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Detection of Oxidants Such as Hydroxyl Radicals and Chlorine Electrogenerated on a BDD Electrode by Simple Methods

Konan Sylvestre Koffi[1], Konan Martin Koffi[2], Foffié Thiery Auguste Appia[1], Sahi Placide Sadia[2], Kouakou Jocelin Kimou[1], Souleymane Kone[1], Lassiné Ouattara[1]

[1]Laboratoire de Constitution et de Réaction de la Matière, UFR SSMT, Université Félix Houphouët Boiguy, Abidjan, Côte d'Ivoire
[2]UFR Environnement, Université Jean Lorougnon Guédé, Daloa, Côte d'Ivoire
Email: syloekonan@gmail.com

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Abstract

The aim of this work is to detect electrogenerated hydroxyl radicals and chlorine by simple and less expensive methods. Preparative electrolyses of perchloric acid ($HClO_4$) and sodium chloride (NaCl) were performed on a boron-doped diamond (BDD) electrode. The hydroxyl radicals were quantified indirectly by assaying the samples from the $HClO_4$ (0.1 M) electrolysis with a 10^{-4} M potassium permanganate solution. The investigations showed that the amount of hydroxyl radicals depends on the concentration of $HClO_4$ and the current density. As for chlorine, a qualitative determination was carried out. A mixture of the electrolyte solution of $HClO_4$ (0.1 M) + NaI (0.2 M) + 2 mL of hexane, taken in this order, leads to a purplish-pink coloration attesting to the presence of Cl_2. The same test was carried out with NaBr and NaI giving pale and very pale pink colourations, respectively, showing that the intensity of the colouration depends on the strength of the oxidant present. In addition, oxidants were detected during the electrooxidation of metronidazole (MNZ). The results showed the participation of electrogenerated hydroxyl radicals. The generation of chlorine has also been proven. Furthermore, the degradation leads to a chemical oxygen demand (COD) removal rate of 83.48% and the process is diffusion-controlled.

Keywords

Electrooxidation, Hydroxyl Radicals, Chlorine, Detection

1. Introduction

Like most countries in the world, Côte d'Ivoire is faced with a real problem of wastewater before it is discharged. Wastewater of various types, including from hospitals, is discharged as such into the environment [1] [2]. Wastewater from hospitals can contain 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 humans [6] [7].

To treat wastewater containing compounds that are difficult to biodegrade, several processes are used. Among these treatment processes, there are the electrochemical advanced oxidation processes. Indeed, advanced oxidation processes are based on the *in-situ* generation of very powerful oxidising agents: hydroxyl radicals. These oxidative species are non-selective and capable of degrading very complex aromatic compounds and non-biodegradable pollutants. Its generation and reactivity for the degradation of persistent pollutants depend essentially on the type of electrode used at the anode. Indeed, for so-called "active" electrodes, the bonds between the electrode surface and the hydroxyl radicals are very strong. Hydroxyl radicals are chemisorbed on the surface of this type of electrode. As a result, they do not participate effectively in the degradation of organic compounds. On the other hand, for non-active anodes, hydroxyl radicals are physisorbed on the surface of the anode, and are therefore very labile. With this type of electrode, hydroxyl radicals are available and participate significantly in the degradation of pollutants of all kinds. Previous work in our laboratory has shown that the degradation of organic pollutants on a BDD electrode led to its mineralisation, while a conversion of the parent compound was achieved on DSA electrodes [8]-[12].

Hydroxyl radicals are very reactive with organic compounds and have a very short lifetime in the nanosecond range [13] [14]. This makes their detection very difficult. In addition, due to their high reactivity, they can easily destroy or disrupt the sensing elements of detection devices, preventing them from generating and transducing trustworthy signals [15] [16]. In recent years, several techniques have been used for the detection of hydroxyl radicals. These include electron spin resonance spectroscopy [17] [18], electrochemical sensors [19], fluorescent detectors [20] [21] and hydroxylation of aromatic compounds [22]. All these methods are very accurate but have some inherent disadvantages such as cost and complexity.

The environment contains many ions including chloride ions. The effect of chloride ions on the efficiency of electrooxidation of organic compounds has been extensively studied in our previous work [8]-[11]. The results obtained showed that the presence of chloride ions had a significant positive impact on the degradation of organic compounds. This is the case for the degradation of amoxicillin on RuO_2, IrO_2 and Pt-RuO_2-IrO_2 electrodes. The rate of chemical oxygen demand abatement (Δ(COD)) determined after 10 hours of electrolysis for each of the DSA

electrodes mentioned is 4.53% (RuO_2), 2.47% (IrO_2) and 0.83% (Pt-RuO_2-IrO_2) in the absence of NaCl and 40.71%, 71.65% and 73.79% in the presence of NaCl on RuO_2, IrO_2 and Pt-RuO_2-IrO_2 respectively [8] [9] [11]. These different results show that chloride ions are powerful oxidising agents. In solution, chloride ions can take various forms depending on the pH of the medium. We can have Cl_2 (Ph < 3), Cl_2 (pH < 3), HClO (3 < pH < 8) and ClO^- (pH > 8) according to Equations (1) to (3) [23]:

$$2Cl^- \rightarrow Cl_2 + 2e^- \quad (1)$$

$$Cl_2 + H_2O \rightarrow HClO + Cl^- + H^+ \quad (2)$$

$$HClO \leftrightarrow ClO^- + H^+ \quad (3)$$

Techniques for the qualitative detection of oxidative chlorine species generally include iodometry, colorimetric, amperometric and electrochemical methods [24]-[27]. Generally, many detection methods have some disadvantages related to the use of many types of reagents that may produce higher toxicity, high detection limit, difficulty of operation, and cost of equipment.

In this work, the aim is to determine hydroxyl radicals and chlorine by alternative, simple and less expensive methods. For this purpose, an indirect quantitative determination of hydroxyl radicals will be carried out by volumetric determination of hydrogen peroxide during the preparative electrolysis of perchloric acid. In addition, a qualitative determination will be carried out to detect chlorine during the preparative electrolysis of sodium chloride. Subsequently, the *in-situ* generation of hydroxide radicals and chlorine will be demonstrated during the electrolysis of metronidazole (MNZ) in perchloric acid. The qualitative test for the detection of the oxidants Br_2 and I_2 will also be performed during the electrolysis of NaBr and NaI, respectively.

2. Experimental Method

2.1. Chemicals

Perchloric acid (Panreac) and sodium chloride (Problabo) were used as supporting electrolyte and prepared with distilled water. Hydrogen peroxide 35% (Sharlau) was determined by potassium permanganate (Panreac) for the monitoring of hydroxyl radicals at Scharlau. Sodium iodide (99.5%) and hexane (95% - 97%) were manufactured by Sigma-Aldrich and Ensure respectively. Metronidazole, manufactured by Exphar SA of Belgium, was purchased from a pharmacy in Abidjan in tablet form. The pH was adjusted using H_2SO_4 (Sigma-Aldrich) and NaOH (Panreac). The sodium bromide was manufactured by Panreac.

2.2. Electrochemical System for Anodic Oxidation

A volume of 250 mL under magnetic stirring and at laboratory temperature, covered with aluminum foil, was introduced into an electrochemical cell. Boron-doped diamond electrode was used at the anode and zirconium at the cathode. Both electrodes have a surface area of 16 cm^2. Concentrations of 0.1 M $HClO_4$, and NaCl

were electrolysed individually for the *in-situ* determination of hydroxyl radicals and chlorine. Subsequently, preparative electrolysis of 0.1 M $HClO_4$ + 0.1 g/L metronidazole (MNZ) was performed for COD monitoring as well as oxidant detection. The experimental setup for the preparative electrolysis is shown in Figure 1.

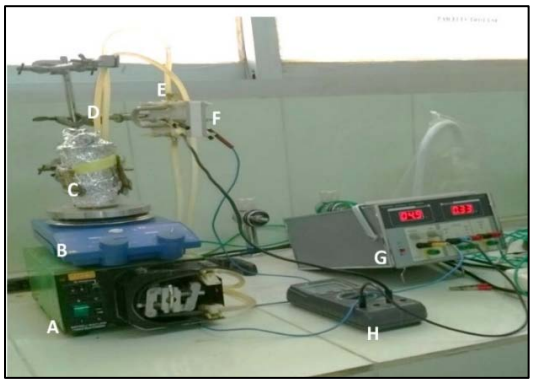

Figure 1. Experimental set-up for preparative electrolysis (A: peristaltic pump; B: magnetic stirrer; C: solution tank; D: beaker containing solution; E: solution recirculation pipe; F: electrochemical cell; G: generator; H: multiparameter).

2.3. Quantitative and Qualitative Detection of Oxidants

2.3.1. Quantitative Detection of Hydroxyl Radicals

For the detection of hydroxyl radicals, several detection methods, both direct and indirect, can be used. In our work, an indirect and simple method for the detection of $^{\cdot}OH$ was considered: the volumetric determination of hydrogen peroxide by potassium permanganate ($KMnO_4$). For this purpose, 10 mL of the samples, taken at well-defined times, were dosed with 0.1 M $KMnO_4$ in the presence of 10 mL 0.1 M H_2SO_4. The turn is reached when the initially colourless solution turns pink. Furthermore, a calibration curve for H_2O_2 concentrations ranging from 0 to 1 mM as a function of the volume of $KMnO_4$ poured in was established before the preparative electrolysis. The curve obtained is a straight line of equation $[H_2O_2] = 0.0473V_{KMnO4} - 0.0386$, with a correlation coefficient R^2 of 0.9961 which is close to 1 attesting to the good linearity of the method.

2.3.2. Qualitative Detection of Chlorine

The aim of this work is also to determine the presence of chlorine during the electrolysis of a sodium chloride solution (0.1 M) in order to identify chlorine in an unknown medium. The experiment was carried out at an acidic pH because according to the probaix diagram for chlorine, chlorine exists in the following pH range [0, 4.5].

The initial pH of the sodium chloride solution is 6.833. A 1 M sulphuric acid solution was used to adjust the pH to 2. The electrolysis of the sodium chloride solution is very suffocating due to the release of chlorine which is toxic. Thus, the detection of chlorine was done by taking a certain volume of NaCl samples to which 1 mL of NaI (0.2 M) and 2 to 5 mL of the hexane solution were added.

After strong agitation of the mixture, the appearance of a pink coloration of the hexane proves the presence of active chlorine (Cl_2). The same test was performed during the preparative electrolysis of NaI and NaBr.

2.4. Monitoring of Degradation by Chemical Oxygen Demand (COD)

The COD of the samples was determined in our experiments using HACH COD tubes. To determine it, 2 mL of sample is taken and put into a COD tube and heated in a digester (HACH) at 150˚C for 120 minutes. After cooling, the COD value is read directly with the DR/6000 spectrophotometer (HACH). The COD reduction rate is determined using this formula:

$$\Delta(\mathrm{COD}) = \left((\mathrm{COD}_0 - \mathrm{COD}_t)/\mathrm{COD}_0\right)*100 \quad (4)$$

where COD_0 and COD_t are respectively the COD at time 0 and t in mgO_2/L.

3. Results and Discussion

3.1. *In-Situ* Determination of Hydroxyl Radicals

3.1.1. Electrolysis of Perchloric Acid

In order to demonstrate the *in-situ* production of hydroxyl radicals, the electrolysis of perchloric acid was carried out under constant stirring for 180 minutes at laboratory temperature (25˚C) and a density of 10 mA/cm^2. 10 mL of $HClO_4$ samples taken at defined time intervals t were determined by 10^{-4} M $KMnO_4$ during the electrolysis. The concentration of H_2O_2 at time t is determined from the relation:

$$N_{H_2O_2} V_{H_2O_2} = N_{KMnO_4} V_{KMnO_4} \quad (5)$$

where N is normality and V is volume.

Figure 2 shows the evolution of the concentration of hydroxyl radicals generated *in-situ* during the electrolysis of 0.1M $HClO_4$. In Figure 2, the concentration of hydrogen peroxide increases during $HClO_4$ electrolysis from 0 mM at t = 0 min to 1.5 mM after 180 min. The electrolysis of $HClO_4$ thus leads to the production of hydrogen peroxide and thus of hydroxyl radicals.

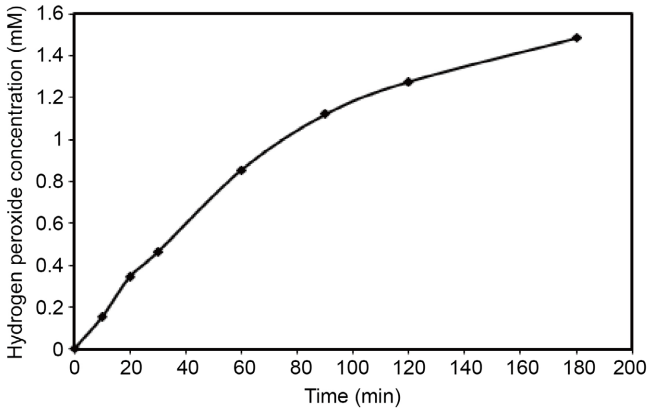

Figure 2. Electrolysis of 0.1 M $HClO_4$ at a current density of j = 10 mA/cm^2.

Figure 3 shows the absorbances of 0.5 M, 1 mM hydrogen peroxide from a 35% commercial hydrogen peroxide solution and a $HClO_4$ sample after 1 hour of electrolysis. A perfect superposition of the absorption curves in the wavelength range from 190 nm to 1100 nm is shown. This shows that the electrolysis of $HClO_4$ leads to the formation of hydrogen peroxide and therefore hydroxyl radicals.

Indeed, during the electrolysis of the supporting electrolyte, water is oxidised. The oxidation of H_2O leads to the formation of hydroxyl radicals (Equation (6)). In the absence of an organic compound, the hydroxyl radicals can only react with each other and form hydrogen peroxide (Equation (7)).

$$2H_2O \rightarrow \cdot OH + OH^- + 2H^+ + e^- \quad (6)$$

$$\cdot OH + \cdot OH \rightarrow H_2O_2 \quad (7)$$

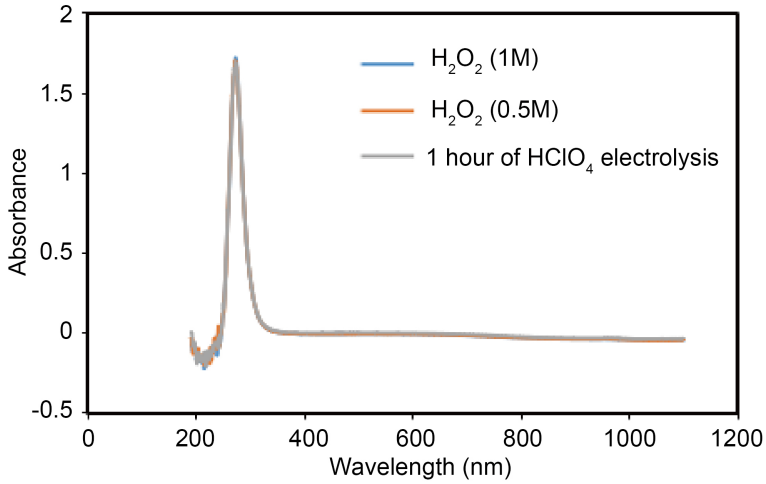

Figure 3. Absorption spectrum of hydrogen peroxide and $HClO_4$.

3.1.2. Influence of the Applied Current

The amount of hydroxyl radicals generated can be influenced by various parameters including the applied current density. The influence of the applied current (current density 3.125, 5 and 10 mA/cm^2 respectively) on the production of hydroxyl radicals was investigated by monitoring the concentration of hydrogen peroxide during the electrolysis of 0.1 M $HClO_4$. The results obtained are presented in Figure 4.

It can be seen from this figure that the production of hydroxyl radicals becomes important with the applied current. For an applied current, the production of hydrogen peroxide, and therefore of hydroxyl radicals, increases with the duration of the electrolysis. Indeed, Gnamba et al showed that the rate of degradation of amoxicillin on the boron-doped diamond electrode (BDD) increased with the imposed current density. This is related to the hydroxyl radicals formed, the amount of which depends on the imposed current.

The generation of hydroxyl radicals on the BDD occurs as follows:

$$BDD + H_2O \rightarrow BDD(\cdot OH) + H^+ + e^- \quad (8)$$

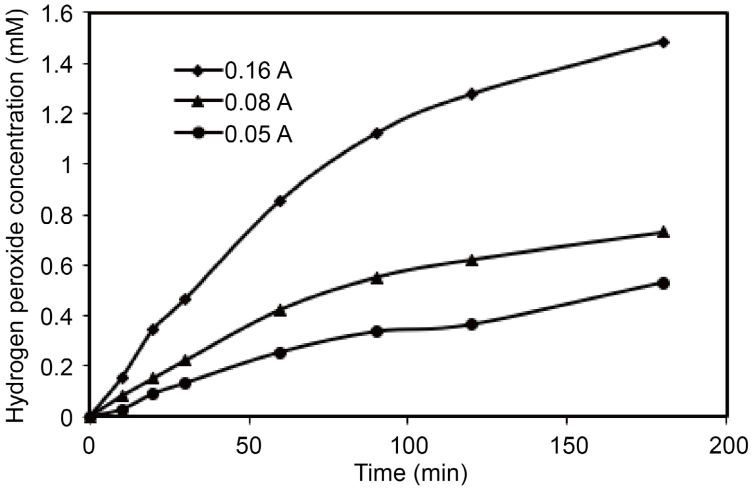

Figure 4. Influence of current (0.05 A, 0.08 A, 0.16 A) on H_2O_2 production for 0.1 M $HClO_4$.

3.1.3. Influence of $HClO_4$ Concentration

Electrolysis of several concentrations (0.1 M, 0.2 M, 0.4 M) of perchloric acid was performed on the BDD at a current density of 5 mA/cm² for 180 min. **Figure 5** shows the hydrogen peroxide concentration versus time curves. In **Figure 5**, it can be seen that the concentration of H_2O_2, initially zero for all investigated concentrations, increases to 0.723, 1.10 and 1.915 mM after 180 min of electrolysis for 0.1, 0.2 and 0.4 M 0.1 M $HClO_4$ respectively. This shows that the initial concentration of $HClO_4$ plays an important role in the production of hydroxyl radicals.

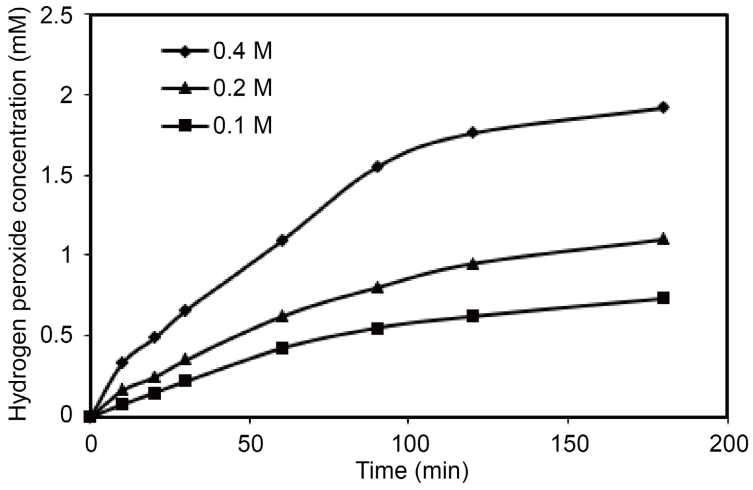

Figure 5. Influence of $HClO_4$ (0.1 M, 0.2 M, 0.4 M) on hydrogen peroxide production at 5 mA/cm².

3.2. *In-Situ* Determination of Chlorine

3.2.1. Qualitative Detection

Chlorine detection was investigated by degradation of a sodium chloride solution (0.1 M) under a current density of 10 mA/cm². In order to promote chlorine

generation, the initial pH (6.833) was reduced and maintained at 2 using 1 M $HClO_4$. The electrode used at the anode for NaCl electrolysis was boron-doped diamond (BDD). After 15 minutes of electrolysis, a suffocating and very unpleasant odour characteristic of chlorine release was noted. After 30 min of electrolysis, NaCl samples were taken and tested for Cl_2. NaI and hexane were added to the NaCl electrolysis samples. The photo in **Figure 6** shows the photo of the NaCl sample after 30 minutes of electrolysis (tube A), the tube containing the NaCl (30 minutes) + NaI sample (tube B). The third tube C contains a mixture of NaI + NaCl (30 minutes) + 1 mL of hexane and tube D, NaI+ NaCl (30 minutes) + 2 - 5 mL of hexane.

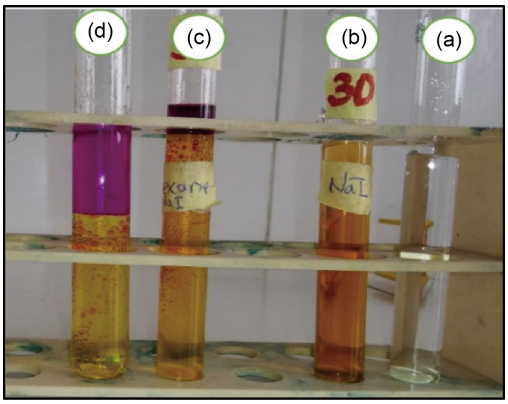

Figure 6. Photo of Cl_2 test.

According to this picture, the addition of NaI to the NaCl sample gives a yellow coloration indicating the presence of an oxidant. The addition of hexane (2 - 5 mL) to the NaCl + NaI mixture gives a pinkish-purple colouration. This would indicate the presence of the oxidant Cl_2. It should be noted that a very suffocating odour is given off during the electrolysis of NaCl. To confirm that chlorine is responsible for the pinkish-purple colouration observed, the same test was carried out during the electrolysis of some solutions containing halogens (NaI and NaBr).

Electrolysis of NaBr concentration (0.1 M) under a current density of 10 mA/cm^2 was performed. The electrode used was boron-doped diamond (BDD). During this electrolysis, a 5 mL sample was taken after 30 minutes of electrolysis. In order to highlight the purplish-pink coloration of the hexane, NaI (0.2 M) and hexane were added to the samples of the NaBr electrolysis. The result obtained is shown in **Figure 7**.

The colour of the NaBr electrolyte solution is pale green (**Figure 7(a)**). The addition of NaI (0.2 M) (**Figure 7(b)**) to this solution transforms this green colour (bromine water colour) into yellow, indicating the presence of an oxidant, in this case Br_2. The addition of hexane to the mixture (NaBr + NaI) (**Figure 7(c)**) leads to a very pale pink colouration on the surface of the mixture (**Figure 7(c)**). This could be characteristic of the presence of a weak oxidant (Br_2) in the reaction medium.

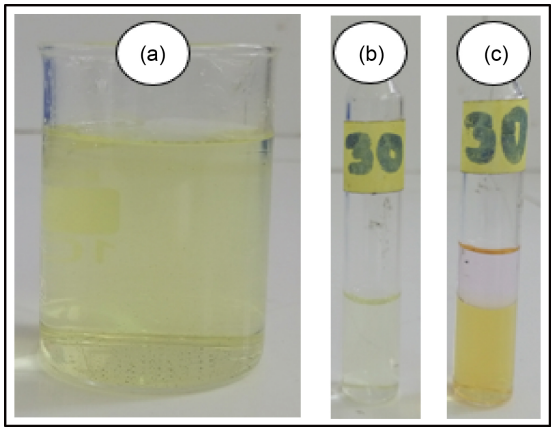

Figure 7. (a) Staining of the NaBr (0.1 M) electrolyte solution after 1 hour of electrolysis; (b) Staining of NaBr (0.1 M) electrolyte solution after 30 minutes of electrolysis; (c) Electrolyte solution mixture of 5 mL 0.1 M NaBr + 1 mL 0.2 M NaI + 2 mL hexane.

The electrolysis of NaI concentration (0.1 M) was carried out under a current density of 10 mA/cm^2. The electrode used was boron-doped diamond (BDD). A sample of the NaI solution was taken after 30 minutes of electrolysis. To highlight the purplish-pink coloration of the hexane; NaI (0.2 M) and hexane were added to the sample taken from the NaI electrolysis. The result obtained is shown in **Figure 8**.

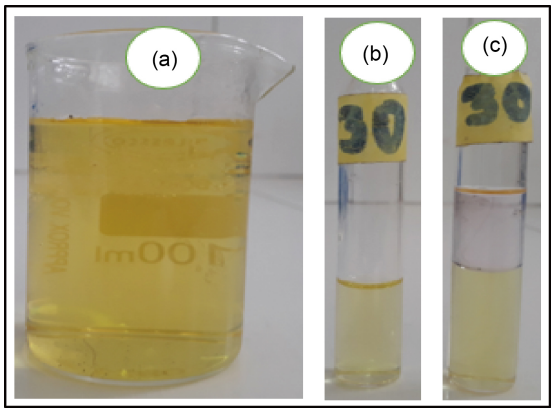

Figure 8. (a) Coloration of the NaI (0.1 M) electrolyte solution after 1 hour of electrolysis; (b) Coloration of NaI (0.1 M) electrolyte solution after 30 minutes of electrolysis; (c) Electrolyte solution mixture of 5 mL 0.1 M + NaI 1 mL 0.2 M + NaI 2 mL hexane.

The coloration of the NaI solution after 30 minutes of electrolysis is orange-yellow (**Figure 8(a)**) characteristic of the presence of I_2. This colouration is maintained with the addition of NaI (**Figure 8(b)**), attesting to the presence of an oxidant, I_2. The addition of hexane leads to a very pale pink coloration on the surface of the mixture (**Figure 8(c)**). This could be characteristic of the presence of a weak oxidant (I_2) in the reaction medium.

The chlorine detection test was carried out on the electrolytic solutions of NaCl, NaBr and NaI. From these investigations, it appears that the test is positive with all these solutions indicating the formation of oxidants during preparative electrolysis. However, the vivid purplish-pink colouration obtained in the NaCl case, highlighting the electrogeneration of chlorine, in contrast to the very pale pink colouration obtained in the case of NaBr and NaI would show a selectivity of this method. This technique can therefore be applied to the detection of chlorine.

3.2.2. Electrolysis of Perchloric Acid

The electrolysis of 0.1 M $HClO_4$ was performed on the DDB electrode at a current density of 10 mA/cm^2.

In order to demonstrate the presence of chlorine during the electrolysis of perchloric acid, 10 mL of the reaction mixture was taken and 1 mL of NaI (0.2 M) and 2 mL of hexane were added. The mixture was stirred vigorously and then left to stand to allow decantation. The photo in Figure 9 shows the mixture of the electrolyte solution, NaI and hexane.

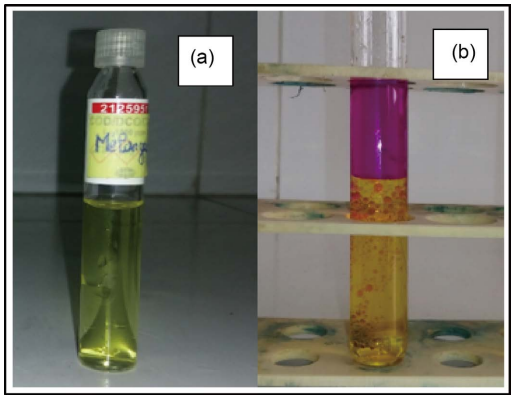

Figure 9. (a) Electrolyte solution mixture of 10 mL 0.1 M $HClO_4$ + 1 mL 0.2 M NaI; (b) 10 mL 0.1 M + $HClO_4$ electrolyte solution mixture 1 mL 0.2 M + NaI 2 mL hexane.

In Figure 9(a), mixing the 0.1 M $HClO_4$ and 0.2 M NaI electrolyte solution gives a yellow coloration. The addition of hexane leads to a purplish-pink coloration on the surface of the mixture (Figure 9(b)). This is characteristic of the presence of Cl_2 in the mixture. Indeed, the initial pH of the reaction medium was 0.865 and was maintained below 2.5 throughout the electrolysis. This confirms the formation of Cl_2 during the electrolysis of 0.1 M $HClO_4$. Compared to NaCl electrolysis, 0.1 M $HClO_4$ electrolysis does not cause a suffocating odour to be released.

The formation of chlorine can be summarised as follows (Equation (9)):

$$4HClO_4 \rightarrow 2Cl_2 + 7O_2 + 2H_2O \quad (9)$$

3.3. Degradation of MNZ: Identification of Hydroxyl Radicals and Chlorine

In-situ detection of hydroxyl radicals and chlorine was investigated during

electrolysis of HClO4 (0.1 M) containing 0.1 g/L metronidazole (MNZ) under a current density of 10 mA/cm^2.

3.3.1. Identification of Hydroxyl Radicals

To detect the hydroxyl radicals, 10 mL of the sample mixture ($KClO_4$ + MNZ) was assayed at different times with $KMnO_4$ of 10^{-4} M concentration. The results are shown in Figure 10.

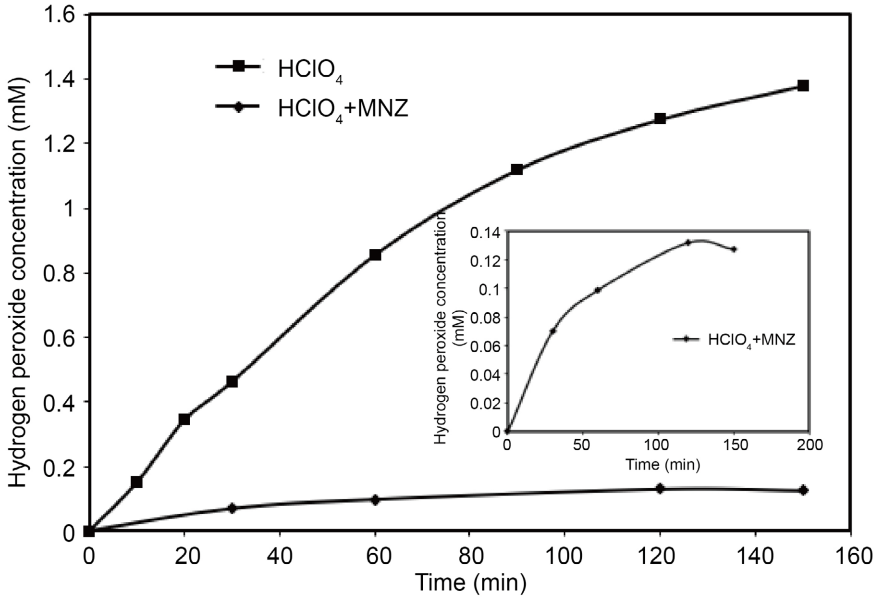

Figure 10. Comparison between electrolysed $HClO_4$ and electrolysed ($HClO_4$ + MNZ). Inset: Evolution of hydrogen peroxide during electrolysis of MNZ in $HClO_4$.

According to this figure, the concentration of hydrogen peroxide increases from 0 to 0.13 mM after 120 minutes of electrolysis and then remains almost constant until 150 minutes (inset in Figure 10). This shows that hydroxyl radicals are formed during the degradation of MNZ on boron-doped diamond. However, the amount of hydroxyl radicals detected during the degradation of MNZ is much lower than that detected during the electrolysis of $HClO_4$.

For example, for 60 minutes of electrolysis, the amount of radicals detected in $HClO_4$ alone is almost 9 times that detected in the case (MNZ + $HClO_4$). This difference could be explained by the fact that the hydroxyl radicals generated during the electrolysis of MNZ participate significantly in the degradation of the organic compound (metronidazole).

The degradation of MNZ (0.1 g/L) in a 0.1 M $HClO_4$ solution on the DDB at a density of 10 mA/cm^2 was monitored by measuring the COD. The results obtained are shown in Figure 11.

The COD evolution curve obtained decreases exponentially. The decrease in COD during electrolysis implies that the MNZ is degraded on the BDD below 10 mA/cm^2. This degradation leads to a COD removal rate of 83.48% after 180 minutes of electrolysis.

The limiting current density, determined by Equation (6), for the degradation of MNZ is 0.473 mA/cm^2, which is lower than 10 mA/cm^2. The degradation of MNZ was essentially controlled by mass transfer, i.e. limited by diffusion. This can explain the exponential curve of the COD.

$$J_{lim} = 4Fk_dCOD \quad (10)$$

where F is faraday constant (96458 C/mol); k_d is mass transfer coefficient (cm/s) and COD in mol O_2/L.

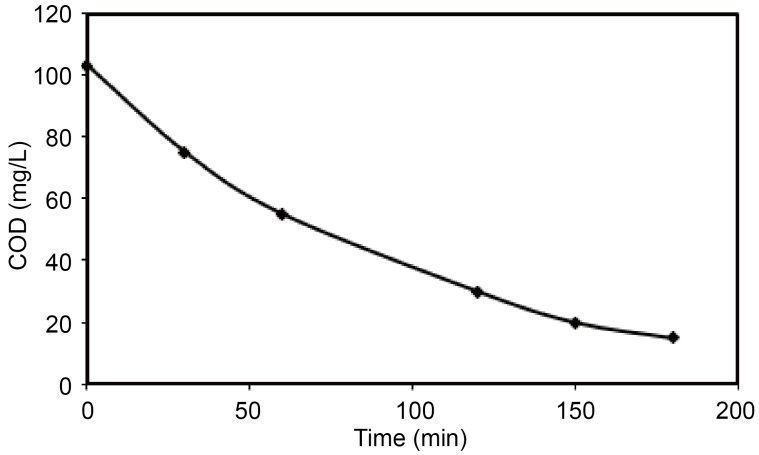

Figure 11. Evolution of COD during degradation of 0.1 g/L MNZ under a current density of 10 mA/cm^2. Supporting electrolyte $HClO_4$ 0.1 M, T = 25˚C.

3.3.2. Identification of Chlorine

In **Figure 12**, mixing the solution of electrolysed MNZ in 0.1 M $HClO_4$ and 0.2 M NaI gives a yellow coloration. The addition of hexane leads to a purplish-pink coloration on the surface of the mixture. This is characteristic of the presence of Cl_2 in the mixture. Indeed, the initial pH of the reaction medium was kept below 2.5 throughout the electrolysis. The purplish-pink colouration is characteristic of the presence of Cl_2 in the reaction medium during the electrolysis of MNZ in 0.1 M $HClO_4$.

Figure 12. Electrolyte solution + a quantity of NaI + hexane at T = 25˚C.

4. Conclusions

The objective of our work was to establish alternative methods for the *in-situ* detection and quantification of the oxidants •OH and Cl_2. To achieve our objective, these oxidants were detected in the absence and presence of metronidazole. The *in-situ* determination of hydroxyl radicals during the electrolysis of a 0.1 M perchloric acid ($HClO_4$) solution was performed. The results obtained show that the electrolysis of $HClO_4$ leads to the production of hydroxyl radicals. The quantification of hydroxyl radicals was done by dosing the electrolysed solution with a $KMnO_4$ solution. The amount of hydroxyl radicals produced depends on some parameters such as the current density and the initial concentration of $HClO_4$. This amount of •OH increases with a current density ranging from 3.125 to 10 mA/cm^2 and then with the increase of the initial $HClO_4$ concentration.

Chlorine was detected by colorimetric determination. The results obtained showed that the presence of chlorine is proven by a purplish-pink coloration of the hexane. The formation of Cl_2 was also demonstrated during the electrolysis of 0.1 M $HClO_4$. We also carried out the electrooxidation of metronidazole (0.1 g/L) in a 0.1 M $HClO_4$ solution on the DDB at a density of 10 mA/cm^2 and monitored it by measuring the COD. The electrolysis of metronidazole showed that hydroxyl radicals and chlorine were produced and contributed to its degradation.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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