# Treatment of a Tunisian textile effluent containing Bromothymol Blue dye using anodic oxidation on Boron Doped Diamond electrode

Malak Maamar[a,b,*] and Nizar Bellakhal[a]

*[a] Research Unit of Catalysis, Electrochemistry, Nanomaterials and their Applications and Didactic (CENAD), National Institute of Applied Sciences and Technologies (INSAT), Carthage University, 1080 Tunis, Tunisia.*
*[b] Department of Chemistry, Bizerte Faculty of Sciences (FSB), Carthage University, 7021 Zarzouna, Tunisia.*

**Abstract:** In the present study, Anodic oxidation (AO) as an Advanced Oxidation Process (AOP), was applied to degrade and mineralize a synthetic solution of a textile dye, Bromothymol Blue (BTB) on a Boron Doped Diamond (BDD) anode. An industrial discharge, sampled from a Tunisian textile industry containing BTB, was then treated, at the same operating conditions by AO. The effect of key parameters such as current density, reaction medium pH, treatment time, bubbling and cathode nature was investigated for the synthetic BTB solution. Discoloration yield was optimal and it reached 99% after 60 min of BTB treatment at pH 3, using a carbon felt as a cathode, operating at 60 mA cm$^{-2}$ as current density and maintaining bubbling during the electrolysis. BTB mineralization was investigated under these optimal conditions by monitoring the discoloration, the Chemical Oxygen Demand (COD) and the Total Organic Carbon (TOC) during 360 min of treatment, recording 100% of discoloration, 67% of COD abatement and 59% of TOC abatement. Thereupon the optimization of BTB synthetic dye solution, AO method was applied to oxidize an industrial textile effluent. Results found after 360 min of treatment at the same optimal conditions showed almost 94% of discoloration, 59% and 52% of COD and TOC removal respectively. The energy consumption per unit COD mass (EC$_{COD}$) of the AO was also calculated for the treatment of both BTB synthetic solution and the Tunisian textile effluent. 0.7 kWh (g COD)$^{-1}$ and 0.91 kWh (g COD)$^{-1}$ were found respectively after 360 min of treatment.

**Keywords:** Bromothymol Blue, Advanced Oxidation Process, Anodic Oxidation, Boren Doped Diamond anode, Textile Effluent
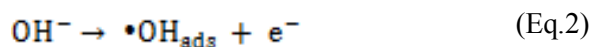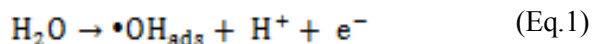
## INTRODUCTION

Textile industries are considered as one of the most polluting sectors worldwide. This is mainly due to the high discharge volume of textile, the intensity of its colors, its high organic contents in addition to its persistence and low biodegradability [1-5]. In fact, they represent a major risk to the aquatic ecosystem and therefore to the living beings [6-8]. Hence, solving the pollution issues caused by the textile industries has become an environmental priority.

Several methods of wastewater treatment, including physical, chemical and biological technologies, attempted to treat these releases. However, in most cases, these traditional wastewater treatments technologies are non-destructive or ineffective for the total removal of toxic and recalcitrant textile dyes due to the chemical stability of these pollutants [9,10]. Moreover, the cost of these traditional processes and their production of secondary waste products such as sludge may need further disposal as well as refractory toxic chemicals [11-13].
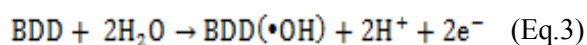
Recently, a growing interest was granted to Anodic Oxidation (AO) method to treat biologically refractory organic pollutants [14-16]. Considering its high oxidation efficiency, its fast reaction rate and its simple use and feasibility compared to conventional processes. AO is based on the generation of very reactive species hydroxyl radicals •OH which have high oxidation potential ($E^0$(•OH/H$_2$O) = 2.8 V/NHE) adsorbed on the surface of a high anode O$_2$ over potential by water oxidation in an acidic or neutral medium (Eq.1) and hydroxide ion in basic medium (Eq.2) [17].

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* Corresponding author, e-mail address : malakmaamar@hotmail.fr

$$H_2O \rightarrow {}^{\bullet}OH_{ads} + H^+ + e^- \qquad \text{(Eq.1)}$$

$$OH^- \rightarrow {}^{\bullet}OH_{ads} + e^- \qquad \text{(Eq.2)}$$

This process efficiency depends highly on the anode choice which must be characterized by a high $O_2$ evolution over potential. For this reason, typical electrodes such as graphite, platinum and the dimensionally stable anodes are not effective enough for pollutant oxidation. Electrodes such as $PbO_2$, $SnO_2$ and $TiO_2$ are inexpensive and easy to fabricate. They have been tested and they gave satisfactory results for AO process. However, they present a poor electrochemical stability [18-20].

In this context, a more promising anode was developed, the Boron Doped Diamond (BDD) thin film electrodes. They have high current efficiency, high oxygen evolution over potential, low capacitance, and show an important electrochemical stability [21]. It is suggested that the organics can be incinerated to carbon dioxide by the hydroxyl radical $^{\bullet}OH$ electro-generated from water oxidation (Eq.3) [22]:

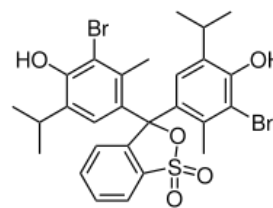$$BDD + 2H_2O \rightarrow BDD({}^{\bullet}OH) + 2H^+ + 2e^- \quad \text{(Eq.3)}$$

Several toxic pollutants such as surfactants [23], herbicides [24, 25] and dyes [26, 21] were successfully mineralized by AO using BDD electrode.

Bromothymol Blue (BTB) (Figure 1), communally used as a pH indicator, is a textile dye derivative [27, 28] widely used in Tunisian textile industry [29, 30]. It presents dangerous synergic effects with azo based dyes making its mineralization necessary. BTB treatment was performed by numerous processes such as electro-Fenton process [31], electro-polymerization [32], plasma [33], photo-Fenton process [34] and photo-catalytic process [35].

Nevertheless, there is no information reported in the literature to date concerning the degradation of BTB by AO on BDD anode.

This paper introduces AO on BDD anode in order to degrade BTB until its total mineralization. The optimization of various parameters was carried



**Figure 1:** Chemical structure of BTB

out. The color intensity, the chemical oxygen demand and the total organic carbon removal percentages were determined. In order to test its effectiveness, this optimized process was applied for treating a Tunisian textile effluent. The energy consumption per unit chemical oxygen demand mass of the AO was determined for the treatment of BTB synthetic solution and for a Tunisian textile effluent.

**MATERIALS AND METHODS**
**1. Chemicals**
The BTB (4,4'-(1,1-Dioxido-3H-2,1-benzoxa-thiole-3,3-diyl) bis (2-bromo-6-isopropyl-3-methylphenol) was purchased from Reactifs Ral. Its chemical structure and its main characteristics are given respectively in Figure 1 and in Table I. Anhydrous sodium sulfate ($Na_2SO_4$) was used as an inert supporting electrolyte, purchased from Acros Organics. Analytical grade diluted sulfuric acid ($H_2SO_4$) and sodium hydroxide (NaOH) were used to regulate the pH and were provided from Sigma-Aldrich. All the other chemicals were bought from Sigma-Aldrich.

**2. Experimental procedure**
The experiments were performed in an open, undivided and cylindrical cell containing 250 mL of BTB solution. BTB initial concentration was fixed at 100 mg $L^{-1}$ (1.6 x $10^{-4}$ M). The ionic strength was maintained constant by adding 5 x $10^{-2}$ M of $Na_2SO_4$.

The carbon felt piece (Carbone Lorraine RVG 4000 Mersen) was used as a cathode (25 $cm^2$). It was placed on the inner wall of the cell. The BDD anode (5 $cm^2$) was placed in the center of the cell. Solution

**Table I:** Characteristics of BTB

| Characteristics | Molecular formula | Molecular weight (g $mol^{-1}$) | Solubility in water (g $L^{-1}$) |
|---|---|---|---|
| Data | $C_{27}H_{28}Br_2O_5S$ | 624.381 | 10 |

pH values were adjusted to the desired level using dilute sulfuric acid and sodium hydroxide solutions. A Mettler Toledo EL20 pH-meter was used for pH measurements. A moderate compressed air was bubbled for 10 min through the cell to saturate the solution in oxygen, prior to the electrolysis. The bubbling as well as the magnetic stirring was maintained throughout the experiment. The current was kept at the desired level with a Gwinstek GPS-3303 stabilized power supply. Samples were withdrawn at regular electrolysis times.

# 3. Analytical determinations
## 3.1. Color removal measurements

The effectiveness of color removal was monitored by measuring its absorbance using Jouan VP1020 UV spectrophotometer at an absorbance detection of 433 nm which is the maximum wavelength of the acid form of BTB.

The color removal degree of the investigated solutions was determined using the following formula (Eq.4):

$$\% \text{ Color removal} = \left(1 - \left(\frac{C_t}{C_0}\right)\right) \times 100 \qquad (\text{Eq.4})$$

Where $C_0$ is the initial concentration of BTB and $C_t$ is its concentration at treatment time t (min).

## 3.2. Chemical Oxygen Demand removal measurements

Chemical Oxygen Demand (COD) measurements were taken by sampling 2 mL of the treated solution. Aliquots of an acidic solution (1 mL) containing $K_2Cr_2O_7$ and $HgSO_4$ were added to the treated samples followed by the addition of 3 mL of a concentrated mixture of $H_2SO_4$ and $AgSO_4$. These solutions were heated at 150°C for 120 min in a COD block reactor to complete the oxidation of the remaining organic matter. Finally, the COD value was monitored using Hanna photometer COD.

COD removal percentage was estimated using the following formula (Eq.5):

$$\% \text{ COD removal} = \left(1 - \left(\frac{COD_t}{COD_0}\right)\right) \times 100 \qquad (\text{Eq.5})$$

Where $COD_0$ and $COD_t$ are the measures of the chemical oxygen demand at reaction time (0 and t) of BTB AO treatment.

## 3.3. Energy Consumption

The Energy Consumption per unit COD mass ($EC_{COD}$) is obtained from (Eq.6), used for electrochemical techniques based on COD removal and operating at constant applied current [36]:

$$EC_{COD} = \frac{E_{cell}It}{\Delta COD_t V_s} \qquad (\text{Eq.6})$$

Where $EC_{COD}$ is the energy consumption per unit COD mass (kWh (g COD)$^{-1}$), $E_{cell}$ is the average cell voltage (V), I is the applied current (A), t is the electrolysis time (h), $(\Delta COD)_t$ is the corresponding decays in COD (mg $O_2$ L$^{-1}$) and $V_S$ is the solution volume (L).

## 3.4. Total Organic Carbon removal measurements

The solutions were filtered on Sartorius Minisart 0.4 µm GF prefilters. Total Organic Carbon (TOC) was measured by means of a TOC-V$_{CPH-CPN}$ Total Organic Analyzer Schimadzu. Organic carbon compounds were combusted and converted to $CO_2$, which was detected and measured by a non-dispersive infrared detector (NDIR). Dissolved Nitrogen compounds were combusted and converted to NO which was then mixed with Ozone chemiluminescenece for detection by a photomultiplier. Reproductible TOC values were always obtained using the standard NPOC (Non Purgeable Organic Carbon) method. For every sample, each measurement was duplicated.

TOC removal percentage was estimated using the following formula (Eq.7):

$$\% \text{ TOC removal} = \left(1 - \left(\frac{TOC_t}{TOC_0}\right)\right) \times 100 \qquad (\text{Eq.7})$$

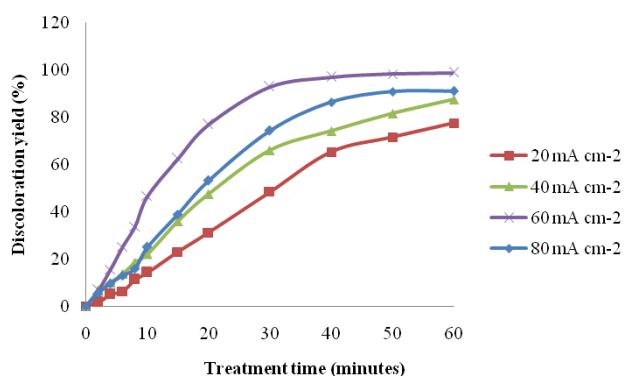Where $TOC_0$ and $TOC_t$ are the measures of the total organic carbon at reaction time (0 and t) of BTB AO treatment.

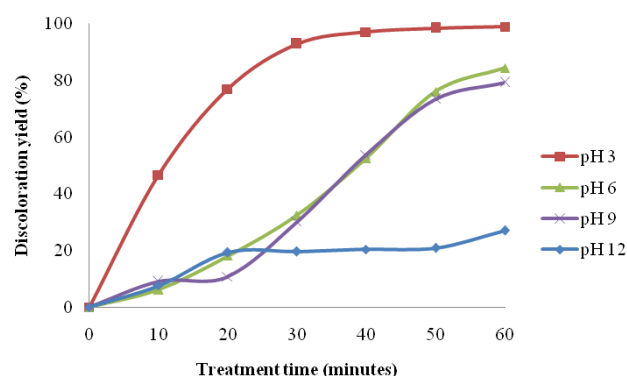# RESULTS AND DISCUSSIONS
## 1. Optimization of BTB AO on BDD anode
### 1.1. Effect of applied current on the AO of BTB on BDD anode

The effect of applied current on the AO of BTB at BDD anode was investigated at different current values in a range of 20 to 80 mA cm$^{-2}$. The results are depicted in Figure 2.

It can be clearly seen from Figure 2 that the discoloration curves evolve exponentially for all current values. The discoloration yield increase by raising the applied current densities from 77 to 99% for 20 and 60 mA cm$^{-2}$, respectively. This result is due to the oxidizing power associated with the
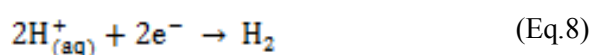
**Figure 2:** Effect of applied current density
on the AO of BTB on BDD anode
[BTB] = 1.6 x $10^{-4}$ M; [Na$_2$SO$_4$] = 5 x $10^{-2}$ M; pH = 3;
Treatment time = 60 min; V = 250 mL



**Figure 3:** Effect of the reaction medium pH
on the AO of BTB on BDD anode
[BTB] = 1.6 x $10^{-4}$ M; [Na$_2$SO$_4$] = 5 x $10^{-2}$ M;
D = 60 mA cm$^{-2}$;
Treatment time = 60 min; V = 250 mL

enhancement of H$_2$O$_2$ electro-generation and •OH regeneration rates (which are adsorbed at the BDD surface) according to (Eq.1) [37].

However, at 80 mA cm$^{-2}$, a drop of 7% in the discoloration efficiency was recorded. Indeed, working at value superior to limiting current of pollutant oxidation, the portion of over current can be used to generate parasitic reaction as recombination of radicals. Furthermore, consumption of protons and modifications in the medium pH may be another cause of this decrease according to (Eq.8) [31]:

$$2H^+_{(aq)} + 2e^- \rightarrow H_2 \qquad \text{(Eq.8)}$$

As a consequence, 60 mA cm$^{-2}$ is the optimal current density for BTB synthetic solution discoloration by AO on BDD anode.

### 1.2. Effect of the reaction medium pH on the AO of BTB on BDD anode

Solution pH is a key factor for wastewater treatment. Many studies reported the influence of pH in the removal effectiveness of AO, depending on the chemical structure of the organic molecules

**Table II:** BTB solution's color at different pH and $\lambda_{max}$

| pH | BTB solution's color | $\lambda_{max}$ (nm) |
|---|---|---|
| Acidic | Orange | 433 |
| Neutral | Green | 618 |
| Basic | Blue | 648 |

and also on electrode materials [38,39]. Indeed, experiments were conducted to study the effect of the medium pH in the range of 3-12 on the AO of BTB. BTB is an acid-base dye. Its solution's color depends on the medium pH (Table II). Thus, the BTB concentration monitoring was performed according to the maximum theoretical wavelength at which absorbs the solution. The found values were confirmed by a UV-Visible scan.
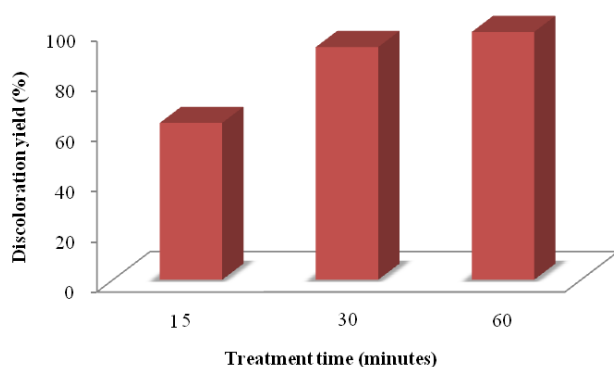
It is clear from Figure 3 that the acidic medium gives the most favorable discoloration yield of BTB synthetic solution by AO. Indeed, an exponential trend was observed for the evolution of the discoloration yield depending on electrolysis time. This behavior can be explained by the enhancement of hydroxyl radicals production by the AO of water on BDD anode, occurring most likely at acidic pH (Eq.2) [40,8].

Consequently, the optimal pH for the dis-coloration of BTB synthetic solution by AO on BDD anode was equal to 3.
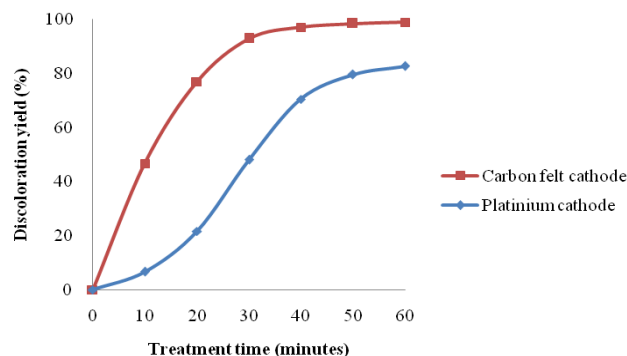
### 1.3. Effect of treatment time on the AO of BTB on BDD anode

The effect of treatment time on the AO of BTB on BDD anode was investigated and the obtained results are shown in Figure 4.

This figure demonstrates that an increasing duration of electrolysis enhances the discoloration of BTB synthetic solution, due to a higher production of hydroxyl radicals in the medium which are able to attack the initial molecule and the by-products electrogenerated. In fact, a higher discoloration yield of BTB synthetic solution can be achieved when the treatment time varies from

**Figure 4:** Effect of the treatment time
on the AO of BTB on BDD anode
[BBT] = 1.6 x $10^{-4}$ M; [$Na_2SO_4$] = 5 x $10^{-2}$ M;
D = 60 mA $cm^{-2}$; pH = 3; V = 250 mL



**Figure 6:** Effect of the cathode type
on the AO of BTB on BDD anode
[BBT] = 1.6 x $10^{-4}$ M; [$Na_2SO_4$] = 5 x $10^{-2}$ M;
D = 60 mA $cm^{-2}$; pH = 3;
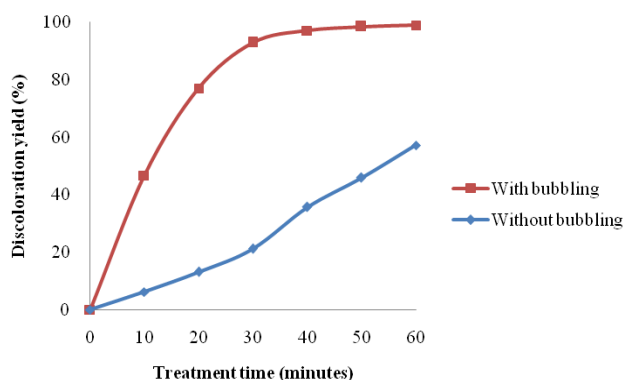Treatment time = 60 min; V = 250 mL

15 to 60 minutes. Indeed, a discoloration yield of 63% was reached after 15 minutes while 99% were obtained after 60 minutes [41].

Therefore, 60 minutes is the optimal treatment time for BTB synthetic solution discoloration by AO on BDD anode.

### 1.4. Effect of bubbling on the AO of BTB on BDD anode

In order to understand the bubbling effect on the AO of BTB on BDD anode, two experiments were carried out: the first with bubbling and the second without bubbling. Figure 5 reports the found results.

Figure 5 reveals an obvious enhancement of the oxidation rate of bubbling experience reaching a

discoloration yield of 99% than that obtained without bubbling (57%). This can mostly be due to the presence of $O_2$ which enhanced $H_2O_2$ electro-generation and as a consequence •OH regeneration rates [42].

Conclusively, bubbling is a critical parameter prerequisite in the AO of BTB on BDD anode, which was kept throughout all the experiments.

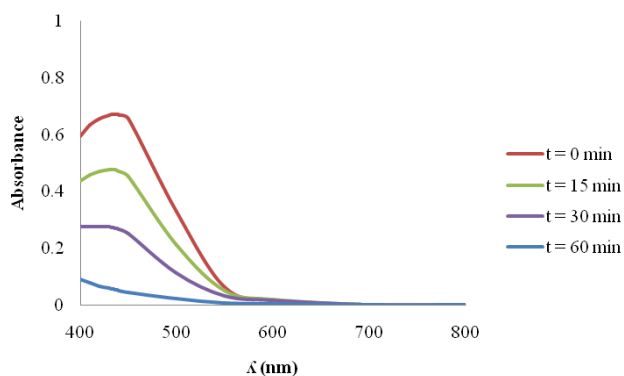### 1.5. Effect of the cathode type on the AO of BTB on BDD anode

The effect of the cathode type on the AO on BDD anode was investigated. For this purpose, a comparison was conducted between the carbon felt cathode and a platinum cathode for the BTB AO on BDD anode. The curves depicted in Figure 6 reveal that BTB synthetic solution discoloration is better with a carbon felt cathode (99%) than with a platinum one (83%). This result was explained in literature by a greater surface area and a very porous texture of carbon felt which allows a better adsorption of $O_2$ comparing to platinum. Furthermore, the carbon felt is characterized by a significant electrolytic activity leading to a higher efficiency of $H_2O_2$ production [43].

Consequently, a carbon felt cathode was used as an optimal condition for BTB synthetic solution discoloration by AO on BDD anode.

### 1.6. Optimal conditions for the AO of BTB on BDD anode

Under the optimal conditions determined previously (D = 60 mA $cm^{-2}$, pH = 3, treatment time = 60 min, a carbon felt cathode and maintaining bubbling) for the AO of BTB on BDD anode, the visible spectra was plotted (Figure 7) for many treatment times (0, 15, 30 and 60 min).
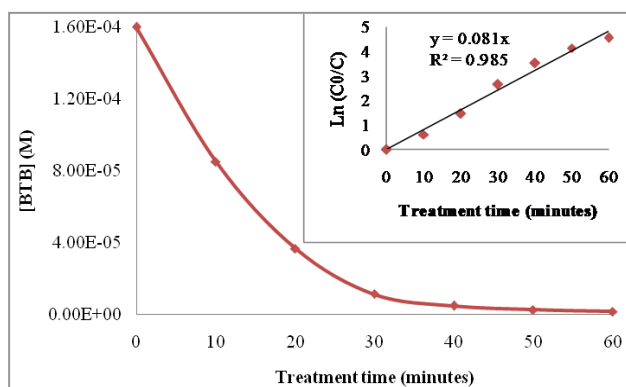


**Figure 5:** Effect of bubbling on the AO
of BTB on BDD anode
[BBT] = 1.6 x $10^{-4}$ M; [$Na_2SO_4$] = 5 x $10^{-2}$ M;
D = 60 mA $cm^{-2}$; pH = 3;
Treatment time = 60 min; V = 250 mL

**Figure 7:** Spectra obtained under optimal conditions for the AO of BTB on BDD anode
[BBT] = 1.6 x $10^{-4}$ M; [Na$_2$SO$_4$] = 5 x $10^{-2}$ M;
D = 60 mA cm$^{-2}$; pH = 3;
Treatment time = 60 min; V = 250 mL

Figure 7 reported the visible scan of BTB solutions before and after treatment by AO, at several electrolysis durations. It showed a gradual decrease of the 433 nm band, corresponding to the BTB acid form, as function of treatment time, until its total disappearance. The spectra obtained confirm the previous results found in this paper.
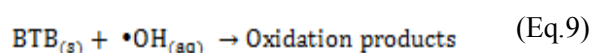
### 2. Kinetic studies

Under optimal conditions (D = 60 mA cm$^{-2}$, pH = 3, treatment time = 60 min, a carbon felt cathode and maintaining bubbling), the evolution of BTB concentration as function of treatment time by AO on BDD anode was followed and is represented in Figure 8.



**Figure 8:** Evolution of BTB concentration as function of treatment time by AO on BDD anode under optimal conditions
[BBT] = 1.6 x $10^{-4}$ M; [Na$_2$SO$_4$] = 5 x $10^{-2}$ M;
D = 60 mA cm$^{-2}$; pH = 3;
Treatment time = 60 min; V = 250 mL

The kinetics of BTB synthetic solution discoloration was followed during 60 minutes of treatment by AO on BDD anode. In order to determine the reaction order, many calculations were carried out. Table III summarizes the main results ($R^2$ and $k_{app}$) related to each reaction order.

The experimental kinetic can be satisfactorily described by a pseudo-first order reaction kinetic (Table III, insert Figure 8), assuming a quasi-stationary state for hydroxyl radical •OH concentration:

$$BTB_{(s)} + \,^{\bullet}OH_{(aq)} \rightarrow Oxidation\ products \qquad (Eq.9)$$

$$V = \frac{-d[BTB]}{dt} = k_{abs}[^{\bullet}OH][BTB] = k_{app}[BTB] \qquad (Eq.10)$$

With BTB Bromothymol Blue, $k_{abs}$ the absolute rate constant and $k_{app}$ the apparent rate constant ($k_{app} = k_{ads}[^{\bullet}OH]$).

The apparent kinetic rate constant value $k_{app}$ for the oxidation of BTB corresponds to the slope of the linear fit of ln([BTB]$_0$/[BTB]) versus time. The found $k_{app}$ (0.081 min$^{-1}$) was calculated from linear regression of the pseudo-first order kinetic model with related coefficient $R^2$ equal to 0.985 (Table III, insert Figure 8). This value is in agreement with other apparent rate constant for hydroxylation reactions of aromatic compounds with hydroxyl radicals. Indeed, $k_{app}$ for the anodic oxidation on BDD anode of Reactive Black 5 dye is 0,835 min$^{-1}$ [44]. Furthermore, the apparent rate constant values of different chlorophenoxy herbicides (4-chlorophenoxyacetic acid, 4-chloro-2-methyl-phenoxyacetic acid, 2,4-dichlorophenoxyacetic acid and 2,4,5-trichlorophenoxyacetic acid) treated with anodic oxidation using a BDD anode are 5.4 x $10^{-3}$ min$^{-1}$, 7 x $10^{-3}$ min$^{-1}$, 7.1 x $10^{-3}$ min$^{-1}$ and 6.6 x $10^{-3}$ min$^{-1}$, respectively [45].

The determination of the reaction order was also conducted by our team for BTB synthetic solution discoloration by electro-Fenton process, another AOP [31]. The same ascertainment was

**Table III:** Study of the reaction order

| Reaction order | $R^2$ | $k_{app}$ (min$^{-1}$) |
|:---:|:---:|:---:|
| 0 | 0.757 | 2 x $10^{-6}$ |
| 1 | 0.985 | 0.081 |
| 2 | 0.852 | 9829 |

performed. Indeed, BTB synthetic solution discoloration by electro-Fenton process followed a pseudo-first order kinetic model. The apparent rate constant obtained was equal to 0.186 min$^{-1}$ [31]. Comparing this value to that found for BTB synthetic solution discoloration by AO, we can notice that the latest apparent rate constant is higher than the one related to AO. Therefore, we can confirm that the kinetic of electro-Fenton process is faster than the AO one.

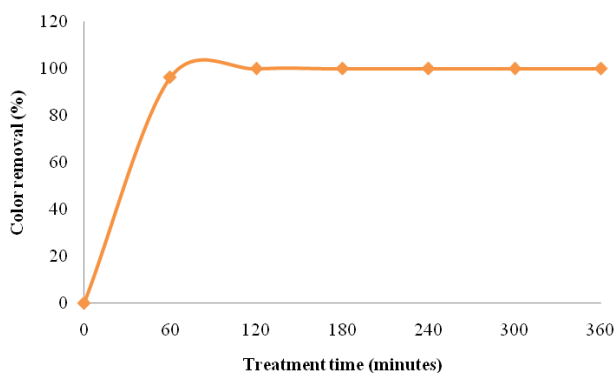### 3. Mineralization of BTB synthetic solution by AO on BDD anode
### 3.1. Evolution of color removal

The mineralization of BTB synthetic solution was monitored by solution color abatement during AO treatment. The experiment was carried out under optimal operating conditions determined previously as described above in this study. Figure 9 presents the results related to this experiment.
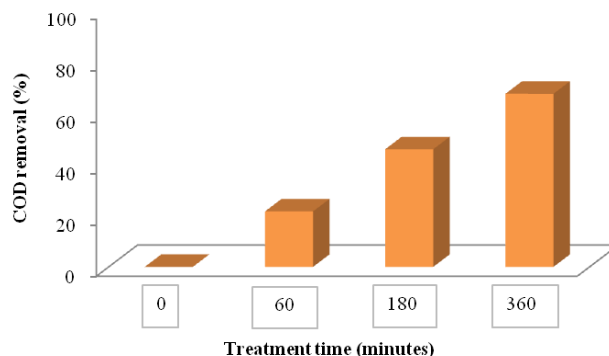
It can be seen on this figure that after 360 minutes of treatment by AO, BTB synthetic solution was completely discolored. This result is consistent with the Tunisian law NT.106.002 for the protection of the environment [46]. Similar observations were already reported for the treatment of other textile dyes [47].

### 3.2. Evolution of COD removal

The evolution of COD removal percentage during the mineralization of BTB in aqueous synthetic solution is shown in Figure 10 as function of treatment time by AO on BDD anode. COD results provided us with information about the BTB oxidation efficiency of the AO during 360 minutes.



**Figure 10:** Evolution of the COD removal percentage of a synthetic solution of BTB treated with AO on BDD anode
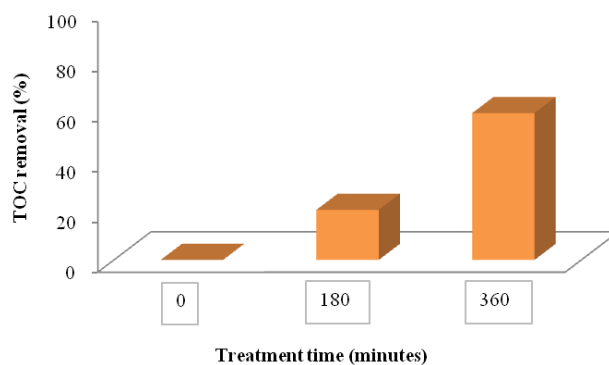
The initial COD value of 118 mg O$_2$ L$^{-1}$ for BTB synthetic solution decreased gradually at the beginning of the treatment giving rise to a removal of 22% in just 60 minutes. Half of BTB amount was oxidized after 180 minutes and 67% was reached at the end of BTB treatment by AO on BDD anode. This result is consistent with the Tunisian law NT.106.002 for the protection of the environment [46]. It is important to notice that it could be improved by increasing the treatment time.

### 3.3. Evolution of TOC removal

The TOC abatement of BTB synthetic solution is a relevant parameter of its mineralization. It was also performed during AO treatment. Figure 11 presented the results related to this experiment.

Notice that after 180 minutes of treatment by AO on BDD anode, the TOC removal percentage was equal to 20%. 59% was the TOC abatement of this synthetic solution of BTB after 360 minutes of



**Figure 9:** Evolution of the color removal percentage of a synthetic solution of BTB treated with AO on BDD anode



**Figure 11:** Evolution of the TOC removal percentage of a synthetic solution of BTB treated with AO on BDD anode

**Table IV:** Energy consumption of BTB oxidation by AO

| Treatment time (minutes) | $EC_{COD}$ (kWh (g COD)$^{-1}$) |
|---|---|
| 60 | 1.02 |
| 180 | 0.87 |
| 360 | 0.70 |

mineralization. This result is in accordance with the ones found in literature concerning the degradation of dyes with AO [48]. This result would be improved if the treatment time is increased.
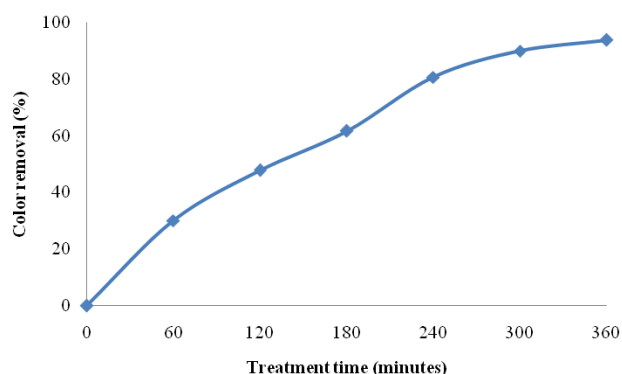
### 3.4. Energy consumption

Once the oxidation and the mineralization efficiencies of the AO on BDD anode were proven, it is essential to evaluate the energy consumption of this process. This part of the paper investigates the $EC_{COD}$ of the BTB oxidation by AO on BDD anode. The results are summarized in Table IV.

The energetic cost of BTB oxidation by AO on BDD anode was equal to 1.02 kWh (g COD)$^{-1}$ within 60 minutes and it decreases to reach 0.7 kWh (g COD)$^{-1}$ after 360 minutes, which is in agreement with the findings in literature [49]. This decrease is a consequence of a good oxidation and mineralization of the solution.

### 4. Application of AO to treat a Tunisian textile effluent containing BTB

To better analyze the viability of AO, the mineralization of a Tunisian textile effluent containing BTB was monitored by color solution, COD and TOC abatements, during AO treatment. The experiments were carried out under optimal operating conditions determined previously.

### 4.1. Evolution of color removal

Figure 12 reveals an obvious enhancement of the color removal for the Tunisian textile effluent containing BTB as function of treatment time.

94% of the color removal was achieved after 360 minutes of treatment. The slight decrease of this value in comparison with the synthetic dye solution is a consequence of the non-selective engagement of the radicals in the degradation of other organic molecules present in wastewater. This result is in accordance with forgoing studies for the treatment of textile wastewaters [47]. Moreover, it is consistent with the Tunisian law NT.106.002 for the protection of the environment [46].
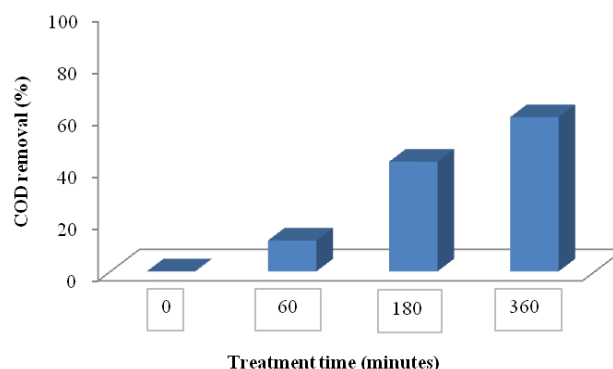
### 4.2. Evolution of COD removal

The extent of the oxidation was monitored by estimating the COD removal percentage during the mineralization of the Tunisian textile effluent containing BTB at optimal conditions. The results depicted in Figure 13 reveal that the COD percentage removal increases with the progress of treatment time.

After 60 minutes of treatment, the COD removal percentage, for this Tunisian textile effluent was around 12% of the initial value (227 mg $O_2$ $L^{-1}$). In fact, this percentage increases by increasing the treatment time to 360 minutes, giving a COD removal degree of 59%. This expected result is due to the complexity of the matrix of this effluent which contains several recalcitrant molecules likely to be oxidized. Conclusively, increasing the electrolysis time allows a better COD removal percentage.

### 4.3. Evolution of TOC removal

To emphasize the mineralization of the textile effluent, the TOC abatement was also performed. The corresponding results are reported in Figure 14.



**Figure 12:** Evolution of the color removal percentage of a Tunisian textile effluent containing BTB treated with AO on BDD anode



**Figure 13:** Evolution of the COD removal percentage of a Tunisian textile effluent containing BTB treated with AO on BDD anode

**Figure 14:** Evolution of the TOC removal percentage of a Tunisian textile effluent containing BTB treated with AO on BDD anode

An abatement of 15% was achieved after the first 180 minutes. It then increases to 52%, when treatment time was expended to 360 minutes. This result exposes not only the electrolysis time influence on the TOC abatement, but also the fact that this effluent is rich of dyes mixture and recalcitrant organic molecules. As concluded previously, a better result would be obtained by increasing the treatment time.

### 4.4. Energy consumption

The $EC_{COD}$ of the AO was calculated for the mineralization of this Tunisian textile effluent containing BTB. The related results are presented in Table V.

This Tunisian textile effluent which contains BTB dye has an energetic cost equal to 1.24 kWh (g COD)$^{-1}$ at the beginning of the electrolysis and reaches 0.91 kWh (g COD)$^{-1}$ after 360 minutes. The AO on BDD anode seems to be less costly for important treatment times due to the increase of hydroxyl radicals accumulation and therefore the decrease of recalcitrant molecules amount. This satisfactory result emphasizes the fact that this effluent has been successfully mineralized [50].

**Table V:** Energy consumption of AO of a Tunisian textile effluent containing BTB

| Treatment time (minutes) | $EC_{COD}$ (kWh (g COD)$^{-1}$) |
|---|---|
| 60 | 1.24 |
| 180 | 1.05 |
| 360 | 0.91 |

## CONCLUSION

The AO of BTB on a BDD anode was investigated in this study. Optimal conditions were fixed, and are as follow: 60 mA cm$^{-2}$ as applied current density, a pH equal to 3, a treatment time of 60 minutes, a three-dimensional carbon felt as a cathode, as well as bubbling air before and during the treatment. In fact, working under these optimal conditions, allowed a maximum discoloration yield of 99%.

Moreover, a total discoloration was observed after 360 minutes of treatment, as well as an abatement of 67% of the COD initial value and 59% of the TOC initial value.

When applied to a Tunisian textile effluent containing BTB dye, the color intensity decrease, the COD and the TOC removal reached respectively the interesting percentages of 94%, 59% and 52% after 360 minutes of treatment by AO on BDD anode. These values are lower than the ones obtained for BTB synthetic solution, which was expected considering the nature of effluent containing a complex matrix of several recalcitrant molecules likely to be oxidized.
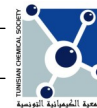
The $EC_{COD}$ of the oxidation of both BTB synthetic solution and a Tunisian textile effluent containing BTB by AO on BDD anode were determined. 0.7 kWh (g COD)$^{-1}$ and 0.91 kWh (g COD)$^{-1}$ were respectively found after 360 minutes of treatment. The final $EC_{COD}$ value related to the Tunisian textile effluent is higher than that of BTB synthetic solution. This is due to the complex mixture of dyes and recalcitrant organic molecules in the industrial effluent requiring more energy input.

Conclusively, the previous results insure the effectiveness of the AO treatment using BDD anode, considering it as a promising environmentally friendly technology for the remediation of wastewaters containing BTB textile dye.

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