

Detection and quantification of diiodine during the electrooxidation of pharmaceuticals on a boron-doped diamond electrode (BDD)

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Abstract:

Oxidative species play a very important role in the degradation process of organic pollutants. However, their detection and quantification are often very complex. In this work, the aim is to determine qualitatively and quantitatively the diiodine (I_2) generated *in situ* during an electrochemical process by the starch-poisoning test and by spectrophotometry, respectively. Thus, for quantification, a simple, linear, reliable and accurate technique with a detection limit of 0.0023 mM and a quantification limit of 0.007 mM was used. Preparative electrolysis of NaI leads to the *in situ* generation of diiodine characterized by a very rapid increase in the concentration of I_2 during the first 20 minutes of electrolysis followed by a quasi-constant evolution of the concentration of I_2 until 240 minutes. The degradation of metronidazole (MNZ) (0.1 g/L) in the presence of NaI (0.05 M) in $KClO_4$ medium (0.1 M) leads to the *in situ* generation of I_2 with a maximum concentration reached (1702 mg/L) after 5 minutes of experiment. After this date, a rapid decrease of I_2 in the medium is observed, which reflects the participation of I_2 in the MNZ degradation process. The contribution is positive from I_2 and it allows to reach 100% of the chemical oxygen demand ($\Delta(COD)$) abatement rate against 83.48% in its absence. In addition, diiodine is generated during the electrolysis of telebrix (TLX) (1 g/L). The release of I_2 is evidenced by the end-of-electrolysis coloration of TLX being identical to that obtained during NaI electrolysis, by the maximum wavelength of the TLX samples being identical to that of I_2 and by the starch stain test being positive.

Keywords: Spectrophotometry; Electrooxidation; Diiodine; Detection.

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1. Introduction

Like most countries in the world, Ivory Coast is faced with a real problem of wastewater treatment before discharge. Wastewater of various types, including from hospitals, is discharged as such into the environment [1, 2]. Hospital wastewater can contain, among other things, heavy metals (mercury, silver, chromium, nickel, cobalt, etc.) and organic molecules, some of which, such as antibiotics, are difficult to biodegrade [3 - 5]. This constitutes a danger to the environment and to humans [6, 7]. To treat wastewater containing compounds that are difficult to biodegrade, several processes are used. These treatment methods include advanced electrochemical oxidation processes. Indeed, advanced oxidation processes are based on the *in situ* generation of very powerful oxidising agents such as hydroxyl radicals and diiodine. Diiodine is an important element in environmental protection studies of human health [8]. Diiodine is also a micronutrient and is mainly present as iodate (IO_3^-), iodide ion (I^-), volatile organic diiodine such as methyl iodide ($\text{CH}_3\text{-I}$), methylene diiodide (CH_2I_2) as well as diiodine (I_2). All these molecules are found in plants and animals as they are transferred and deposited on the soil and in water from sea water [9]. Diiodine is an essential micronutrient for humans and other mammals for the synthesis of the thyroid hormones T3 and T4. These hormones play a crucial role in the development and maturation of the nervous system and in the regulation of the

metabolism of most tissues [10]. Its use as a disinfectant is a method that has been widely used by individuals living in very hostile environments, soldiers at war, adventure travelers who have difficult access to drinking water [11]. The environment contains many ions including iodide ions. The effect of iodide ions on the efficiency of electrooxidation of organic compounds has been studied in previous work [12]. The results obtained showed that the presence of I^- had a significant impact on the degradation of organic compounds. The presence of recalcitrant organic compounds, specifically pharmaceuticals, in wastewater degrades the quality of our ecosystem, which would have a negative impact on human health [13 - 15]. For their degradation we will use an advanced electrooxidation process which is an electrochemical method. Electrooxidation or anodic oxidation of organic pollutants is usually performed in the anode compartment of a split cell or in an undivided cell, using an anode such as Pt, PbO_2 , SnO_2 [16, 17] and Boron Doped Diamond [18].

The focus of the present investigation is to determine and quantify diiodine using a spectrophotometric method. This method will allow us to quantify the diiodine generated *in situ* during the preparative electrolysis of a sodium iodide solution. In addition, we will use this method to monitor the degradation of metronidazole (MNZ) in perchloric acid during its preparative electrolysis.

Finally, we will monitor COD and diiodine production during the preparative electrolysis of telebrix (TLX). To our knowledge, such a study has not been the subject of a scientific publication.

2. Experimental method

2.1. Chemicals

Perchloric acid (Panreac) and diiodine (Problabo) were used as supporting electrolyte and prepared with distilled water. The hydrogen peroxide (35%), used for monitoring hydroxyl radicals, was manufactured by Scharlau. Sodium iodide (99.5%) and hexane (95-97%) were manufactured by Sigma-Aldrich and Ensure, respectively. Metronidazole ($C_6H_9N_3O_3$, in tablet form) which is a product of the Exphar SA laboratory in Belgium and telebrix ($C_{12}H_{11}I_3N_2O_5$, diiodine contrast solution) were purchased in a pharmacy in Abidjan. The pH was adjusted using H_2SO_4 (Sigma-Aldrich) and NaOH (Panreac).

2.2. Electrochemical system for electrooxidation

For the electrooxidation, an undivided reactor has been used under a galvanostatic regime. The system worked under a batch operation mode. The simulated wastewater was fed with a peristaltic pump into the electrochemical reactor at a flow rate of 2.08 mL s^{-1} . All the

electrooxidation experiments were conducted at room temperature in an open, cylindrical, covered with aluminum foil and undivided glass cell of 250 mL capacity with magnetic stirring. Boron-doped diamond electrode was used at the anode and zirconium at the cathode. The two electrodes have a surface area of 16 cm^2 . A 0.05 M NaI solution was electrolysed and then we proceeded to the detection of the diiodine produced *in situ*. Then, preparative electrolysis of $HClO_4$ (0.1 M) + 0.1 g/L metronidazole (MNZ) and preparative electrolysis of $HClO_4$ (0.1 M) + 0.1 g/L metronidazole (MNZ) + NaI (2.10^{-4} M) were carried out in order to monitor COD as well as the effect of the oxidant diiodine (I_2) on MNZ degradation. Preparative electrolysis of 1 g/L of telebrix (TLX) in a 0.1 M $KClO_4$ solution was also carried out in order to monitor its degradation and then quantify the I_2 produced during the electrolysis time. The experimental set-up used for the preparative electrolysis is shown in Figure 1.

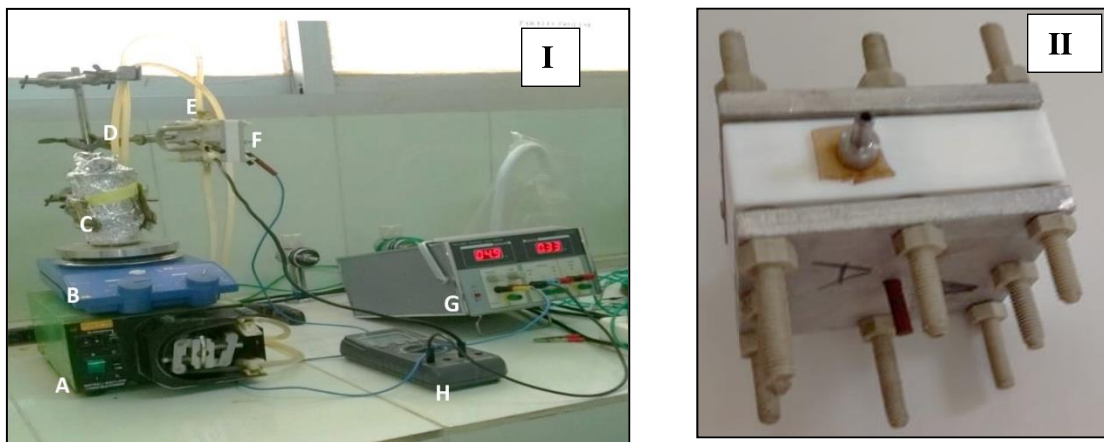


Fig. 1. (I) Experimental set-up for preparative electrolysis (A: peristaltic pump, B: magnetic stirrer, C: solution tank, D: beaker containing solution, E: solution recirculation pipe, F: electrochemical cell, G: generator, H: multiparameter); (II) photo of electrochemical cell.

2.3. Analytical method

2.3.1. Quantification of diiodine

For the quantification of *in situ* generated diiodine, the spectrophotometric method was used. It consisted in monitoring the concentration of diiodine generated *in situ* during the electrochemical process. A calibration curve to monitor the concentration of diiodine was established. For this purpose, different concentrations of diiodine were obtained by dilution from a 0.1 M solution of I_2 . The absorbance of different concentrations of solutions to be analyzed in our experiments were determined with the help of previously used and very well washed COD tubes. For the determination of absorbances and peak wavelengths, 4mL of the different samples of solution are taken and put into a clean empty COD tube. After cleaning of these tubes, the absorbance values are read directly with the

DR/6000 spectrophotometer. The measure of these absorbances allowed us to know the maximum wavelength of diiodine and to draw the diiodine calibration curve which will permit to follow the concentration of diiodine produced over time.

2.3.2. Qualitative identification of *in situ* generated diiodine

For the *in situ* detection of diiodine, we used the starch test. The solution used for this test was obtained by dissolving 5 g of powdered starch in 50 ml of distilled water and mixing it with the aid of a magnetic bar. Some time later, we collected the supernatant (starch solution). A drop of this solution in contact with a diiodine solution (solution I_3^- and yellow in color) gives it an intense blue color. This is because starch is a ligand for the I_3^- ion.

2.3.3. Determination of chemical oxygen demand and limiting current demand

The chemical oxygen demand (COD) of the samples was determined using the HACH COD tubes by the "reactor digestion" method. The principle consists in taking 2 mL of samples at predefined dates which are introduced into a HACH tube and then heated in a digester at 150 °C for 120 minutes. After cooling, the COD value is read directly with the DR/6000 spectrophotometer of the HACH product. The chemical oxygen demand abatement rate was determined by the formula (Eq. (1)) below.

$$\Delta(\text{COD}) = \frac{\text{COD}_i - \text{COD}_f}{\text{DCO}_i} \quad (1)$$

With $\Delta(\text{COD})$: COD abatement rate; COD_i : initial COD and COD_f : final COD.

In order to know the regime that prevails during preparative electrolysis, the limiting current was calculated by applying the following equation (Eq. (2)) [18, 19]:

$$I_{\text{lim}} = 4Fk_dA\text{DCO} \quad (2)$$

Where; F: Faraday constant (96458 C/mol);

k_d : Mass transfer coefficient (cm/s)

A: surface of the electrode in contact with the solution (cm²) and COD in mol O₂/L.

3. Results and discussion

3.1. Diode adsorption spectrum (I₂), calibration curve and statistical data

Figure 2 shows the absorption spectra of 0.04 and 0.1 mM diiodine solutions. The 0.04 mM diiodine solution was obtained by dilution from the stock solution.

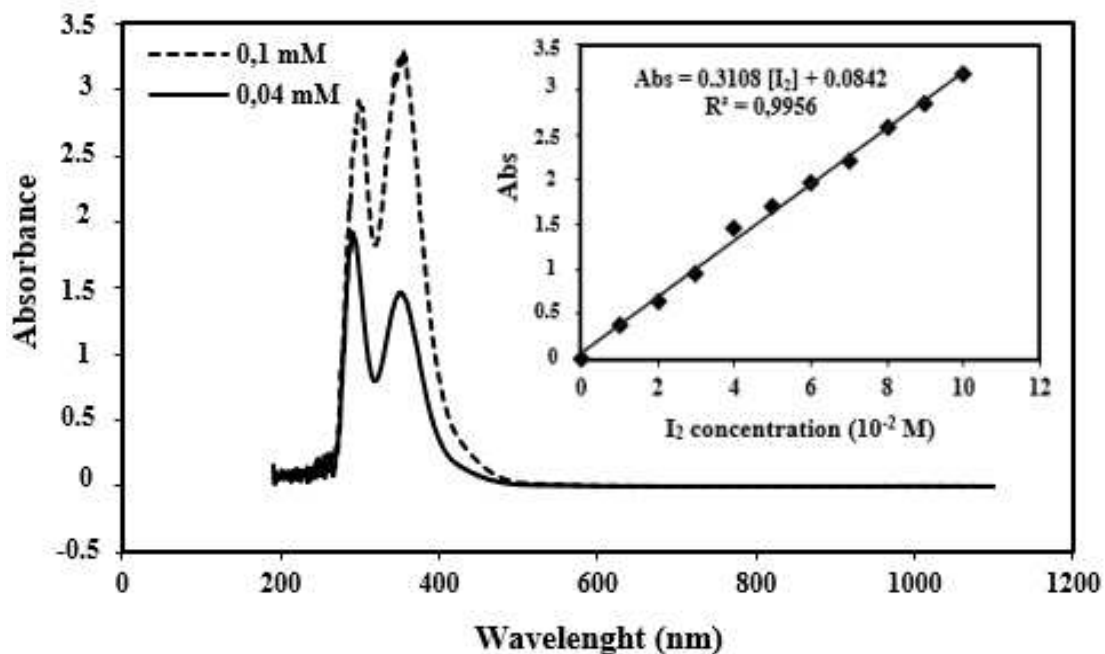


Fig. 2. Absorption spectrum of diiodine samples, inset: The diiodine calibration curve.

From Figure 2, two absorption peaks can be observed in the absorption spectrum of the diiodine solutions (0.04 M and 0.1 M) at wavelengths of 294 nm and 352 nm. These findings have been already reported by others [20, 21].

To establish the calibration curve for I₂, concentrations of diiodine solutions were obtained by dilution of the 0.1 M diiodine stock solution. The absorbance of these solutions were measured at a fixed wavelength of 352 nm. Linear regression of absorbance on concentration gave the line of equation $Abs = 0.3108[I_2] + 0.0842$; Abs is the absorbance and [I₂] in mol/L (insert of Figure 2). The determination coefficient is $R^2 = 0.9956$ attesting to the linearity of the solution preparation method for the concentration range from 0.04 to 0.1 M. Table 1 shows the statistical data of the diiodine concentration curve.

The limits of detection and quantification were determined following the ICH Guide [22]. $LOD = 3.3 \cdot \sigma / S$ and $LOQ = 10 \cdot \sigma / S$ with σ the standard deviation of intersection and S the slope of the calibration curve. The limit of detection

LOD and limit of quantification LOQ of this work are: $LOD = 0.0023$ mM and $LOQ = 0.007$ mM. These LOD and LOQ values are below the lowest concentration of our analysis (0.01 mM), so this indicates a good sensitivity of our analytical method.

To evaluate the reproducibility of our method (Table 2), diiodine concentrations ranging from 0.05 mM to 0.09 mM were prepared. Three independent tests of each concentration were carried out. The concentration found corresponding to each of the concentrations prepared from the regression line equation gives a percentage of $(99.75 \pm 0.03) \%$ with an $RSD = 0.42$ which is less than 1. This shows the reliability of the analysis technique.

Accuracy was investigated by analyzing different diiodine concentrations (0.02, 0.03, 0.04, 0.05 and 0.06 mM) three times intra-day and three times inter-day on three consecutive days. The standard deviation was determined and shown in Table 2. The average RSD in intra-day and inter-day are 0.5564 and 0.1768, respectively, indicating the accuracy of the analysis technique used in this work.

Table 1Statistical data of the calibration curve for the determination of I₂ spectrophotometrically

Parameter	Value
λ_{\max} (nm)	352
Color	yellow brown
Linear range (mM)	0.04 - 0.1
Regression equation	Abs = 0.3108 [I ₂] + 0.0842
Slop (L/mmol)	0.3108
Intercept (b)	0.0842
Limit of detection (mM)	0.0023
Limit of quantification (mM)	0.007

Table 2

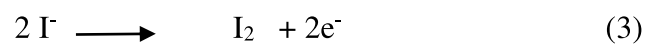
Recovery and precision

Recovery			Precision		
Added level (mM)	Recovery (%) (n = 3)	RSD (n = 3)	Added level (mM)	Inter-day (%) (n = 3)	Intra-day (%) (n = 3)
0.05	100 ± 0.002	0.04	0.02	1.44	0.256
0.06	100 ± 0.053	0.88	0.03	0.608	0.199
0.07	98.57 ± 0.054	0.78	0.04	0.293	0.217
0.08	100 ± 0.011	0.14	0.05	0.08	0.179
0.09	100 ± 0.023	0.26	0.06	0.361	0.033

3.2. *In situ* determination of diiodine

To carry out the *in situ* detection of diiodine, we performed the electrolysis of 0.05 M NaI under a current density of 10 mA/cm² (0.08 A) during 240 min. The evolution of the concentration of I₂ generated during the electrolysis of NaI is shown in Figure 3. The equation $[I_2] = 3.217 \text{ Abs} - 0.271$ of the regression line was used in the determination of the I₂ concentration over time. In this figure, it can be seen that the general trend of the I₂

concentration curve shows two parts: a rapid increase in concentration followed by an almost constant change in concentration after 20 minutes of electrolysis. Indeed, the increase in the curve reflects the formation of I₂ during the first 20 minutes of electrolysis; diiodine is formed according to the following relationship:



The plateau observed after 20 minutes of electrolysis could be explained by the saturation of the solution in I₂.

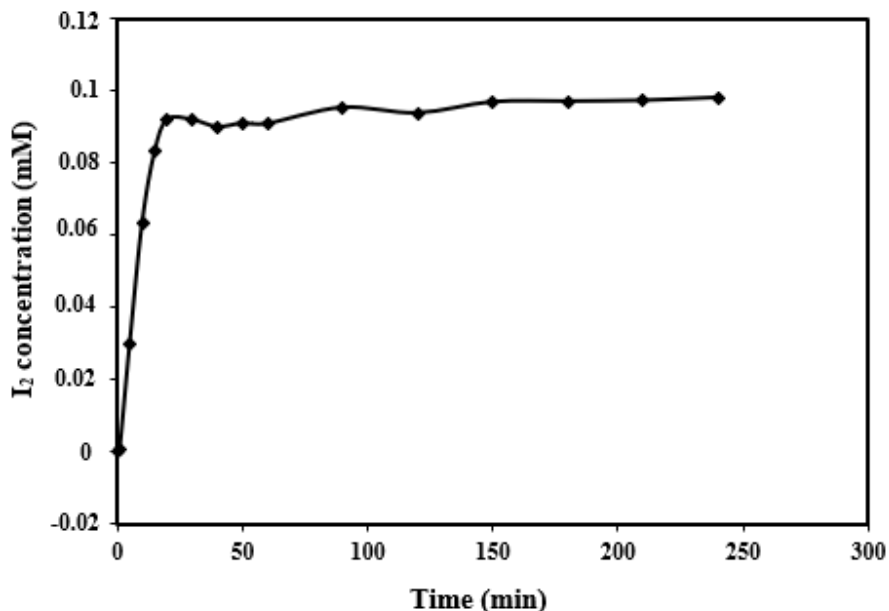


Fig. 3. Evolution of the concentration of I₂ formed during electrolysis of 0.05 M NaI under a current density of $j = 10 \text{ mA/cm}^2$.

3.3. Effect of sodium iodide on the degradation of metronidazole

Metronidazole (0.1 g/L) is a pharmaceutical compound. Its electrolysis was carried out in 0.1 M perchloric acid under a current density of 10 mA/cm^2 in order to evaluate the effect of I₂ on its degradation.

Figure 4 shows the degradation of metronidazole in the absence and the presence of NaI (0.05 M). In this figure, the evolution of the normalized COD (COD*) in the absence and the presence of NaI is presented. The two curves have an exponential appearance. However, the degradation rate of MNZ in the presence of NaI is faster than in its absence. After 3 h of degradation, the following COD removal rates are obtained: 83.48% and 100% in the absence and the presence of NaI, respectively.

In the absence of NaI, the degradation of MNZ would be due to the production of hydroxyl radicals on the DDB surface. Because on the surface of the DDB, hydroxyl radicals are physisorbed and are very labile. Therefore, the hydroxyl radicals will be available and will participate significantly in the degradation of any type of organic pollutants.

In the presence of NaI, the result obtained indicates that the organic compound is completely mineralized. This mineralization would be due to the synergistic effect of I₂ generated from NaI and hydroxyl radicals from the decomposition of water. The contribution of NaI in the mineralization of MNZ could be expressed by the following reaction:

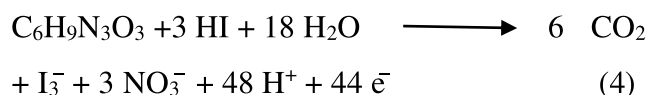


Figure 5 allows us to understand the evolution of the I_2 concentration during the degradation of MNZ in 0.1 M $HClO_4$ medium. The concentration of I_2 increases very rapidly from the first moments of electrolysis until it reaches a maximum after 15 minutes of electrolysis. After this time, there is a rapid decrease in I_2 concentration to 0 after 90 minutes of

electrolysis. This shows that the amount of I_2 produced was completely used to degrade the MNZ.

These results show that, in the diffusion-limited regime and in ($HClO_4 + NaI$) medium, the organic compound is degraded by the combined action of hydroxyl radicals and diiodine (I_2).

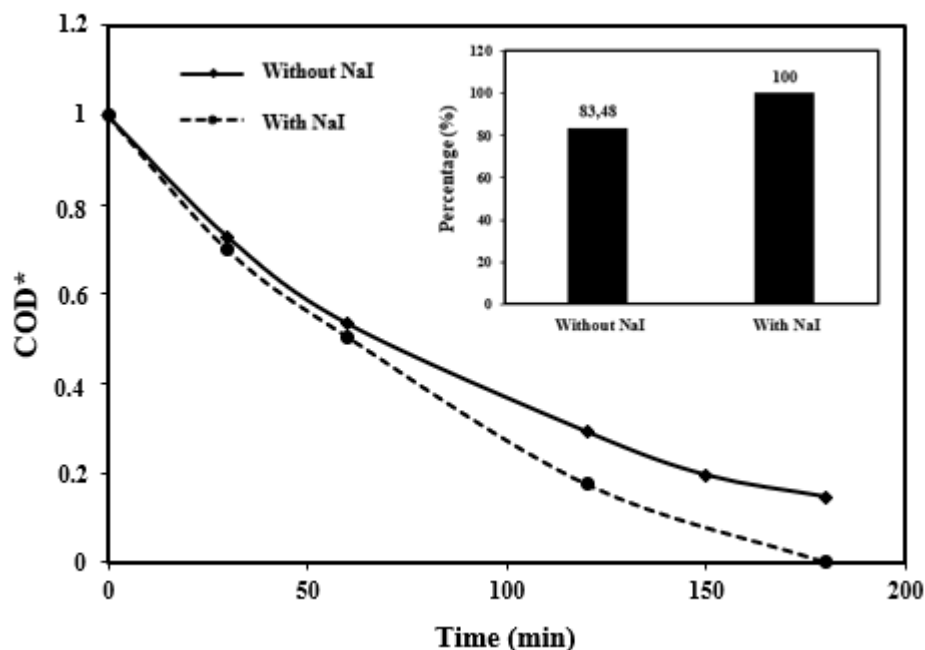


Fig. 4. Evolution of COD during treatment of $[MNZ] = 0.1$ g/L in $HClO_4$ in the absence and presence of 2.10^{-4} M NaI. $j = 10$ mA/cm²; $T = 25$ °C.

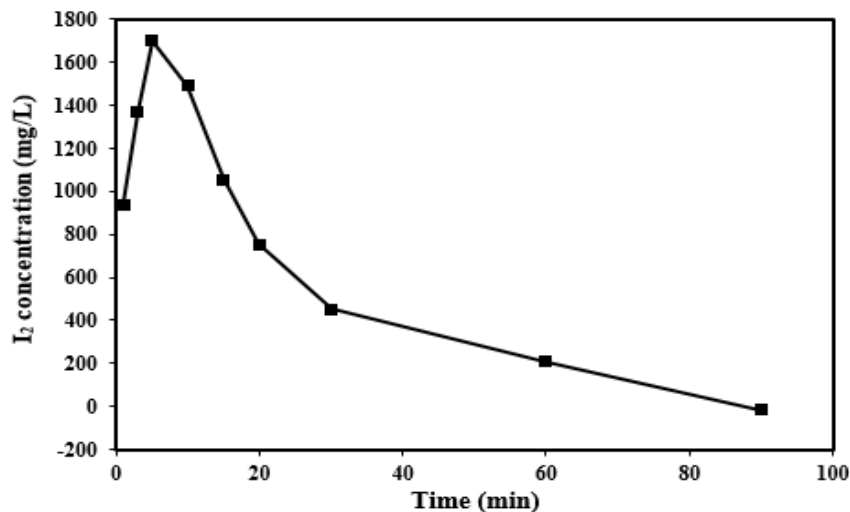


Fig. 5. Evolution of I_2 during electrolysis of the mixture (0.1 g/L MNZ + 0.1M $HClO_4$ + 0.05M NaI) under a current of 10 mA/cm² at $T = 25$ °C.

3.4. Demonstration of *in situ* diiodine generation during the degradation of telebrix

The degradation of 1 g/L of telebrix (TLX), an iodinated contrast medium, was performed in a 0.1 M KClO_4 solution at 3.125 mA/cm² for 3 h.

3.4.1. Staining of the telebrix solution during preparative electrolysis

The coloration of the TLX solution (1 g/L) was monitored during electrolysis. It can be seen that the solution, initially colorless, turns orange-yellow after 1.5 hours of electrolysis. This coloration persists until the end of the electrolysis (3 h) (Figure 6). The change in the initial coloration of the TLX solution would reflect the formation of intermediate compounds during its degradation. The coloration of the final TLX electrolysis solution was compared to that of NaI of initial concentration 0.2 M obtained after 4 hours of electrolysis (Figure 6). It can be seen that these end-of-electrolysis solutions have the same coloration. This would indicate the presence of I_2 in the electrolyzed TLX solution. This result shows that I_2 is released during the degradation of TLX.

Electrolysis of the 1 g/L TLX solution leads to an end-of-reaction solution with the same coloration (orange-yellow) as an end-of-reaction solution of NaI (0.2 M). During the TLX electrolysis, the absorbance of samples taken at different times (0, 30 and 1 h) was measured (Figure 7). A maximum absorption is observed

in the various spectra at a wavelength of 352 nm, with the intensity of the absorption peak increasing with time. This wavelength is the same as that of diiodine, indicating that I_2 is generated during the electrolysis of TLX. The orange-yellow color of the electrolyzed TLX solution and the absorption spectra would attest to the presence of diiodine.

In addition, another test was performed to confirm the presence of diiodine in the reaction medium: the test with starch. Indeed, when starch is added (just a few drops) to a medium containing diiodine, a purplish-blue coloration appears, characteristic of the presence of diiodine. A few drops of starch were added to the 0, 5, 10, 15, 20 and 30 minute samples. The results obtained are shown in the picture in Figure 8.

Samples from 0 to 10 minutes are colorless despite the addition of a few drops of starch. This shows that the starch test is negative from 0 to 10 minutes of electrolysis. After 15 minutes, the addition of starch causes a purplish blue color to appear, indicating the presence of I_2 . Electrolysis of the 1 g/L TLX solution leads to the formation of I_2 showing that there is a release of I^- whose oxidation to I_2 would contribute positively to the oxidation of TLX and probably the reaction intermediates.

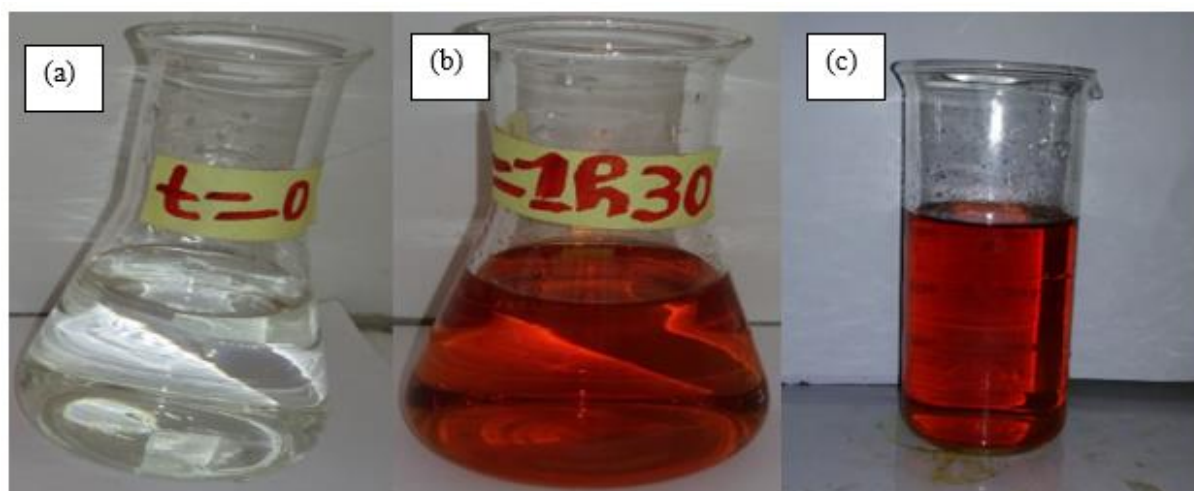


Fig. 6. Photo of the staining : (a) telebrix solutions before the start of electrolysis, (b) the telebrix solution after 1h30 min of electrolysis : solution becomes yellow-orange and persists until 3h, (c) the NaI solution after 4 hours of electrolysis.

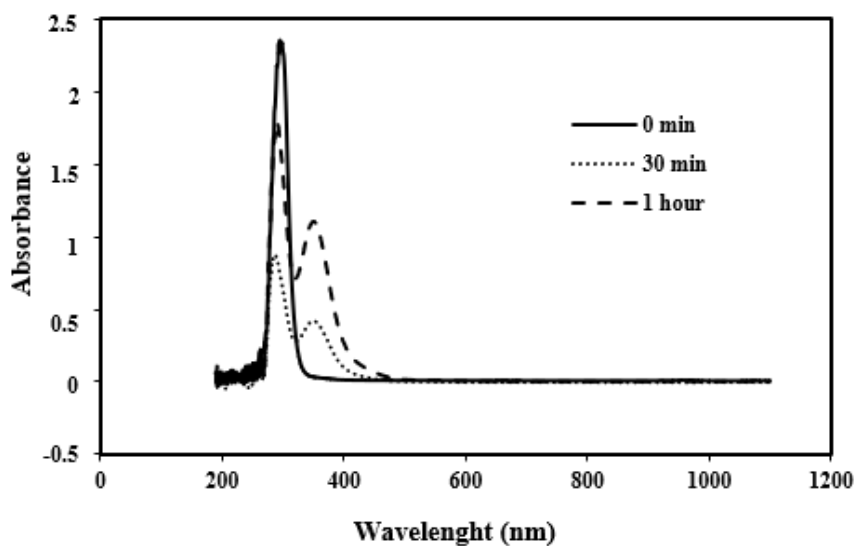


Fig. 7. Absorption spectrum of telebrix samples during electrolysis at 3.125 mA/cm^2 on the DDB for a concentration of 1 g/L .



Fig. 8. Starch test for the demonstration of diiodine formation during electrolysis of the TLX solution.

3.4.2. COD evolution of the telebrix and diiodine production

The degradation of TLX (1 g/L) in a 0.1 M KClO_4 solution on the DDB under a current density of 3.125 mA/cm^2 was monitored by a global parameter: the chemical oxygen demand (COD). The results obtained are presented in Figure 9.

In this figure, it can be seen that the COD decreases over time, from $2458 \text{ mgO}_2/\text{L}$ ($t=0 \text{ h}$) to $1782 \text{ mgO}_2/\text{L}$ after 3 h (180 minutes) of electrolysis. This reflects the degradation of TLX during electrolysis. The figure shows that the more the telebrix degrades, the more diiodine is produced. Indeed, the concentration of diiodine, initially zero, increases during the electrolysis and reaches 0.066 mM after 3 hours of TLX degradation. This indicates the release of I^- leading to the formation of I_2 in the reaction medium during the degradation of the iodinated

contrast product. Furthermore, the COD removal rate ($\Delta(\text{COD})$), calculated by Eq. (1), obtained after 3 h is 26.85%. This low value of $\Delta(\text{COD})$ could mean that the degradation of TLX under this current density does not lead to its mineralization. The limiting current density has been calculated by considering the Eq. (2) where k_d has already been determined in the previous work of our laboratory ($k_d=2.36 \times 10^{-7} \text{ m s}^{-1}$) [23]. The limited current density found is 11.28 mA/cm^2 which is higher than 3.125 mA/cm^2 . Thus, the degradation process of TLX is limited by electron transfer. This may explain the straight COD curve. Indeed, in such a regime, all the imposed current is used for the degradation of the organic compound. In addition, previous work in our laboratory on the degradation of other organic compounds such as amoxicillin has shown that the oxidation process is limited by diffusion [23, 24].

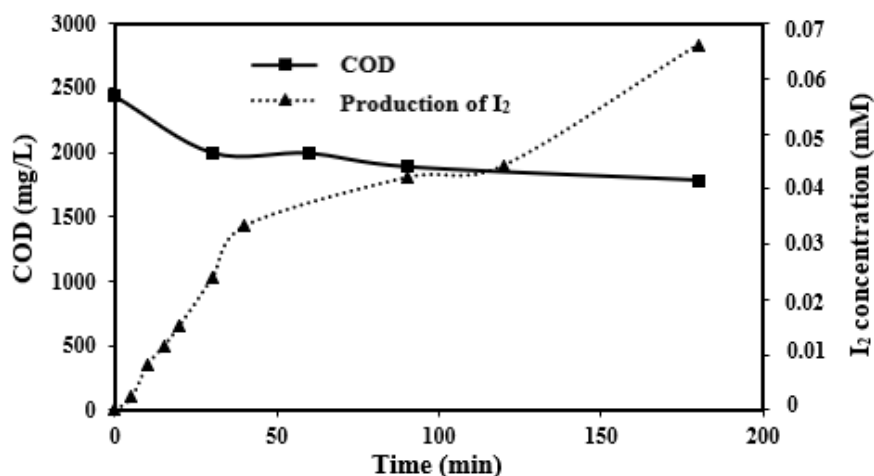


Fig. 9. Evolution of COD during the treatment and production of diiodine by the $[\text{TLX}] = 1\text{g/L}$ concentration telebrix at a current of 3.125 mA/cm^2 and at $T=25^\circ\text{C}$. Electrolyte support: KClO_4 0.1 M.

4. Conclusion

It appears from this work that the analytical technique used for the detection of *in situ* generated diiodine by the electrochemical method is linear, weak and accurate. In addition, the absorption spectrum of diiodine has a maximum peak at 352 nm. The electrolysis of NaI (0.05 M) leads to the production of diiodine whose evolution curve shows two phases: the first phase is faster during the first 20 minutes and the second phase is almost stationary; diiodine was detected in the organic compounds. It should be noted that during the electrolysis of telebrix (1g/L) at a current density of 3.125 mA/cm² and metronidazole (0.1 g/L) at a current density of 10 mA/cm², the participation of this oxidant was noted. The electrolysis of MNZ and TLX was performed on the DDB electrode. From the electrolysis of MNZ, it appears that radicals are produced and contribute to its degradation. In the presence of NaI, degradation under a current density of 10 mA/cm² leads to a 100% removal rate after 3 hours of electrolysis. This removal rate is higher than the removal rate obtained (83.48%) in the absence of NaI. This indicates that the degradation of MNZ occurs through the combined action of I₂ and ·OH leading to the mineralization of MNZ. In addition, the electrolysis of TLX revealed the production of I₂, attested by the starch test, which varies from 0 mM to 0.065 mM after 3 hours.

The limiting current density (11.25 mA/cm²), which is higher than the imposed current density (3.125 mA/cm²), indicates a regime limited by electron transfer. Under this regime, the degradation of TLX leads to an abatement rate of 26.85% after three hours of electrolysis.

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