RAMReS Sciences des Structures et de la Matière Vol. 3 (2021) 1 - 11
http://publication.lecames.org/index.php/mat *ISSN: 2630-1180*

Influence of iodides on the electrochemical oxidation of paracetamol on boron doped diamond electrode

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Received: 18 February 2021 / Received in revised form: 15 April 2021 / Accepted: 12 May 2021

***Abstract*:**

In this work, the influence of iodide on the electrolysis of paracetamol in sulfuric acid medium was carried out using voltammetry. It emerges from this study that for a pH = 0.6, the electrochemical oxidation of paracetamol in the presence of iodide is better than those obtained at pH equal to 3 and 7. This result shows that the oxidative action of the iodide and its derivatives is inhibited when pH increases. The preparative electrolysis of paracetamol in the presence of iodide at a current density of 70 mA/cm^2 showed that the iodide and its derivatives substantially contribute to the oxidation of paracetamol. However, a high concentration of iodide reduces the oxidation kinetics of paracetamol because kinetic constants equal to 0.868 h^{-1}, 2.176 h^{-1}, 1.584 h^{-1} and 0.964 h^{-1} were obtained in the presence of 10 mM PCM containing respectively 0 mM, 10 mM, 50 mM and 100 mM of iodide ions. During electrolysis, the oxidation kinetics of paracetamol have been shown to be a pseudo first order reaction. The current efficiency study has shown that there is less current loss in the presence of iodide.

***Keywords*:** Paracetamol; Iodide; Boron doped diamond; Cyclic voltammetry; Differential pulse voltammetry.

1. Introduction

A healthy, pollutant-free environment is what humanity dreams of for its existential fullness. Unfortunately, with the industrialization of the world for ages, such a life seems unattainable. Indeed, the presence of pharmaceutical products in the environment following their use by humans with the intention of treating oneself is a reality [1, 2]. According to investigations made by the scientific community, this presence has a harmful impact on the well-being of living beings and more specifically on human health [3-6].

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Paracetamol is the most administered drug in the world and the most frequently found pharmatical in water with concentrations reaching 250 µg/L [7-8]. It is found among the drugs that are dangerous for the aquatic environment [8]. Facing with this situation, wastewater decontamination is necessary. The traditional techniques such as biological treatment, coagulation, filtration and chemical treatment are found to be either inefficient or are costly. In this case, new methods of wastewater depollution such as electrochemical methods have been implemented.

According to the literature, electrochemical methods make it possible to effectively clean up wastewater containing non-biodegradable organic compounds [9-14]. Despite the efficiency of the electrochemical method, it is sometimes necessary to associate oxidative species with it in order to reduce the time required for the complete mineralization of pollutants, in other words to minimize losses in electric current. Thus, many studies have been carried out on the influence of inorganic ions on the oxidation of pollutants. Most of these investigations have focused on chloride, ferrous, cuprous, sodium ions, with the exception of iodide ions, whose application in the mineralization of pollutants is not common compared to their counterparts raised [11, 12, 15, 16]. So, in this work we have focused on the influence of iodide on the paracetamol oxidation. The basic principle of an electrochemical measurement is based on the fact that certain molecules or ions can exchange electrons with an electrode, this under analytical conditions well defined in particular by the potential at which this exchange takes place [17]. Among the most recent electrochemical methods, we distinguish voltammetry. Several voltammetry techniques can be used to study the response of an electrochemical system subjected to polarization: linear, cyclic, square wave voltammetry, etc.

Each has a particular modulation of the potential as a function of time. The choice is generally made with regard to the desired information: pulse voltammetry methods are very often used to detect very low concentrations (nanomolar or micro molar) of organic products in solution [18-21].

This work will therefore focus on studying the effect of iodide on the electrochemical oxidation of paracetamol using a boron-doped diamond (BDD) electrode. We chose BDD electrode because previous studies in our laboratory have shown that it can effectively treat wastewater [13, 22]. During this study cyclic voltammetry and differential pulse voltammetry (DPV) will be used as the analysis method.

2. Experimental Methods

2.1. Equipment and electrodes

The voltammetric measurements were performed using an AUTOLAB PGSTAT 20 (Ecochemie) connected to a potentiostat equipped with USB electrochemical interface.

This system is connected to a three-electrode single compartment glass cell and a computer for data storage and processing. A GPES 4 software was employed to get the voltammograms. The glass electrochemical cell consisted of saturated calomel electrode (SCE) and platinum wire as reference and counter electrode respectively. BDD electrode was used as a working electrode. The surface of the BDD in contact with the electrolyte is 1 cm^2. All the pH values were measured with a pH meter HANNA instruments (HI 2211 pH/ORP Meter). All the potentials reported in this paper were given against SHE according to the following equation (1) at an ambient temperature of 25˚C.

$$E_{SHE} = E_{SCE} + 0.25 \quad (1)$$

Where SHE: standard hydrogen electrode; SCE: saturated calomel electrode

2.2. Chemicals

The chemicals used for the electrochemical study are H_2SO_4 (Panreac, 96%), NaOH (Panreac, 98%), H_3PO_4 (Emsure, 85%), H_3BO_3 (Emsure, 99.5%) and CH_3-COOH (Emparta, 99.7%). All solutions were prepared with distilled water, and the experiments were carried out at room temperature at 25°C.

Paracetamol was supplied by BAILY-CREAT (France). A stock solution of $1.32.10^{-2}$ mol/L (2g/L) of paracetamol was prepared by dissolving an accurate mass of the drug in an appropriate volume of H_2SO_4. The working solutions for the voltammetric investigations were prepared by diluting of the stock solution. All solutions were protected from light and used within 24 h to avoid decomposition. Distilled water was used to prepare all the solutions.

2.3. Setup for Britton Robinson buffer medium preparation

A 0.04 M Britton Robinson buffer solution was prepared in order to maintain the pH of the withdrawn samples during the electrolysis within a very restricted range. For this purpose, acetic acid, orthophosphoric acid and boric acid were used with the respective amounts of 4.6 mL; 5.4 mL and 4.9713 g.

The preparation of this buffer solution was done as follows: (i) Heating a certain amount of water in a glass beaker to a temperature of around 70°C using a water bath. (ii) Dissolution of boric acid in this quantity of heated water. (iii) Let the solution containing boric acid cool. (iv) Transfer this solution into a 2000 mL flask containing the above-mentioned quantities of acetic acid and orthophosphoric acid. (v) Fill with distilled water to the mark, then homogenize.

In 99 mL of this Britton Robinson buffer solution we put 1 mL of samples from electrolysis at pre-established time intervals. After homogenization of this solution, its voltammetric curve with differential pulse is determined in order to have an idea of the paracetamol concentration.

3. Results and discussion

3.1. Cyclic voltammograms

Figure 1a shows cyclic voltammograms of BDD electrode in the presence of PCM (2.5 mM) in H_2SO_4 (0.3 M). We note the appearance of an oxidation peak at 1.15 V/SHE. A rapid increase in the current related to the oxygen evolution reaction started at 2.5 V.

Figure 1b shows the voltammetric curves relating to the influence of iodide on the behavior of BDD in sulfuric acid (0.3 M) medium between -0.35 and 3 V/SHE in the presence of paracetamol (2.5 mM). This figure shows that the potential of the peak observed at 1.25 V/SHE in the absence of iodide increases in presence of I^-. We also note that the intensity of this peak increases with the concentration of iodide ions. This figure also shows another oxidation peak around 2.5 V/SHE whose potential and current intensity increase with iodide concentration that peak could be related to the oxidation of I^-. From this result it is observed that the current intensity of the peak located at around 2.5 V/SHE is approximately five times greater than that located at 1.25V/SHE. Thus, it is reasonable to suggest that the ratio of the number of electrons exchanged during the two successive oxidation reactions remains the same.

Consequently, the appearance of the first peak could be attributed to the oxidation reaction of I^- to I_2 and that of the second to the oxidation of I_2 to iodate (IO_3^-) [23].

$$I^- \rightarrow 1/2\, I_2 + e^- \quad (2)$$

$$1/2\, I_2 + 3H_2O \rightarrow IO_3^- + 6H^+ + 5e^- \quad (3)$$

Furthermore, in the absence of paracetamol (Figure 2), it is noted that the intensity linked to the oxidation wave in the presence of I^- of the species produced at 2.5 V/SHE is high compared to a containing 2.5 Mm of paracetamol; which reflects the participation of iodate in the paracetamol oxidation. At around 1.45 V/SHE the product I_2 catalyses the PCM oxidation process and the excess of I_2 process less than produced in PCM from I^- solution, indego oxidation to IO_3^-.

The effect of pH (pH = 0.6; 3 and 7) on the voltammetric response of BDD anode was studied in a sulfuric acid medium in the presence of 2.5 mM PCM and 50 mM iodide. Figure 3 gives the voltammetric curves resulting from this study. We notice a decrease in the anode peak currents. It lets appear at high potential a lowering of the current. From these observations, it follows that the oxidative action of iodide and its derivatives is inhibited when the pH increases.

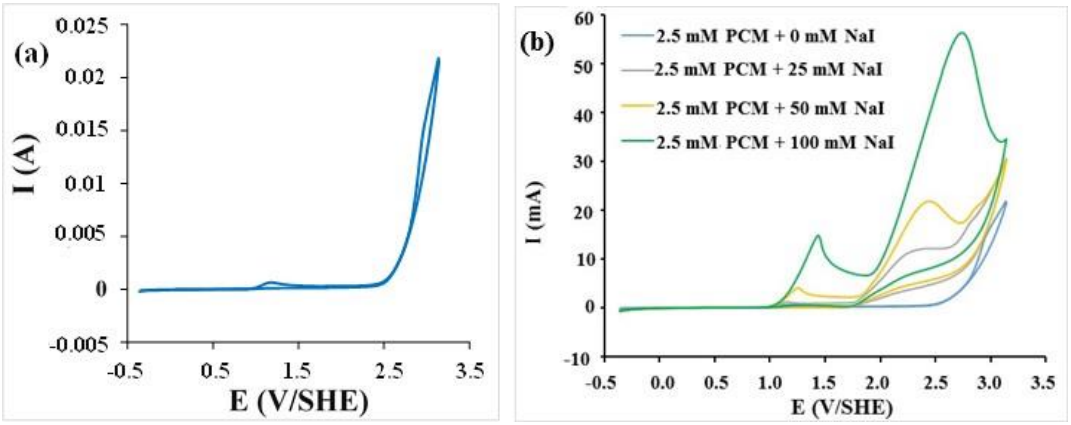

Fig. 1. (a) Voltammogram of paracetamol (2.5 mM); (b) Influence of iodide on the voltammogram in the presence of paracetamol (2.5 mM); v = 100 mV / s; T = 28 °C; pH = 0.6.

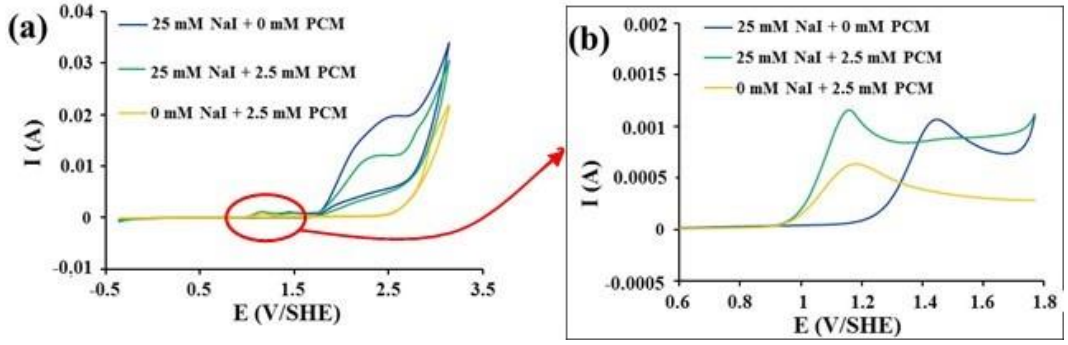

Fig. 2. Paracetamol oxidation and iodide oxidation; v = 100 mV/s; T = 28 °C; pH = 0.6.

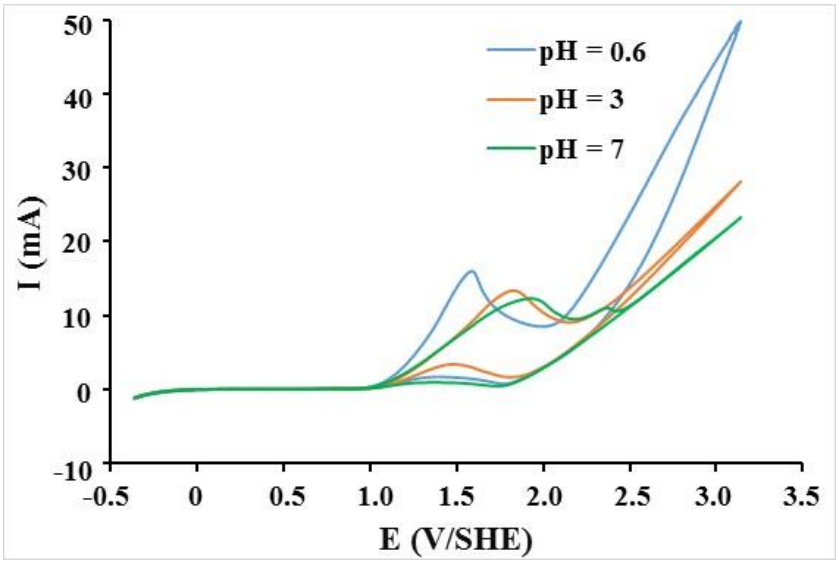

Fig. 3. Influence of pH combined with that of iodide (50 mM) on the behavior of BDD in the presence of paracetamol (2.5 mM); v = 100 mV/s; T = 28 °C.

3.2. Electrolysis

Figure 4 shows the differential pulse voltammograms resulting from the study of the effect of iodide on the electrochemical degradation of paracetamol in sulfuric acid medium at 70 mA/cm^2. In this figure, there are two peaks located at approximately 0.9 and 1.8 V/SHE which can be attributed to the oxidation peak respectively of paracetamol and iodide. There is a simultaneous oxidation *versus* time of paracetamol and iodide during treatment.

The oxidation kinetics of paracetamol (10 mM) in the absence and presence of iodide were described using the pseudo-first-order model (Figure 5b): $-\ln(C/C_0) = kt$ [24]; where C and C_0 are the concentrations of PCM in the solution at time t and 0 (h), respectively, k is the rate constant (h^{-1}).

Figure 5b shows that the curves of $-\ln(C/C_0)$ as a function of time (0 to 1.5 h) are straight lines that pass through the origin of the coordinate system. The results of rate constant and R^2 are displayed in Table 1. This table shows that the determination coefficients of these lines are 0.996, 0.998, 0.990 and 0.971, respectively for 0 mM, 10 mM, 50 mM and 100 mM of iodide. These results indicate that the oxidation kinetics of paracetamol is a pseudo first order reaction in the presence and absence of iodide. Table 1 also shows that the kinetic constants associated with the oxidation of PCM are 0.868 h^{-1}, 2.176 h^{-1}, 1.584 h^{-1} and 0.964 h^{-1}, respectively in the presence of 0 mM, 10 mM, 50 mM and 100 mM iodide. Thus, the presence of iodide improves the oxidation of paracetamol; but at high concentrations, there is a progressive decrease in the oxidation kinetics. During electrolysis we assist in addition to iodide, the formation of iodine (I_2) and iodate (IO_3^-) thus increasing the number of species involved in the oxidation of PCM [23]. Most of the electrochemical treatments of pollutants involve side reactions which improve or inhibit the mineralization reaction of the parent compound under very specific operating conditions [9, 25]. Thus, we have studied the electrolysis of iodide to ensure that they are involved or not in the electrochemical oxidation of paracetamol.

Table 1
Oxydation kinetics parameters of 10 mM PCM in the absence and presence of iodide

[I^-] (mM)	k (h^{-1})	R^2
0	0.868	0.996
10	2.176	0.998
50	1.584	0.990
100	0.964	0.971

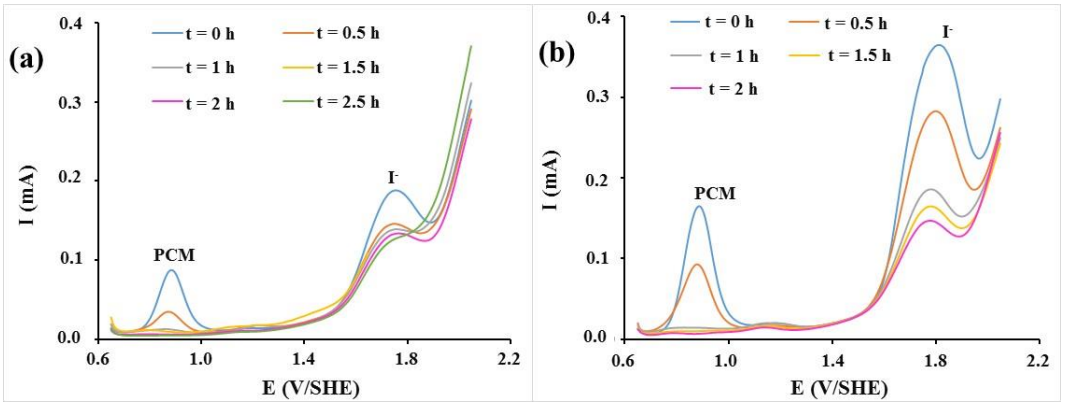

Fig. 4. Differential pulse voltammetric curves of paracetamol (10mM) in sulfuric acid (0.3 M) in the presence of iodide (10 mM) (a); 50 mM (b); j = 70 mA/cm^2; T = 28 °C.

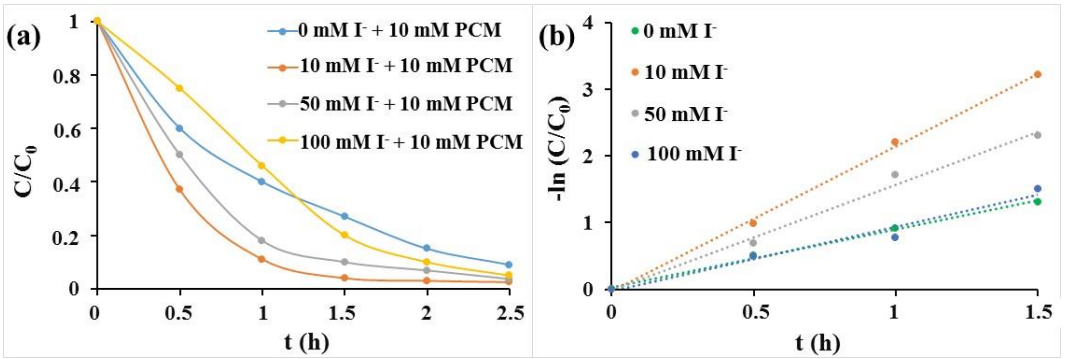

Fig. 5. Influence of iodide concentration on the electrolytic oxidation of PCM (10 mM) in sulfuric acid (0.3 M); j = 70 mA/cm^2; T = 28 °C.

Figure 6 shows the results of the electrolysis of iodide (50 mM) in the absence of paracetamol under a current density of 70 mA/cm^2 in 0.3 M sulfuric acid. In this figure, we observe the presence of two anodic peaks. The first peak corresponds to iodine molecule associated with a potential of 0.5 V/SHE and that of the iodate associated with a potential of 1.2 V/SHE. This result has been obtained in a iodide solution prior to its electrolysis process. During electrolysis, these two species are gradually oxidized and their elimination kinetics are those of a pseudo first order reaction, as shown in Figure 5b. From these results, it is possible to claim that during the electrolytic oxidation of PCM in the presence of iodide, on the one hand iodine and iodate are involved in it, and on the other hand they lead to undesirable electrochemical reactions. This latter tendency can have a negative impact on the organic compound oxidation for a high concentration of iodide in the sense that in such a situation its oxidation will not be predominant. The evolution of the current ratio I/Im of the peak currents of I_2 and I^- during the electrolysis was determined. Figure 6b shows the obtained results. This figure confirms that the I_2 and I^- concentrations decrease during the electrolysis of paracetamol. This clearly shows that they participate in the degradation of PCM.

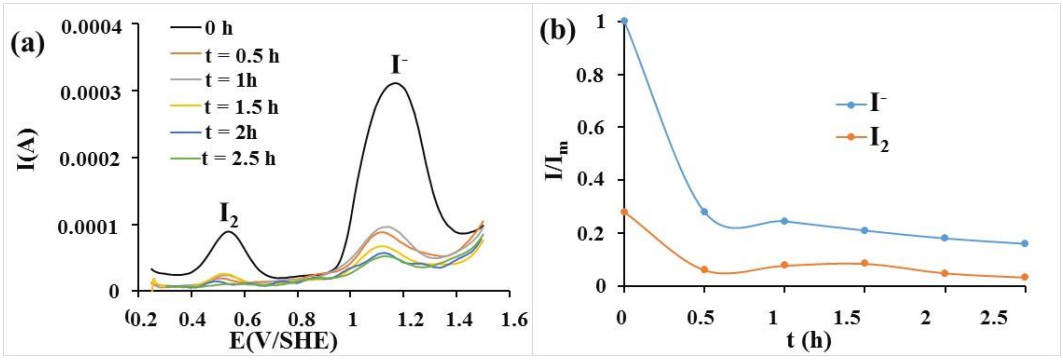

Fig. 6. Electrolysis of iodide (50 mM) in the absence of paracetamol; j = 70 mA/cm^2; flow rate= 2.7mL/s; T = 28 °C.

Figure 7 highlights a comparative study of the iodide oxidation during electrolysis in the absence and presence of paracetamol under a current density of 70 mA/cm^2 in sulfuric acid medium (0.3 M). It shows faster oxidation kinetics in the presence of paracetamol. In fact, the current intensity ratios (I/I_m) determined after 2.5 h of electrolysis are 0.16 and 0.39, respectively in the presence and in the absence of paracetamol. This shows that iodide is involved in the oxidation of paracetamol. Monitoring the color of the solution that contains paracetamol and iodide, enabled us to note that after 0.5 h of electrolysis, the solution which was colorless at the start takes on an intense brown coloring which becomes gradually discolored until a pale yellow color is obtained after 2.5 hours as shown in figure 8. Indeed, this gradual change in color confirm the involvement of iodide in paracetamol oxidation.

The current efficiency of the electrolysis of paracetamol was studied. The results are presented in Fig. 9. In this figure, it can be seen that the current efficiency increases in the presence of iodide. This indicates that there is less current loss in the presence of iodide.

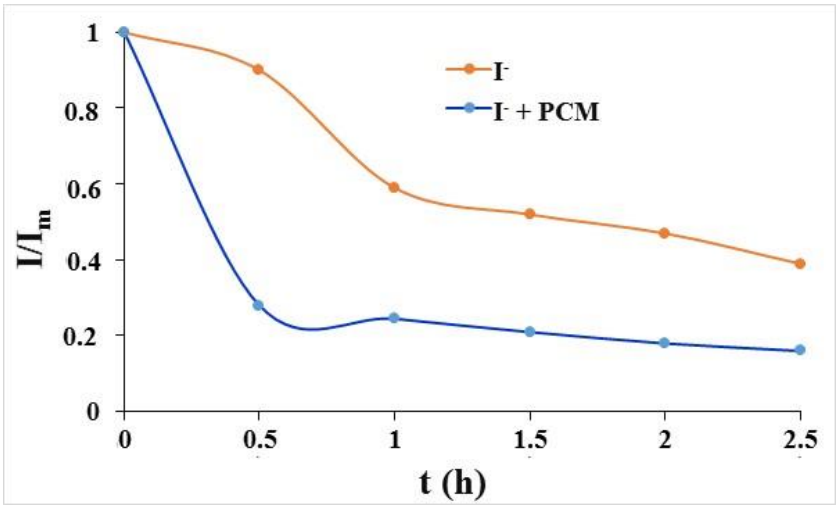

Fig. 7. Involvement of the activity of iodide in the electrolytic oxidation of paracetamol (10 mM); j = 70 mA/cm^2; flow rate = 2.7 mL/s.

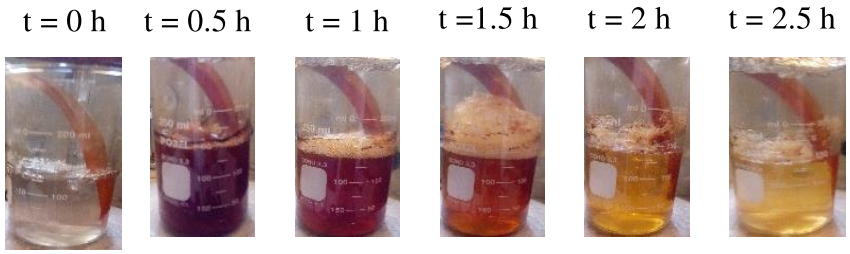

Fig. 8. Evolution of the coloration of the paracetamol solution containing 10 mM of iodide during electrolysis.

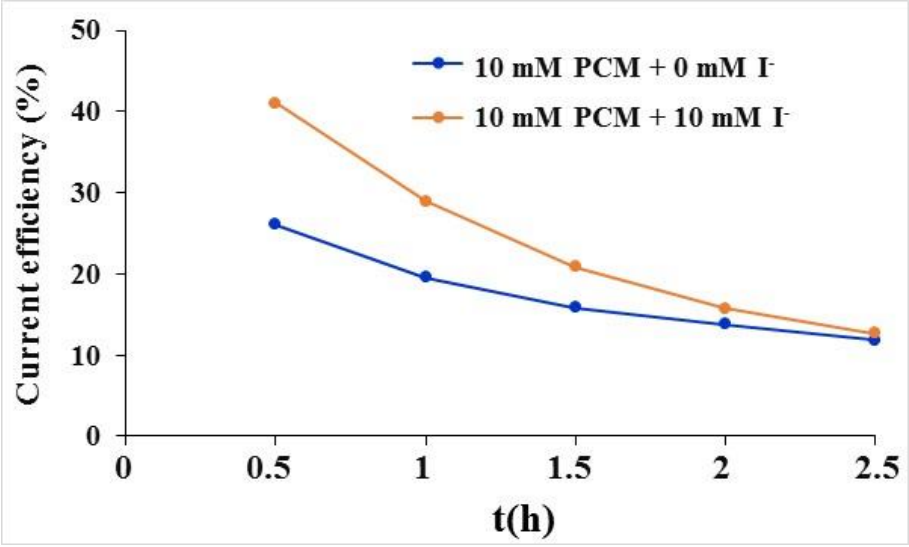

Fig. 9. Influence iodide on the current efficiency; j = 70 mA/cm^2; flow rate = 2.7 mL/s.

4. Conclusion

Voltammetric measurements have shown that iodide (I^-) are oxidized to iodine (I_2) and iodate (IO_3^-). It has also been shown that iodate, diodine and iodate participate in the oxidation of paracetamol. It emerges from this study that the oxidative action of iodide and its derivatives is inhibited when the pH increases. Preparative electrolysis of paracetamol in the presence of iodide at a current density of 70 mA/cm^2 using differential pulse voltammetry as an analytical method, reported that iodide and its derivatives substantially contribute to the oxidation of paracetamol. However, a high concentration of iodide reduces the oxidation kinetics of paracetamol because kinetic constants equal to 0.868 h^{-1}, 2.176 h^{-1}, 1.584 h^{-1} and 0.964 h^{-1} were obtained in the presence of 10 mM PCM containing respectively 0 mM, 10 mM, 50 mM and 100 mM of iodide. During electrolysis, the oxidation kinetics of paracetamol are a pseudo first order reaction. The current efficiency study has shown that there is less current loss in the presence of iodide.

Aknowledgement

We are very thankful to the Swiss National Funds for its financial support. They funded the project (IZ01Z0_146919) which durability helped this work to be undertaken.

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