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Anodic oxidation of cationic dye on boron-doped diamond (BDD): effect of electrochemical operation parameters

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***Abstract*:**

The aim of this work is to treat simulated wastewater containing a cationic dye by anode oxidation on a non-active electrode. For this purpose, the effect of six independent variables including initial methylene blue (MB) concentration, applied current density, initial pH, temperature, supporting electrolyte concentration and recirculation rate were determined. All experiments were monitored by UV-visible spectrophotometry. The electrode used as anode is boron-doped diamond (BDD). Based on this research, it appears that electrochemical parameters significantly influence the performance of the electrochemical process. In addition, a complete discolouration of the methylene blue solution is achieved under all experimental conditions. Furthermore, the degradation of the organic compound is controlled by mass transport and can be described by pseudo-first order kinetics. In sum, the anodic oxidation process using the BDD electrode represents a satisfactory method for the degradation of methylene blue in aqueous media.

***Keywords*:** Anodic oxidation; Dye; Boron-doped diamond (BDD) electrode; Advanced Oxidation Process (AOP).

1. Introduction

Dyes are widely used in printing, food products, cosmetics, clinical products, and many other sectors but particularly in the textile industries for their chemical stability and ease of synthesis and their variety of colors. However, the alarming increase in water pollution by dyes poses a real danger to aquatic flora and fauna and causes serious problems for humanity [1]. It is caused mainly by heavy industrialization which releases various toxic pollutants into the environment. Like most pollutants, cationic dyes are very harmful and can be found in the effluents of many industries. It is therefore necessary to treat these discharges before they are released into the environment. Biological decontamination processes are the most commonly used in wastewater treatment.

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Indeed, these processes, in which bacteria are the main actors in the degradation process, are relatively inexpensive and easy to set up. Their effectiveness in eliminating pollutants that are more difficult to biodegrade, such as dyes, is questionable. Biological treatment is generally economical and is chosen when the effluent contains biodegradable and non-toxic compounds [2]. Recent researches are oriented towards more efficient techniques for the treatment of these refractory organic pollutants, using advanced oxidation processes, among which electrochemical treatment is particularly promising. Electrochemical oxidation processes have attracted a lot of interest in recent years, mainly because of their low cost, simplicity of implementation, low sludge production, especially because of their high efficiency. As such, they seem to be an interesting alternative for the treatment of refractory compounds [3]. They can be used as a pre-treatment prior to the biological process and can also degrade the material to the ultimate carbon dioxide and water. This process does not require the addition of any hazardous chemical oxidants and the possibility of full recycling of aqueous effluents is particularly attractive from an industrial point of view [4]. This is anodic electrooxidation, which is a commonly used process for the removal of organic pollutants from wastewater [5-7]. However, the efficiency of electrochemical oxidation of dyes in aqueous solutions is highly dependent on the nature of the electrode used [8]. The total degradation of refractory pollutants into carbon dioxide and water is a difficult energy process with a very complex mechanism. The difficulty is to find a stable anode material that allows the degradation of the molecular skeleton to take place and eventually lead to carbon dioxide and water. The use of anodes with specific properties must therefore be considered [4]. It is necessary to work at high potentials, in the field of water discharge, to generate powerful oxidants such as hydroxyl radicals $^{\bullet}OH$ (powerful non-selective oxidant E° $H_2O/^{\bullet}OH = 2.81$ V/ENH) [9]. The material of the anode is therefore the technological lock for this process. In addition to the need for an anode with a high oxygen evolution overvoltage, the materials that can be considered industrially must have good chemical resistance in acidic and caustic environments, as well as a long service life. The anode chosen for its extraordinary electrochemical properties is boron-doped diamond (BDD) [10, 11].

A lot of work on the electrochemical degradation of dyes on BDD has been carried out. Panizza *et al.* [10] studied the anodic oxidation of methyl red on BDD and PbO_2 electrodes. According to their work, the best degradation rate as well as the best effective current is obtained with the BDD. Furthermore, they showed that the hydrodynamic conditions have an effect on the oxidation of the organic compound. Also, Vasconcelos *et al.* [11] investigated the electrochemical oxidation of reactive blue-19 using BDD as anode. They showed that complete discoloration as well as 90% of total organic carbon (TOC) with a significant decrease of the toxicity of the studied dye against *V. fischeri* are achieved. In addition, keto-enolic tautomers, hydroquinone and benzoquinone, benzoic acid, phenol and aliphatic acid, such as oxalic acid are the intermediate reactions they determined by HPLC-MS during the degradation of the blue-19 reagent. Electrochemical oxidation studies on BDD have been performed on other dyes such as crystal violet [12], X-6G dye [13], anthraquinone dye Alizarin Red S [14]. These works have shown the high performance of BDD for dye degradation.

Hence, the aim of this study is to apply the electrochemical method using BDD as an anode to the degradation of a cationic dye derived from phenothiazine, methylene blue (MB). The effect of various electrochemical parameters (initial concentration of the MB, applied current density, initial pH, temperature, supporting electrolyte concentration and recirculation flow rate) on the efficiency of the electrochemical method in terms of solution discoloration is also evaluated. In addition, the current efficiency as well as the energy consumed have been calculated in this work. This work intends to provide a green and efficient method for wastewater treatment of the cationic dye.

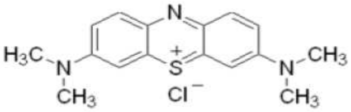
2. Materials and methods

2.1. Chemical products used

Methylene blue, which has the physico-chemical characteristics listed in Table 1, is supplied by Merck. Sodium sulphate is manufactured by Fulka. The sodium hydroxide is from Panreac and the sulphuric acid is from Sigma-Aldrich. These two products made it possible to adjust the pH of the solution. All these chemicals are of analytical grade and used without any purification.

Table 1

Characteristics of the physico-chemical properties of BM [15-17].

Name	Methylene blue or tetramethylthionine chloride
Chemical designation	3,7-bis (dimethylamino) phenazathionium chloride
Family	Basic or cationic dye
Gross formula	$C_{16}H_{18}N_3SCl$
Molar weight (g/mol)	319.86
Solubility in water (g/L) at 25 °C	43.16
Melting point (°C)	100 - 110
Log K_{ow}	5.85
pKa	3.8
λ_{max} (nm)	662 - 665
Structural formula	

2.2. Electrochemical reactor

The electrolysis preparative were carried out in a spherical electrochemical reactor. In this configuration, boron-doped diamond (BDD) and a zirconium plate were used as the anode and the cathode, respectively. These electrodes are disks with a thickness of 0.1 cm and a diameter of 10 cm. The two electrodes are separated by a 1.5 cm thick spacer. This results in an active anode area of 78.54 cm^2. The substrate is a boron-doped polycrystalline silicon disk. The simulated methylene blue solution to be treated is stored in a 250 mL glass beaker covered with aluminium foil, and circulated through the electrochemical reactor via a WATSON MARLOW 505U peristaltic pump. Constant current operations have been possible with FARNELL voltage generator AP 70-3. The current value is monitored with a PROMAX PD-986 multimeter. A manual sampling of 2.5 mL is performed every 30 min for 3 h by 5 mL pipettes for the measurement of the absorbance of the residual BM concentration in order to monitor its degradation. The overall volume of samples taken remains below 10% of the total volume. Note that before each electrolysis, the working electrode is anodically pre-treated (40 mA cm^{-2} for 30 minutes in 0.1 M H_2SO_4) to clean the surface of any adsorbed impurities. The system is then flushed with distilled water.

Figure 1 shows the set-up of the preparative electrolysis.

2.3 Analytical methods

The experiments were monitored by a HACH DR 6000 UV-Visible spectrophotometer. The maximum wavelength of methylene blue determined was $\lambda_{max} = 663$ nm. Measurements of the absorbance of several solutions of methylene blue at known concentrations were carried out to verify the Beer-Lambert law with (Absorbance = 0.119×Concentration + 0.0488 with $R^2=0.9989$). Then, the degradation rate of methylene blue was obtained by equation (1):

$$D\ (\%) = \frac{C_0 - C_t}{C_0} * 100 \qquad (1)$$

Where C_0 and C_t are the dye concentration at initial and t time, respectively.

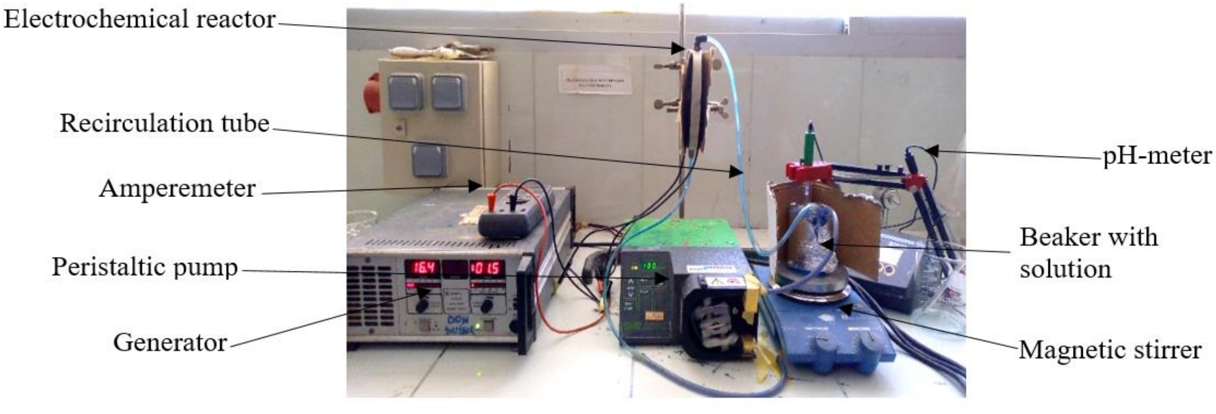


Fig. 1: Device for preparative electrolysis.

The limiting current density (mA/cm²) j_{lim} is given by equation (2) [18, 19]:

$$j_{lim}(t) = n\,.F.k_d.C_t \tag{2}$$

Where *n* is the number of electrons exchanged; *F* is Faraday's constant (Coulomb); k_d is the mass transfer coefficient (m s^{-1}) and C_t is the concentration of methylene blue (mol/L).

The complete combustion reaction of methylene blue is as follows (equation 4) [20]:

$$C_{16}H_{18}N_3SCl + 45\ H_2O \rightarrow 16\ CO_2 + 3\ NO_3^- + SO_4^{2-} + Cl^- + 108\ H^+ + 102\ e^- \tag{3}$$

The expression for the limiting current density becomes (equation (4)):

$$j_{lim}(t) = 102.F.k_d.C_t \tag{4}$$

At t=0 (at the beginning of electrolysis), the limiting current is expressed by the following formula (equation (5)):

$$j_{lim}^0 = 102.F.k_d.C_0 \tag{5}$$

Under galvanostatic, at $J_{appl} < J_{lim}$, the electrolysis is under current control and at $J_{appl} > J_{lim}$, it is controlled by mass transport [18, 19, 21].

Electrochemical oxidation is an energy-intensive process. Its efficiency is one of the inherent factors in water treatment; it is evaluated in terms of specific energy consumption which is calculated according to the equation (6) [22]:

$$EC = \frac{U \times I \times t}{3600 \times V} \tag{6}$$

EC is the Specific energy consumption (kWh/m^3); U is the Potential difference across the electrodes (V); I is the Applied current (A); t is the time after which the experiment takes place (s) and V is the Volume of the solution to be treated (dm^3).

The pseudo-first order kinetic constants were determined using equation (7).

$$\ln\frac{[MB]_0}{[MB]_t} = k_{app\,(MB)} \times t \tag{7}$$

$[MB]_0$ and $[MB]_t$ are the MB concentration at times 0 and t, respectively. $k_{app(MB)}$ is the apparent rate constant of MB.

3. Results and discussion

3.1. Effect of the initial concentration of methylene blue

Due to the fact that industrial textile wastewaters usually contain different concentrations of dyes, it is very important from a practical point of view to study the effect of the initial concentration of the methylene blue (MB) on the performance of the electrochemical oxidation process in removing pollutants. The effect of the initial concentration of the MB was studied over a concentration range of 20-100 mg/L at free pH = 5.9 and a current density of 20 mA/cm². The supporting electrolyte used was 0.1M Na_2SO_4. Figure 2 shows the degradation kinetics of different concentrations of methylene blue. According to this figure, complete discoloration of methylene blue is achieved for all concentrations explored. However, the time to complete discoloration increases with the initial dye concentration. It is 1.5 h; 2 h; 2.5 h and 3 h for 20, 50, 75 and 100 mg/L, respectively. This could be explained by the fact that increasing the initial concentration would require a large number of oxidative species such as hydroxyl radicals. Indeed, the BDD electrode is an electrode with a high oxygen release potential on which the hydroxyl radicals resulting from the decomposition of water are labile and therefore participate in the oxidation of the organic compounds. In addition, the gradual decrease in the efficiency of MB degradation with its initial concentration may also be due to competitive reactions between the dye molecules and those of the intermediates formed during the electrolysis process. The dye molecules and intermediates ones will compete to react with the hydroxyl radicals $^{\bullet}OH$ at the electrode surface and other oxidative species present in the reaction medium.

In addition, the imposed current density of 20 mA/cm² (k_d = 2.3610^{-7} m/s [3]) is above the limiting current densities determined in this work, which are 0.14; 0.363; 0.545 and 0.726 mA/cm² for 20, 50, 75 and 100 mg/L, respectively. This implies that the mass transport process controls the electrodegradation process of methylene blue [19].

During electrolysis, the evolution of the degradation of an aqueous solution of methylene blue (50 mg/L) during electrooxidation was monitored qualitatively by UV-Visible spectroscopy. The result is shown in Figure 3. It is noted that the elimination of methylene blue by electrochemical oxidation is fast. The absorbance peak at λ_{max} = 663 nm decreases very rapidly during the 0.5 hours of electrolysis and then disappears completely after one hour of electrolysis. The same phenomenon is observed for compounds absorbing in the length between 220 and 280 nm. The disappearance of the wavelength at 663 nm would mean that there no longer exists conjugative bond.

Fernandes *et al.* [23] showed that degradation of C.I. acid orange 7 (40 mg/L) on BDD in Na_2SO_4 medium led to a complete disappearance of absorbance at the maximum wavelength [23].

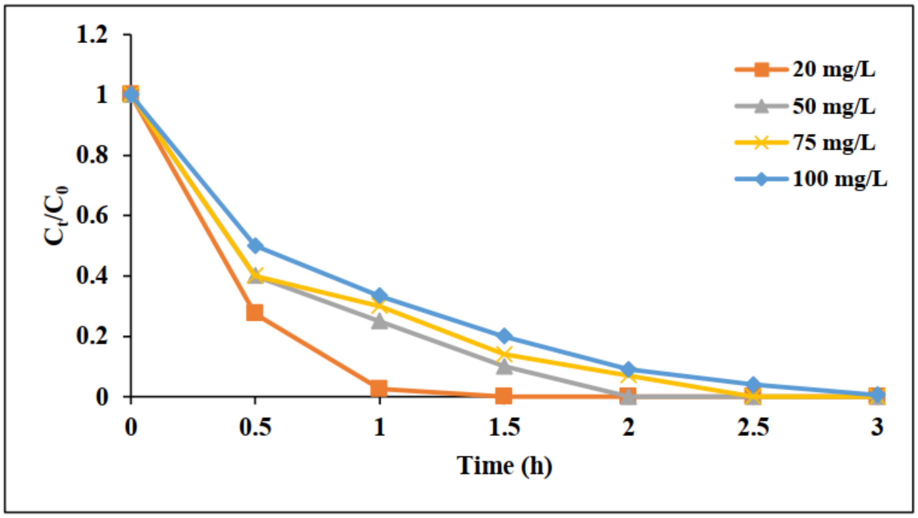


Fig. 2. Kinetic rate of degradation of different concentrations of MB on the BDD electrode. Operation conditions: j = 20 mA/cm²; Flow rate = 23.27 L/h; [Na_2SO_4] = 0.1 M; V = 0.25 L; Ambient temperature: 25 °C and free pH = 5.9.

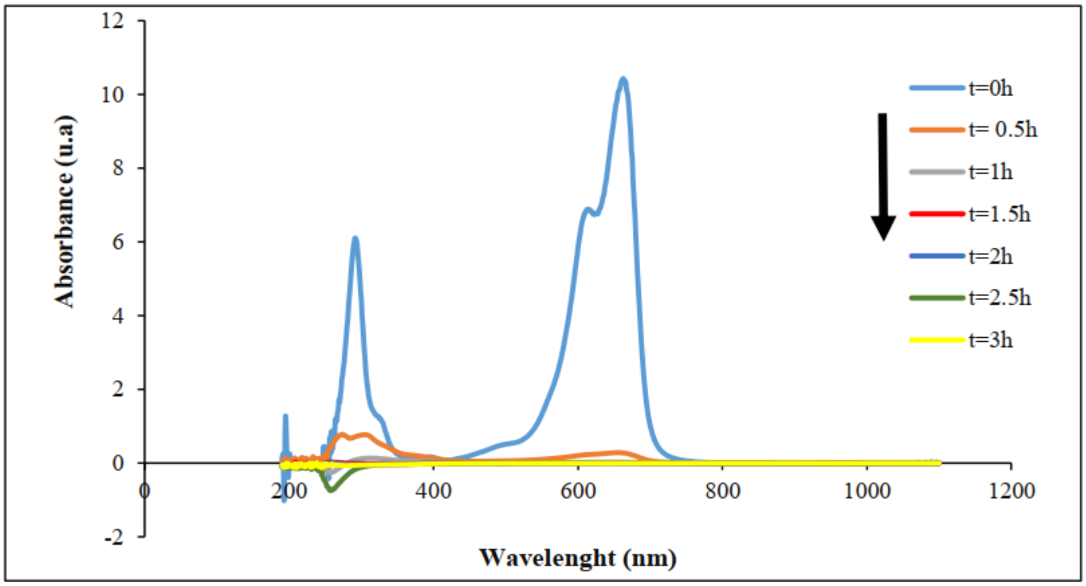


Fig. 3. UV-Visible spectrum of BM during preparative electrolysis treatment. Operation conditions: j = 20 mA/cm²; Flow rate = 23.27 L/h; [Na_2SO_4] = 0.1 M; V = 0.25L; Ambient temperature: 25 °C and free pH = 5.9.

3.2. Effect of applied current density

The applied current density is a very important parameter in electrochemistry. Thus, its effect was investigated on the degradation of 50 mg/L for the following values: 5; 10; 20 and 50 mA/cm². Figure 4 shows that the degradation of MB is significantly improved with increasing applied current density.

Figure 5 shows the degradation rates of MB after 1h30 (A) and 03h (B) of electrolysis. The degradation rates of methylene blue after 1h30 hours of electrolysis are 48.4; 73.6; 90 and 94.94% for 5, 10, 20 and 50 mA/cm², respectively. Furthermore, 20 and 50 mA/cm² lead to a very fast degradation of the dye with degradation rates close to 100%. By continuing the degradation until 3 h, the rates of degradation go up and range from 97.4 and 100% (Figure 5(B)). However, it should be noted that the MB degradation is only improved by 10.78% and 0.06% at 20 and 50 mA/cm², respectively. After 3 hours of electrolysis. On the other hand, for low current densities, a strong improvement of color removal is observed with 101.2% and 33.83% for 5 and 10 mA/cm².

Table 2 shows the Energy Consumption (EC) determined for the treatment of one m^3 of methylene blue solution for different current densities. The calculated EC values are 23.52; 63.36; 159.36 and 514.80 kWh/m^3 for 5, 10, 20 and 50 mA/cm², respectively. These values show that the EC rises with the applied current density. Compared to 50 mA/cm², 20 mA/cm² seems to be the optimal current density in this study. In fact, the energy cost for 50 mA/cm² is 3.23 times higher than that of 20 mA/cm² while the dye degradation rates under these two current densities are approximately the same for the same electrolysis time.

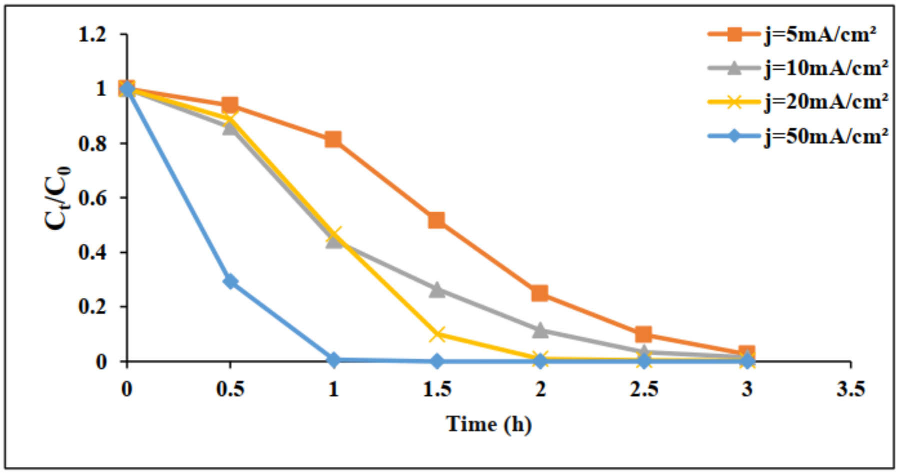


Fig. 4. Evolution of C_t/C_0 as a function of time under different current densities. Operation conditions: Volume of solution = 0.25 L; Flow rate = 23.27 L/h; [MB] = 50 mg/L; Free pH = 5.9; Ambient temperature: 25 °C; $[Na_2SO_4]$ = 0.1 M.

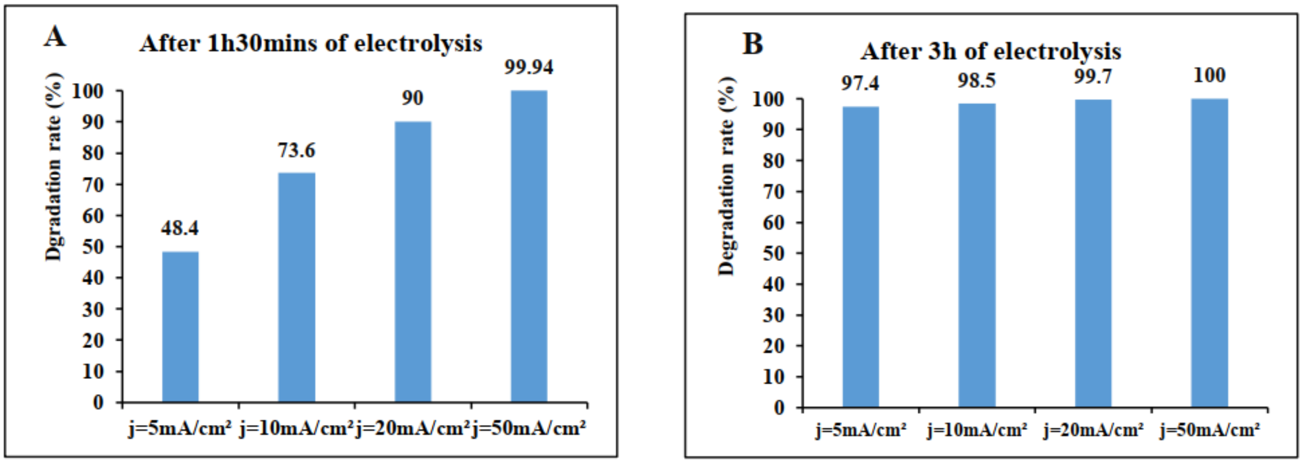


Fig. 5. Histograms of the effect of current density on the rate of degradation under the Operation conditions: [MB] = 50 mg/L; V = 0.25L; Flow rate = 23.27 L/h; Free pH = 5.9; $[Na_2SO_4]$ = 0.1 M; Ambient temperature: 25 °C.

Table 2

Energy consumption at different current densities.

Current density (mA/cm²)	5	10	20	50
EC (kWh/m^3)	23.52	63.36	159.36	514.80

3.3. Effect of initial pH

The initial pH is of major importance in wastewater treatment. In anode oxidation studies, a number of reports concern the influence of the pH of the solution, but the results obtained are diverse and even seem contradictory because of the different structures of the compounds studied and also the nature of the electrode material used [25]. Some authors report that oxidation is favorable in an acidic environment [26]. On the other hand, others state that the efficiency of the process is increased in alkaline medium [27]. In other studies, it has been found that the effect of pH on the oxidation of organic compounds is negligible [28]. Referring to the literature, it can be said that the effect of pH is highly dependent on the nature of the compound, the electrodes and the study medium (electrolytes) [29].

In this work, the effect of initial pH was investigated for an initial concentration of 50 mg/L and a current density of 20 mA/cm². The pH values were between 2 and 12. The methylene blue solutions were prepared in 0.1 M Na_2SO_4.

Figure 6 shows the evolution of MB degradation as a function of pH. The rate of degradation in the acid medium is observed to be higher than that obtained in the neutral medium and in the alkaline medium. The degradation is almost complete for the different pH values considered after 3 h of treatment. The different results show that the highest degradation rate is reached at acidic pH (pH= 2) after 2 hours of electrolysis with 99.88% of MB degradation (insert in Figure 6). This pH is followed by pH 5.9; 7; 9 and 12 with 99.62%; 97.8%; 95.3% and 90% of the elimination of MB color removal rate. The decrease in the rate of degradation as the pH increases may be due to the fact that the increase in pH promotes the polymerization reaction of the intermediate reactions on the surface of the BDD electrode that leads to the partial passivity of the electrode [30]. According to Dai *et al.* [31], the acidic media (low pH) would be more favorable for the degradation of pollutants than the alkaline conditions. Indeed, in an acidic environment, hydroxyl radicals would be produced in large quantities and the O_2 release reaction would be inhibited by H^+, which would result in an improvement in the degradation of the organic compound. In addition, the better degradation rate of MB obtained at pH = 2 and 5.9 could be linked to its pKa, which is 3.8, between 2 and 5.9. It would be more susceptible to electrophilic attack in this pH range. Such observations were made by Appia *et al.* [32] for the degradation of amoxicillin on a DSA type electrode. Moreover, the oxidation potential of the hydroxyl radical is higher under acidic conditions (+2.85 V) than under alkaline conditions (+2.02 V) [33].

The plot of ln (C_t/C_0) *versus* degradation time is shown in Figure 7. It can be seen that this plot is in very good agreement with pseudo first order kinetics with correlation coefficients tending towards 1 (Table 3).

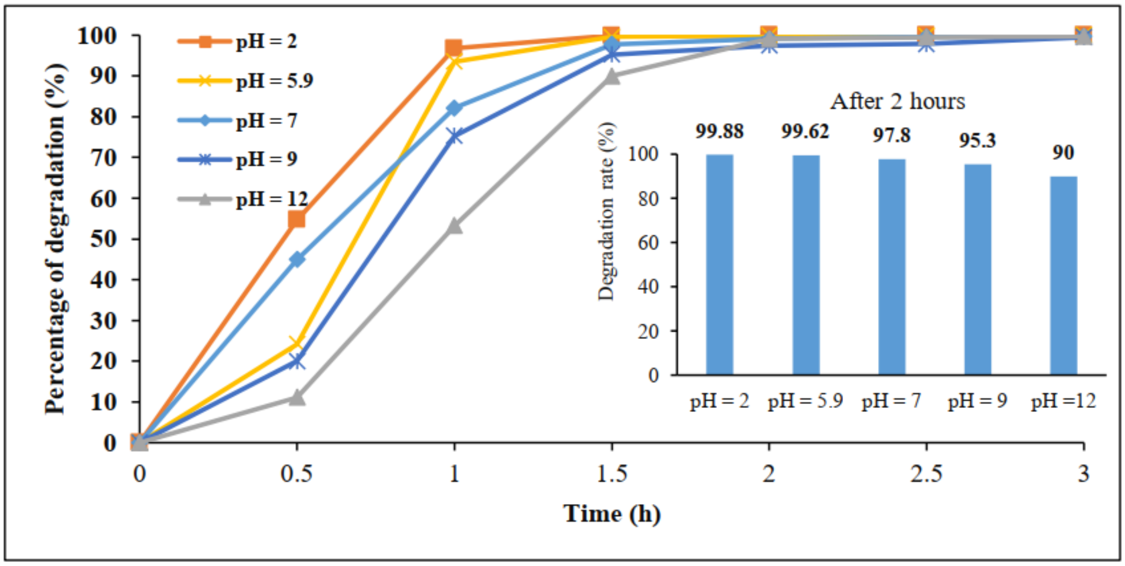


Fig. 6. Effect of pH on percentage degradation as a function of time, Insert: Histogram of the effect of pH on degradation rate. Operation conditions: [MB] = 50 mg/L; j = 20 mA/cm²; [Na_2SO_4] = 0.1 M; Flow rate = 23.27 L/h; V = 0.25 L; Ambient temperature: 25°C.

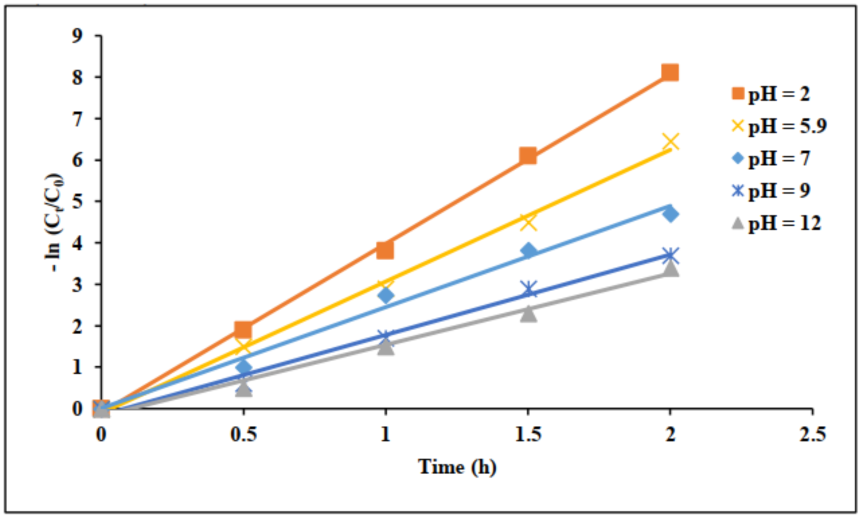


Fig. 7. - ln (Ct/C0) = f (t) at different initial pH.

Table 3

Apparent rate kinetic constant determined as a function of pH.

pH	k (h^{-1})	R²
2	4.0800	0.9988
5.9	3.1780	0.9957
7	2.4430	0.9874
9	1.9380	0.9895
12	1.7206	0.9873

The evolution of the coloration of the 50 mg/L BM solution at pH = 2 (A) and 12 (B) is presented in Figure 8. For the MB solution at pH=2, discoloration is effective after 30 minutes of electrolysis, whereas at pH=12, coloration is persistent, changing from purplish blue to violet at 30 minutes and then becoming colorless after 2 hours.

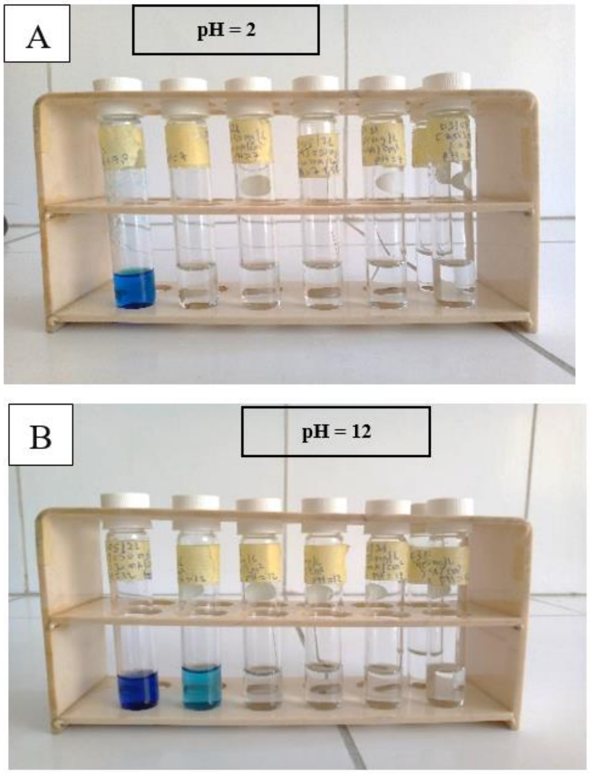


Fig. 8. Evolution of the staining of the methylene blue solution at pH=2 (A) and pH=12 (B).

3.4. Effect of temperature

Under our experimental conditions, the effect of temperature was studied for an initial BM concentration of 50 mg/L on the BDD under 20 mA/cm². The solutions were prepared in 0.1 M Na_2SO_4. The different temperatures were 12; 25; 50 and 72 °C, continuously monitored with a thermometer. The temperature is of great importance, as it would favor the degradation of the MB. The Figure 9 shows that increasing the temperature enhanced the discoloration of the MB solution within the investigated temperature.

The plotting of - ln (Ct/C0) as a function of time (insert in Figure 9) gives straight lines for all temperatures. The apparent methylene blue degradation rate constant represents the slope of each line obtained. The values of the apparent degradation rate constant of MB at different temperatures are collected in Table 4. The different determination coefficients R² tend towards 1, indicating that the MB degradation is pseudo first order. Moreover, the rate constant is strongly temperature dependent. It rises with an increase in temperature. This finding can be explained in terms of the electrogeneration of inorganic oxidising agents such as $S_2O_8^{-2}$, which are very strong reagents, from Na_2SO_4, following equation (8) [34, 35].

$$2SO_4^{2-} \rightarrow S_2O_8^{2-} + 2e^- \qquad (8)$$

The influence of temperature on the reaction rate allows us to determine the activation energy. According to the literature, the reaction rate increases exponentially with temperature. The apparent activation energy (Ea) was calculated from the empirical Arrhenius equation (Equation (9)) [20]:

$$K_{app} = K_o \exp[-\frac{E_a}{RT}] \qquad (9)$$

k_{app}: apparent electrochemical degradation rate constant (h^{-1}); k_0 : pre-exponential factor of the empirical Arrhenius equation (h^{-1})
Ea: apparent activation energy of the degradation reaction (kJ mol^{-1}); R: ideal constant gas (8.314×10^{-3} kJ mol^{-1} K^{-1}); T: absolute temperature of the solution (K).

Equation (9) gives equation 10:

$$\ln K_{app} = \ln K_o - \frac{E_a}{RT} \qquad (10)$$

From the representation in the Figure 10, it is possible to determine the activation energy, which is 11.69 kJ mol^{-1}. This lower value of Ea suggests that the electrooxidation of MB is controlled by diffusion [36].

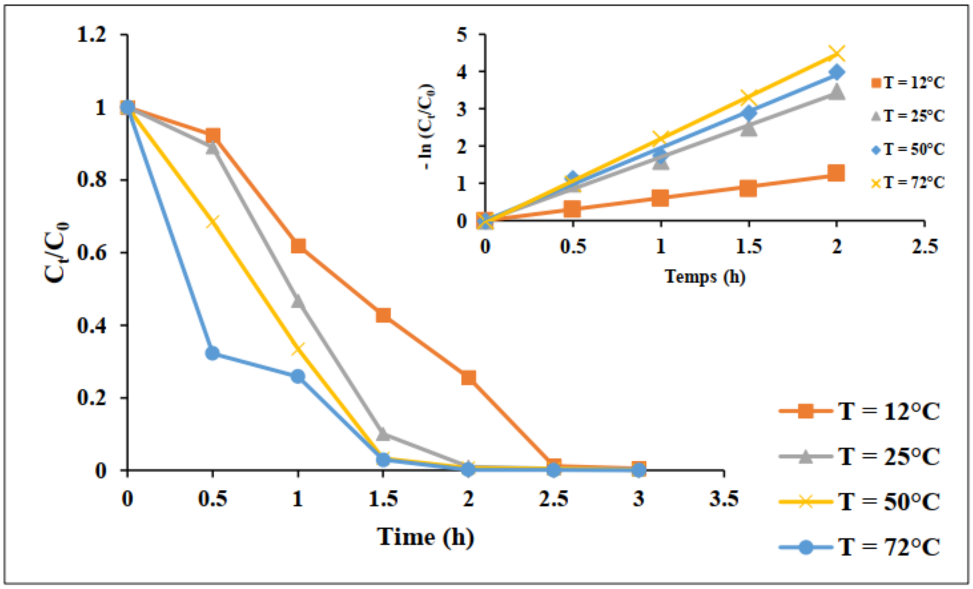


Fig. 9. Plots of (C_t/C_0) against time. Insert: - ln (C_t/C_0) = f (t). Operation conditions: [Na_2SO_4] = 0.1 M; j = 20 mA/cm²; V = 0.25 L; pH = 5.9; Flow rate = 23.27 L/h and Ambient Temperature: 25 °C.

Table 4
Effect of temperature on the degradation kinetics of the methylene blue solution.

Temperature (°C)	k_{app} (h^{-1})	R²
12	0.6103	0.9562
25	1.7080	0.9922
50	1.9534	0.9943
72	2.2600	0.9991

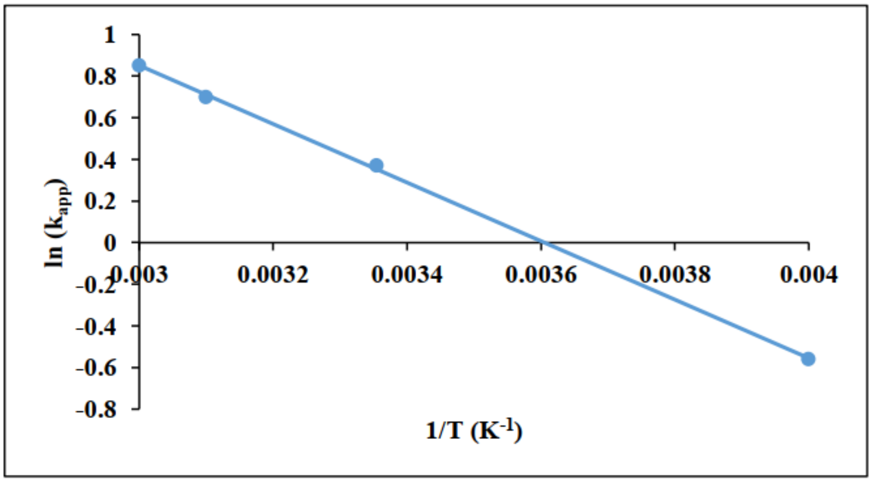


Fig. 10. Arrhenius plot of the degradation rate constant of MB.

3.5. Effect of the concentration of the supporting electrolyte

The investigations were carried on the effect of the concentration of Na_2SO_4, under 20 mA/cm² for an initial MB concentration of 50 mg/L. For this purpose, electrolysis experiments with different concentrations of 0.01, 0.1, 1 and 2 M Na_2SO_4 were performed. According to Figure 11, the degradation rate of MB increases with increasing Na_2SO_4 concentration (0.01 to 1 M) in the first instance. Then, this rate decreases for a Na_2SO_4 concentration higher than 1 M.

According to Nidhees and Gandhimathi [37], increasing the concentration of Na_2SO_4 (from 0.01 M to 1 M in this work) promotes the formation of peroxodisulphate ions ($S_2O_8^{2-}$) by recombination of $SO_4^{\bullet-}$ according the equation (9). The peroxodisulfate ions formed also participate in the degradation of the methylene blue molecules. However, further increasing the concentration of the supporting electrolyte to 2 M favors the consumption of the hydroxyl radical following its trapping by SO_4^{2-} ions (equation (11)), and thus leading to a decrease in the efficiency of the electrochemical process.

$$HO^{\bullet} + SO_4^{2-} \rightarrow OH^- + SO_4^{\bullet-} \qquad (11)$$

The average potential for each concentration of Na_2SO_4 was monitored and reported in the Table 5. We have noted that the average potential decreases when the concentration of Na_2SO_4 increases. Increasing the concentration of the supporting electrolyte allows a decrease in voltage, thus reducing energy consumption. However, there is evidence of foaming and a change in color of the MB solution from purplish blue to violet for the 2 M sodium sulphate concentration according to Figure 12.

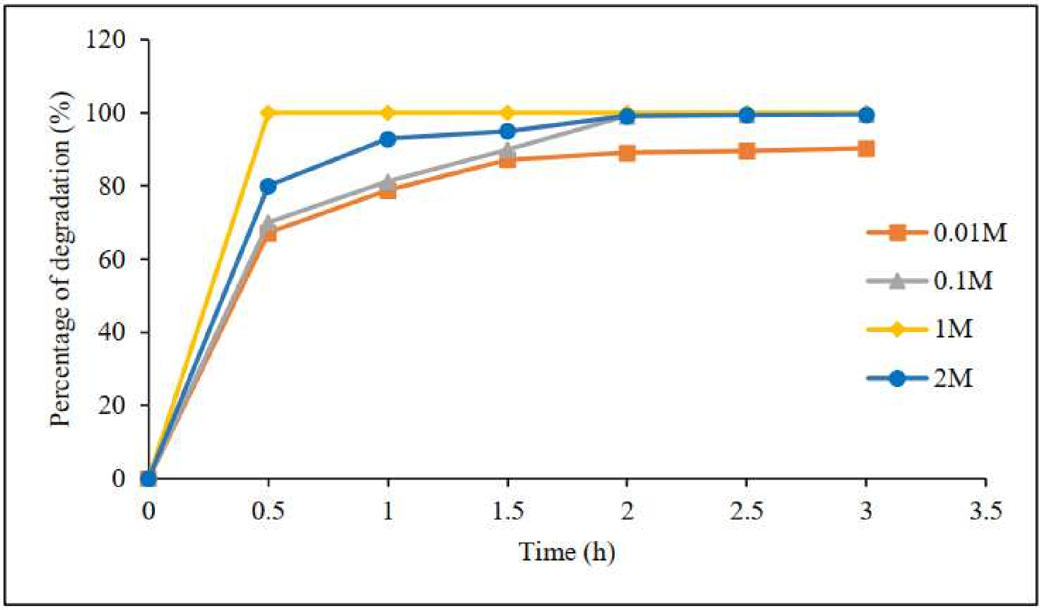


Fig. 11. Effect of supporting electrolyte (Na_2SO_4) concentration on percentage degradation with time. Operation conditions: [MB] = 50 mg L^{-1}; j = 20 mA cm^{-2}; Free pH = 5.9; Flow rate = 23.27 L/h and Ambient temperature: 25 °C.

Table 5
Effect of supporting electrolyte concentration on the electrochemical degradation of methylene blue.

$[Na_2SO_4]$ (M)	0.01	0.1	1	2
U (V)	16.5	8.3	7.1	6.8
j (mA/cm²)		20		

Fig. 12. Staining of a solution MB for $[Na_2SO_4]$ = 2M.

3.6. Effect of recirculation rate

In order to examine the effect of solution flow rate and thus contact time on the electrochemical degradation of MB, electrolysis experiments were performed at different flow rates (4.07; 12.63; 23.27 and 30.43 L/h). As shown in Figure 13, the percentage of degradation increases with decreasing of flow rate. A high flow rate leads to a difficult degradation of the organic compound. From the graphs -ln C_t/C_0=f(t) (insert of Figure 13), it can be assumed first order pseudo-kinetics. The different apparent rate constants are recorded in Table 6. From this table, we can see that the kinetic constant decreases as the flow rate increases. This suggests that the contact time plays an important role in the electrooxidation of MB on a boron-doped diamond electrode. Furthermore, these results show that the hydrodynamic conditions significantly affect the performance of the process used. This shows that the degradation of methylene blue on the BDD electrode is effectively controlled by mass transport under our working conditions [37].

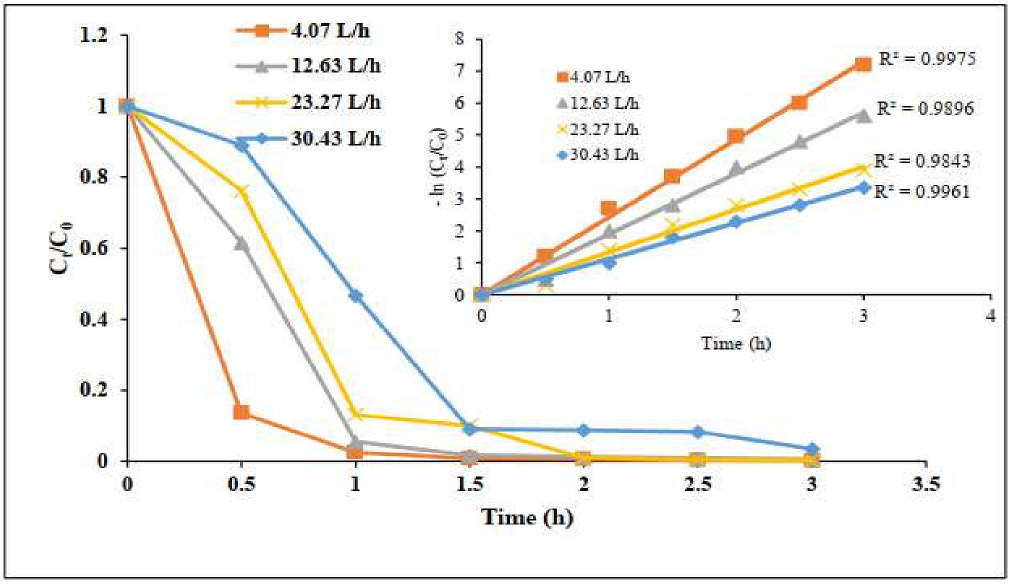


Fig. 13. Electrolysis of [MB] = 50 mg/L on BDD as a function of time at different flow rates, C_t/C_0 = f (t). Operating conditions: $[Na_2SO_4]$ = 0.1 M; Ambient temperature: 25°C; pH = 5.9; j = 20 mA/cm² and Volume of solution: 0.25 L. Insert: – ln (C_t/C_0) = f (t).

Table 6
Effect of flow rate on the electrochemical degradation of methylene blue.

Flow rate (L/h)	4.07	12.63	23.27	30.43
k_{app} (h^{-1})	2.4340	1.9008	1.3363	1.1255
R²	0.9975	0.9896	0.9843	0.9961

4. Conclusion

The degradation of methylene blue by the electrochemical method using BDD as anode was investigated by studying the effect of several parameters, namely the initial MB concentration, applied current density, initial pH, temperature, supporting electrolyte concentration and recirculation flow rate. The results obtained showed that the oxidation of methylene blue is significantly influenced by these parameters. The electrooxidation process of methylene blue is controlled by mass transport and a complete discoloration of the solution is obtained in all experimental conditions of this work. The main results obtained proved that the electrochemical oxidation degradation using a BDD anode of MB follows pseudo-first order kinetics. However, this work requires further investigation to confirm the reaction products (mineralisation of the organic compounds).

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