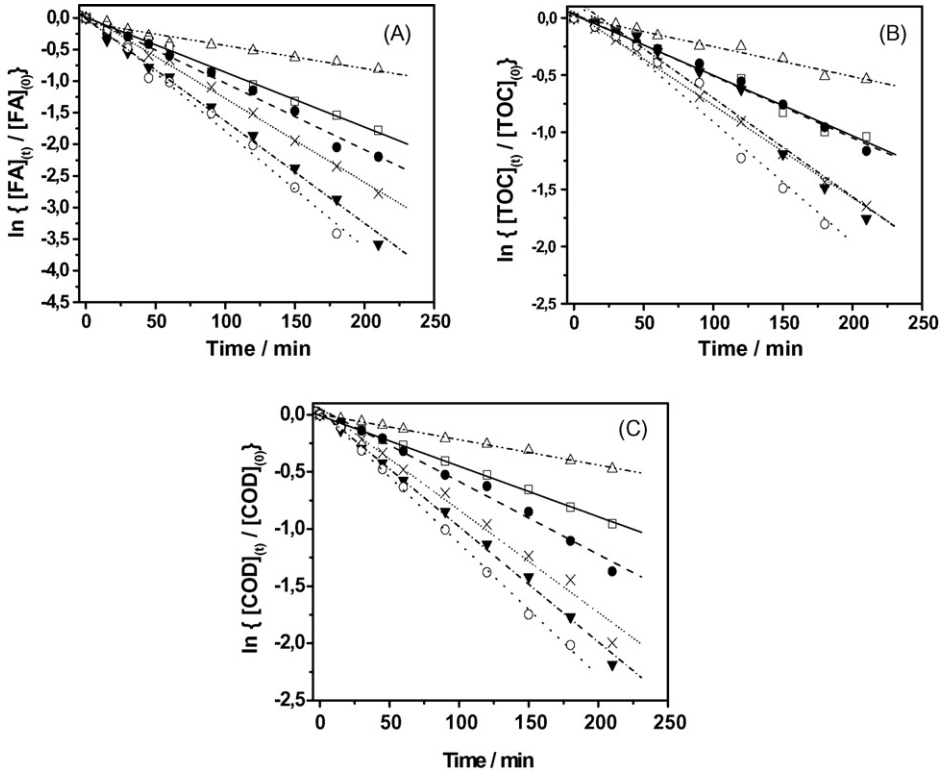

Fig. 3. Linearized concentration profiles of (A) FA, (B) TOC and (C) COD as a function of electrolysis time in different current densities: (△) 25 mA cm^{-2}, (□) 50 mA cm^{-2}; (●) 75 mA cm^{-2}; (×) 100 mA cm^{-2}; (▼) 125 mA cm^{-2}; (◯) 150 mA cm^{-2}. Data from Fig. 2.

Table 2
Values of the average mass transport coefficient resulting from the formaldehyde electrooxidation experiments as a function of current densities

i (mA cm^{-2})	Cell potential (V)	k_m ($\times 10^{-5}$/m s^{-1})		
		FA	TOC	COD
25	1.6	0.78 (r^2 = 0.958)	0.56 (r^2 = 0.978)	0.47 (r^2 = 0.997)
50	2.2	1.87 (r^2 = 0.998)	1.14 (r^2 = 0.993)	0.95 (r^2 = 0.999)
75	2.8	2.26 (r^2 = 0.994)	1.16 (r^2 = 0.995)	1.37 (r^2 = 0.994)
100	3.3	2.86 (r^2 = 0.999)	1.74 (r^2 = 0.999)	1.93 (r^2 = 0.993)
125	3.8	3.48 (r^2 = 0.997)	1.86 (r^2 = 0.980)	2.17 (r^2 = 0.998)
150	4.2	3.97 (r^2 = 0.995)	2.28 (r^2 = 0.988)	2.50 (r^2 = 0.998)

Fig. 4 presents the evolution of FA and COD concentration profiles over the electrolysis time at 100 mA cm^{-2}. Linear fitting of experimental points does not allow an accurate determination of the concentration-time couple where the change in kinetics occurs. However, it is possible to observe that this transition indeed occurs between 3 g L^{-1} and 5 g L^{-1} for FA and COD. As shown in Fig. 4, the linear concentration decay occurs when $i_{appl} < i_L$, and when $i_{appl} \geq i_L$ the combustion reaction becomes controlled by mass transfer and follows a pseudo first-order kinetics. Assuming that in the region where $i_{appl} < i_L$ the solution of the differential equation resulting from the mass balance is:

$$C_{(t)} - C_{(0)} = -\frac{k_{app} A}{V} t \quad (14)$$

where C is the concentration of FA or COD, k_{app} is the apparent oxidation rate constant, A the electrode area, and V is the volume

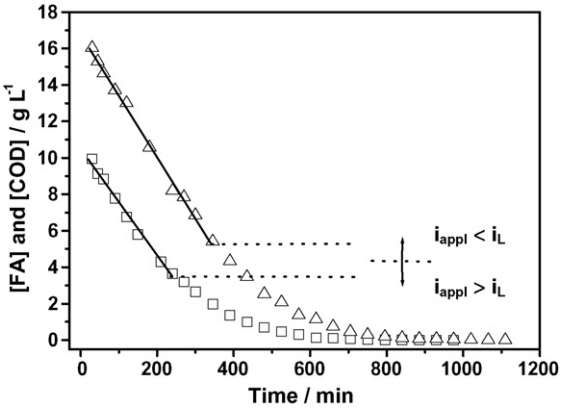

Fig. 4. Changing of reaction kinetic order for (□)FA and (△)COD concentration decay during the electrolysis. Horizontal dot line shows the concentration for which i_{appl} becomes i_L. Φ = 3000 L h^{-1} and i_{appl} = 100 mA cm^{-2}.

of the solution in recirculation. In the region where the zero-order kinetics prevails, FA e COD are removed with k_{app} equal to 6.7 and 7.1 g m^{-2} s^{-1}, respectively.

4. Conclusions

The electrochemical degradation process is a technique that can be applied in the treatment of aqueous waste streams containing FA. Due to the simplicity and low molecular weight of the compound, it is possible to find operation parameters allowing combustion of the compound even with oxide anodes with the commercial composition of $(TiO_2)_{0.7}(RuO_2)_{0.3}$. Thus, it is possible to run the electrodegradation process in mass transport conditions, where removal of FA, TOC and COD follow a pseudo first-order kinetics. As the process is predictable, current densities can be estimated in order to make the degradation process as fast as desirable.

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