



Enhanced electrochemical degradation of a basic dye with Ti/Ru_{0.3}Ti_{0.7}O₂ anode using flow-cell

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ABSTRACT

The present study focuses on the electrochemical oxidation process to degrade the synthetic dye methylene blue (MB) using a dimensionally stable anode(DSA), namely Ti/Ru_{0.3}Ti_{0.7}O₂. The investigated parameters to optimize the COD and color removal were current density, dye concentration, solution pH, supporting electrolyte and temperature. It was found that the highest MB removal rates were attained using both high NaCl concentrations and high current densities, which is explained by the generation of high reactive oxidants such as chlorine and hypochlorite leading to a more rapid electro-degradation. On the other hand, the temperature and pH had no significant influence on the MB removal. The electrical energy consumption (E_e) increased with increasing applied current. These results have great significance because they have proved the applicability of the electrochemical techniques in the treatment of some dangerous pollutants such as methylene blue since high efficiencies in the removal of this pollutant were obtained.

Keywords: Anodic oxidation; Treatment; DSA;Dye

1. Introduction

Effluent discharges from a wide variety of industries that contain large amounts of synthetic organic compounds such as dyes of different concentrations and considerable structural diversity result in significant non-aesthetic pollution and serious health problems and negatively affect natural ecosystems [5,11].

The classic wastewater treatment techniques such as coagulation flocculation, adsorption and biological processes are not able to degrade the majority of these pollutants, more developed methods for the decontamination of dye wastewaters have received an extensive research recently. The advanced oxidative processes (AOP) and in

particular the anodic oxidation are among the techniques in which the hydroxyl radicals (OH^{*}) can lead to the oxidation of these non-biodegradable compounds with a high rate of organic removal and easy implementation with low cost of the required equipment [5,17,29]. In the electrochemical processes, dimensionally stable anodes (DSA)-type electrodes are the most preferred due to their high stability and large production of oxidant species (i.e. Cl₂ and ClO⁻) that can reach current efficiencies as high as 81–93% and higher removal efficiencies of pollutants (as Table 1 shows, with some types of anodes using chloride solutions). However, several researchers have successfully managed to degrade the organic pollutants using these anodes by the production of active chlorine species [4,24,27,33].

These anodic oxidation can be classified either as direct or indirect process. In the direct process, it is not required

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Table 1

Percentage of color removal and COD decays for the indirect electro-oxidation with active chlorine of organic pollutants in chloride solutions using undivided cells with DSA-type anodes

Anode organic pollutant	Initial concentration (mg L ⁻¹)	Experimental conditions	<i>i</i> (mA cm ⁻²)	Color removal (%)	COD decay (%)	Ref
Ti/RuO ₂ anode						
Basic Blue 9	80	1.2 mol L ⁻¹ NaCl, natural pH, 95 min of electrolysis	20	100	94	[43]
Acid Blue 113	160	1.74 mol L ⁻¹ NaCl, pH = 9.0, 90 min of electrolysis	10	– ^a	80	[27]
C.I. Reactive Dyes (Yellow 17 and Blue 4)	– ^a	0.05 mol L ⁻¹ NaCl, pH = 11.0, 3 h of electrolysis	70	99.4	82	[40]
Ti/TiO ₂ –RuO ₂ anode						
Acid Brown 14	330	0.58 mol L ⁻¹ NaCl, pH = 7.0, 2.5 h of electrolysis	30	100	67	[32]
Ti/TiO ₂ –RuO ₂ –IrO ₂ anode						
Reactive Red 141	100	1.5 mol L ⁻¹ NaCl, pH = 6.2–6.5, 2 h of electrolysis	30	100	82.44 ^b	[25]
Reactive Black 5	300	0.008 mol L ⁻¹ NaCl, 15 min of electrolysis	100	100	33	[15]
Reactive Blue 19	400	0.025 mol L ⁻¹ NaCl, pH = 6, 80 min of electrolysis	21.66	100	55.8	[34]

^aNot determined, ^bTOC decay.

to add a large amounts of chemicals to wastewater since the generation of physically adsorbed active oxygen can help the charge transfer to occur. While the indirect process involves the intervention of oxidizing species with an effective action such as chlorine/hypochlorite (see details below) that are generated on the electrode surface which diffuses away from it to interact with organic species in the solution [3,22,42].

For example, the addition of NaCl which is an oxidizing agent can be beneficial to degradation since the following species are formed: chlorine gas (Cl₂) and hypochlorite (OCl⁻). Chlorine gas is formed at the anode according to the following reaction:



The chlorine can react with water at bulk solution to form hypochlorite acid (HOCl) and hypochlorite (ClO⁻):



On the other hand, the choice of the anode is very important. Dimensionally stable anode (DSA) materials containing ruthenium (Ru) and iridium (Ir) have been widely and recently recognized as promising for waste waters treatment [8,26,41]. DSAs are effective for use in treatment systems since they present long lifetimes. It has been also demonstrated that DSAs could be used in the photo-electrochemical oxidation of organic substances and for contaminated effluents [6,7,14,19,20]. The most known and used DSA electrode is the Ti/Ru_{0.3}Ti_{0.7}O₂ anode due to its effectiveness for the oxidation of different dyes such as Reactive Red

[7], Direct Red 81 [36], Acid Violet 1 [37], Reactive Blue 19 [30], Methyl Red [10] and Reactive Orange 16 [12,13].

In the present work, the evaluation of the electrochemically oxidative process of methylene blue using a commercial Ti/Ru_{0.3}Ti_{0.7}O₂ anode has been achieved. The effect of current density, initial pH, supporting electrolyte, temperature and the dye's initial concentration were investigated. The discoloration and the variation of chemical oxygen demand (COD) were followed in order to evaluate the oxidation efficiency.

2. Materials and methods

2.1. Chemicals

All chemicals (Na₂SO₄, NaCl, Ag₂SO₄, HgSO₄, and H₂SO₄) were obtained from SOLVACHIMI and Sigma-Aldrich and used without further purification, deionized water was used in dilutions and preparation of standard solutions.

2.2. Methylene blue dye

The basic dye, methylene blue (noted: MB) (Fig. 1) was prepared by dissolving a required amount in distilled water to get the desired concentrations and different concentrations of supporting electrolytes (i.e. NaCl or Na₂SO₄) were added to the solution. The electrolysis is performed in a solution of 200 cm³ and electrolyte samples were collected at different times during the electrolysis.

2.3. Experimental setup

The electrochemical oxidation of MB was performed using an electrochemical flow-cell with an experimental set

up illustrated in Fig. 2 and previously described in the literature [10,12,38]. The working electrode (WE) was a commercial Ti/Ru_{0.3}Ti_{0.7}O₂ with plate geometric area of 14 cm² (De Nora Company, Brazil), exposed to the solution. A stainless-steel plate of the same area was used as the counter electrode (CE). The reactor was mounted by positioning the electrodes between the Viton and Teflon spacers with variable thickness. The dye solution was pumped vertically through the cell provided by an electric pump at a flow velocity of 30 L h⁻¹. A DC power supply (GW-Instek GPS-3030DD model) was used as the source of constant electric current for the experiments. Before each experiment, the working electrode was generated by the use of a 0.5N H₂SO₄ solution and by applying a current density of 20 mA cm⁻² for a period of 15 min.

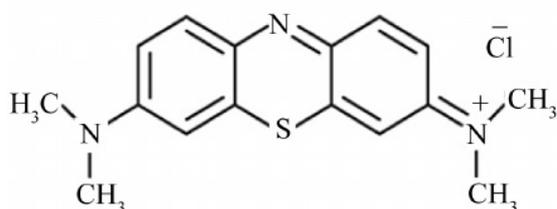


Fig. 1. The molecular structure of methylene blue, with the molecular formula C₁₆H₁₈ClN₃S.

2.4. Analytical procedures

The color removal was followed by the decrease in absorbance using a UV-vis spectroscopy (UV-2300) and by taking sample solutions at different time intervals during the degradation process. The extent of color removal was determined using the following relationship while monitoring the band at $\lambda_{\max} = 664$ nm corresponding to the BM maximum absorption:

$$\% \text{ Color Removal} = \frac{A_0 - A_t}{A_0} \times 100 \quad (4)$$

where A_0 and A_t are the absorbance before and after electrolysis, respectively.

The chemical oxygen demand (COD) of the solution was monitored using a digester (Lovibond RD 125) and a colorimeter (LovibondCheckit direct COD VARIO, Germany), system, diluting the samples in order to avoid the interference of chloride ions.

The COD was monitored according to the standard methods for the examination of wastewater [2]. The COD values of the initial and electrolyzed samples were determined by open reflux, dichromate titration method and diluting the samples in order to avoid the interference of chloride ions.

The variation of chemical oxygen demand (% COD) for the anodic oxidation of the methylene blue was calculated from the values of the COD using the relationship:

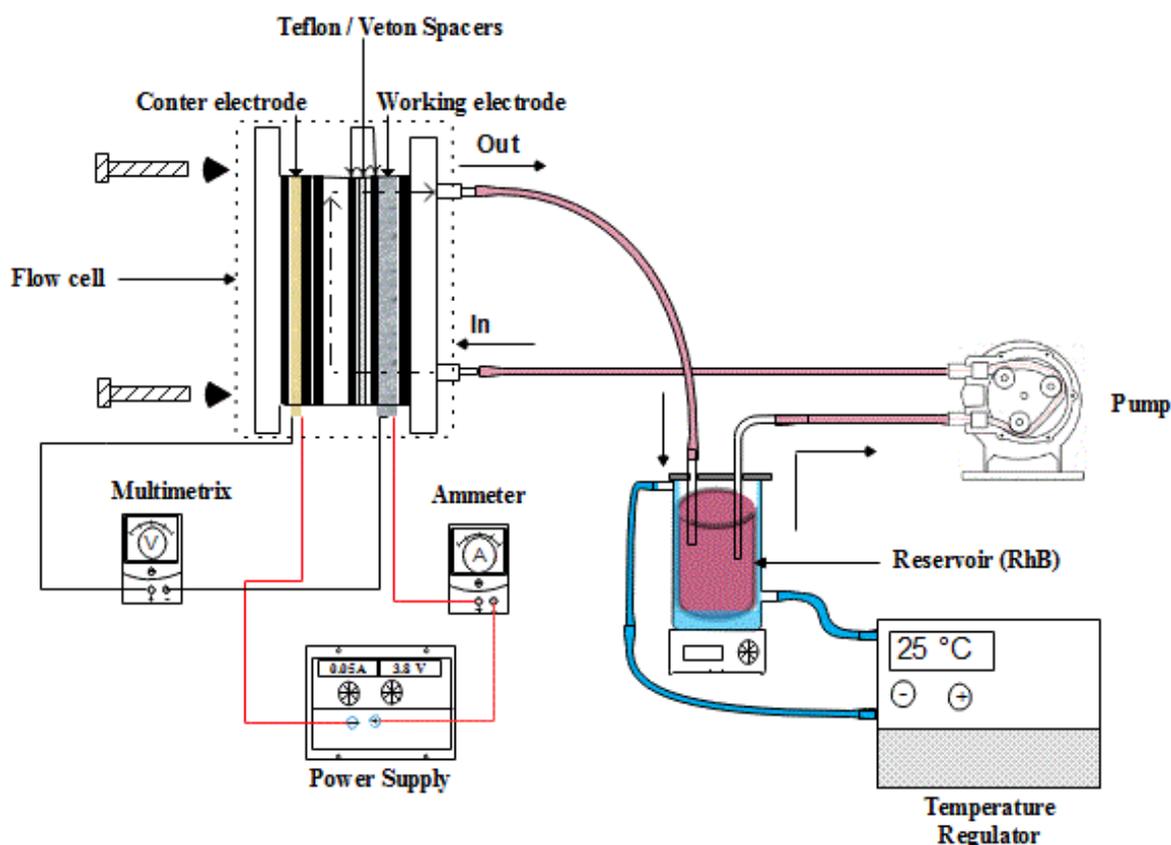


Fig. 2. Schematic representation of the electrochemical setup used in the present study.

$$\% \text{ COD} = \frac{\text{COD}_i - \text{COD}_t}{\text{COD}_i} \times 100 \quad (5)$$

where COD_i and COD_t are the values of COD (mg L^{-1} of O_2) at initial time and at time “ t ”, respectively.

The specific energy consumption (E_c , in kWhm^{-3}) was calculated using Eq. (6):

$$E_c = \frac{U_{\text{cell}} \times I \times t}{3600 \times V} \quad (6)$$

where U is the average cell voltage (V), I is the current (A), t is the treatment time (s), and V is the volume of the treated wastewater (m^3).

3. Results and discussion

3.1. Effect of supporting electrolytes

Different parameters can affect the radicals' generation in electrochemical processes such as the supporting electrolyte nature, this latter can increase the electrolyte conductivity and enhance the treatment efficiency. In this work, NaCl and Na_2SO_4 were the two supporting electrolytes that have been tested, as it is shown in Fig. 3, when 0.1 mol L^{-1} Na_2SO_4 is added to the dye solution, a very low level of color removal of 38% is obtained after 90 min of electrolysis. MB removals were higher in the presence of NaCl [1,13]. Besides, the degradation rate is improved that as the amount of NaCl increases, the conductivity also get increased and, as a result, the operating cell potential is reduced leading to a much lower energy consumption [19].

It is reported that the electrochemical oxidation of organic substances, using DSA electrodes in the presence of chloride ions, is responsible for high pollutant removal rates due to the electro-catalytic evolution of Cl_2 [16,39].

As the presence of NaCl promoted the decolorization on the electrode and to further test the effect of NaCl, different concentrations were used: 0.01, 0.03, 0.05 and 0.08 mol L^{-1} , it was observed that MB removal is increased at high concentration of NaCl at acidic conditions ($\text{pH} = 3$, $i = 0.08 \text{ A}$ and $T = 25^\circ\text{C}$). This can be explained by the indirect oxidation process since NaCl can lead to the formation of both Cl_2 and hypochlorite (ClO^-) according to Eqs. (1)–(3).

These two species can oxidize organic pollutants which in turn contribute to the degradation of the dye in the solution [6]. The same behavior was observed by Malpass et al. [19] during the electrochemical oxidation of a real textile effluent using a DSA electrode. In addition, the intermediates of oxygen evolution may form oxychloro species that can mediate organic destruction (Eqns. (7) and (8)) as described in other studies [21,35]



It is also possible that both the degradation routes Eqns. ((1)–(3)) and (7), (8) play simultaneous roles in the dye removal [21,35].

Plots of MB removal in electrolytes containing different concentrations of Cl^- showed a linear correlation between reaction time and the variation in the concentration logarithm (Fig. 3), signifying that the degradation followed pseudo-first-order kinetics in the presence of NaCl. The rate constant (k) was obtained from the slope of Eq. (9).

$$\text{Ln} \frac{C}{C_0} = k_{\text{app}} t \quad (9)$$

The removal of color follows pseudo first order kinetics, the first order rate plots for the time–concentration profiles in Fig. 3 are presented in the inset. It is obvious that as soon as NaCl is added to the electrolyte, the rate of color removal is increased. The pseudo first order rate constant is obtained from the slope of straight line by plotting the value of $\ln(C/C_0)$ vs. reaction time t .

3.2. Effect of current density

The applied current is one of the important factors that must be considered for scaling up the electrochemical processes. Since we found that the rate of oxidation depends on the amount of NaCl used (and in turn hypochlorite and chlorine), we decided to study the effect of increasing the generation rate of these oxidizing agents, this was achieved by increasing the current from 0.02 to 0.08 by adding 0.08 mol L^{-1} NaCl, that was the maximum concentration that gave the best color removal rates. Previous studies have investigated the effect of the current density and have shown that this late has a strong influence on the rate of color and in turn dye removal. In fact, the current densities increase the rate of formation of the electro-active species formed at the electrode surface [18]. Additionally, the charge needed for the rupture of chromophores increased with increasing current density.

Fig. 4 presents the concentration–time profiles for the degradation of MB, it can be observed that the color removal is enhanced as the current density is increased attaining a complete removal in different times. A high current density simply implies an increase in the amount of electrical energy injected into the system. The refuse, a large energy savings can be realized if low current densities are used (which it is the case in our study), as a result the rate of formation of the electro-active species formed at the

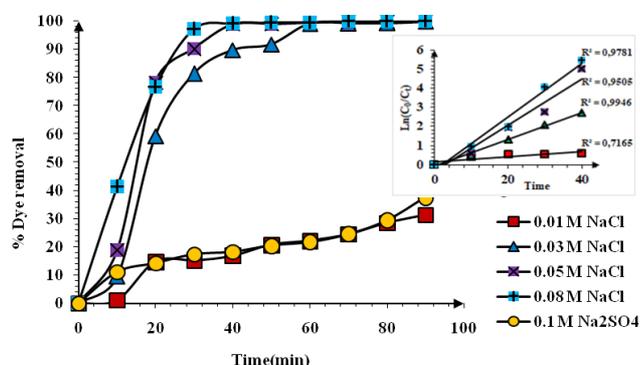


Fig. 3. Percentage of color removal as a function of time at different supporting electrolyte concentrations Na_2SO_4 and NaCl during electrolysis of the MB on the DSA anode (Conditions: $i = 0.08 \text{ A}$, $\text{pH} = 3$, $[\text{MB}] = 100 \text{ mg L}^{-1}$ and Flow-rate = 30 L h^{-1}).

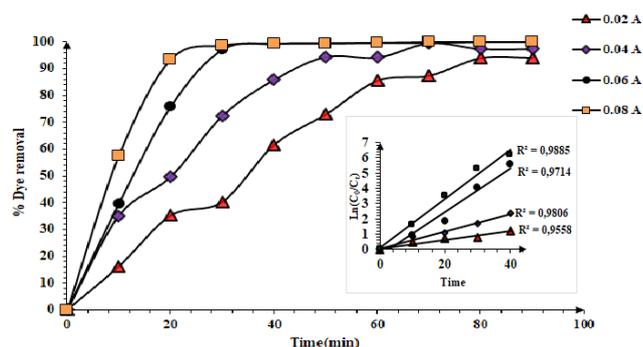


Fig. 4. Effect of current values on the percentage color removal during electrolysis of the MB on the DSA anode (Conditions: $[\text{NaCl}] = 0.08 \text{ mol L}^{-1}$, $\text{pH} = 3$, $[\text{MB}] = 100 \text{ mg L}^{-1}$ and flow-rate = 30 L h^{-1}).

anode surface is more important while increasing the rate of organic degradation [23].

As estimated, increasing the current density has led to a faster de-colorization of the MB solution, due to a greater charge entering the cell and electro-generating more active chlorine. The slope in the plot of $\ln[C(0)/C(t)]$ vs. t leads to the kinetic constant (Fig. 4), it is observed that for all current densities applied, the removal of MB dye solution obeys pseudo-first-order kinetics. Table 2 gives a pseudo-rate constant (K_{app}) of 0.036 min^{-1} ($R^2 = 0.95$) for 0.02 A and 0.121 min^{-1} ($R^2 = 0.95$) for 0.08 A . This suggests that the reaction of degradation rate increase when an increase in the current is attained. Moreover, the concentration of all oxidizing species (Cl_2 , ClO^-) depends on the applied current.

3.3. Effect of temperature

Fig. 5 shows to the influence of the investigated temperatures on color removal, it can be seen that as the temperature increases till 45°C , a small influence in the MB removal has been noticed since almost similar removal percentages were attained, but for temperature ($T = 55^\circ\text{C}$) a less efficient process was observed. At high temperatures, the mass transport controlled reduction of hypochlorite may also be the reason for a decreased de-colorization according to the following cathodic loss reaction [31].



The electrochemical process is expected to get enhanced by the temperature increase since the oxidative species diffusivity coefficient will be improved, but the decomposition reactions of oxidants can also favors the negative effect of the degradation process which depends on the nature of organic pollutants [23].

The slight influence on the degradation as the temperature changes with hydroxyl radicals as oxidants can also be explained by the increase in the chemical reactions rates, in agreement with results already reported [9,28]

3.4. Effect of initial concentration

The fact that the wastewater discharged from different industries has different concentrations of MB dye,

Table 2

Energy consumption, calculated from Eq. (6), per volume of treated effluent, parent first order kinetic constants (k_{app}) and Average cell voltage during MB oxidation at $\text{Ti/Ru}_{0.3}\text{Ti}_{0.7}\text{O}_2$ electrode for different variables in 200 mL synthetic dye solution. $[\text{BM}] = 100 \text{ mg L}^{-1}$, $[\text{NaCl}] = 0.08 \text{ mol L}^{-1}$

Parameters	k_{app} (min^{-1})	Average cell voltage (V)	Energy consumption (kWh m^{-3})
Current			
0.02 A	0.0369	2.03	0.406
0.04 A	0.0544	2.65	1.060
0.06 A	0.1098	3.17	1.902
0.08 A	0.1213	3.45	2.760
Initial pH ($i = 0.08 \text{ A}$)			
3	0.0707	2.33	2.796
5	0.0656	2.72	3.264
8	0.0585	2.36	2.832
11	0.0642	2.42	2.904
Temperature ($i = 0.08 \text{ A}$)			
25°C	0.1375	2.90	2.320
35°C	0.1097	2.23	1.784
45°C	0.1272	2.16	1.728
55°C	0.1081	2.05	1.640
Supporting electrolyte ($i = 0.08 \text{ A}$)			
$0.01 \text{ mol L}^{-1} \text{ NaCl}$	0.0109	2.53	2.024
$0.03 \text{ mol L}^{-1} \text{ NaCl}$	0.0877	2.86	2.288
$0.05 \text{ mol L}^{-1} \text{ NaCl}$	0.0982	3.12	2.496
$0.08 \text{ mol L}^{-1} \text{ NaCl}$	0.1060	3.45	2.760
$0.10 \text{ mol L}^{-1} \text{ Na}_2\text{S}_2\text{O}_4$	0.0108	2.16	1.728

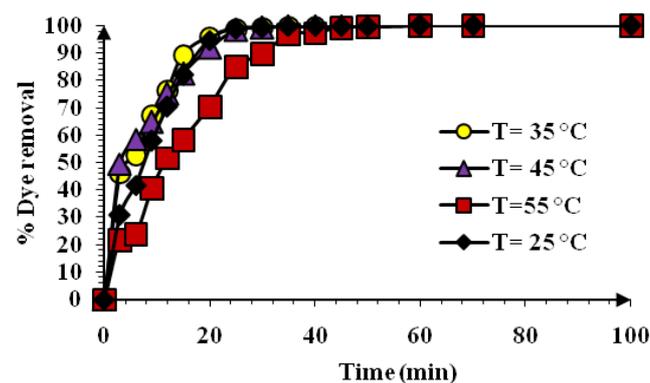


Fig. 5. Percentage of color removal as a function of temperature values during electrolyses of the MB on the DSA anode (Conditions: $[\text{NaCl}] = 0.08 \text{ mol L}^{-1}$, $\text{pH} = 3$ and $[\text{MB}] = 100 \text{ mg L}^{-1}$ and Flow-rate = 30 L h^{-1}).

it is very important, from a practical point of view, to investigate the effect of the initial concentration on the degradation efficiency of MB during the electrochemical process.

The concentration of MB was varied from 100 to 400 mg L⁻¹ (T = 25°C, pH = 3, 0.08 mol L⁻¹ NaCl), Fig. 6 presents the instantaneous variation of the MB concentration as a function of electrolysis time for the different concentrations studied, it can be observed that the two low initial pollutant concentrations 100 and 200 mg L⁻¹ were degraded in 40 and 60 min, respectively, while for high initial concentrations, less efficiencies were obtained, this indicates that both oxidation rate and process efficiency are directly proportional to organic matter concentration, this can be explained by the decrease of the concentration of the oxidizing agent while the MB initial concentration increases.

Furthermore, higher initial MB concentrations may possess a negative effect in the electrochemical reaction, leading to the decrease of the path length of the energy entering the MB solution. As a result, the catalyst surface is reduced, thus, a limited adsorption and less catalytic sites on the catalyst surface are obtained. The competition between MB molecules and intermediates was increased along with the increasing of MB concentration as more intermediates are produced at high pollutant concentrations. Besides, high MB removal at low concentrations can be considered to be of a great importance. For this reason, the initial MB concentration was chosen as 100 mg L⁻¹ in all the experiments.

3.5. pH effect

Solution pH is an important factor having an impact on the kinetics of the electro-catalytic degradation of organic compounds because the pH affects the adsorption/desorption of the organics on the anode. The pH of the electrolyte was followed continuously during the electrolysis and kept at the required value by addition of H₂SO₄ or NaOH solutions as appropriate. In the present work, different pH values were chosen and their effect is discussed.

Fig. 7 shows the changes in relative concentrations of MB and as a function of electrolysis time in experiments in which the dye solution (100 mg L⁻¹ in 0.08 mol L⁻¹ NaCl) was maintained at different pH values (3, 5, 8 and 11) while applying a current density of 0.08 A. These pH values were chosen

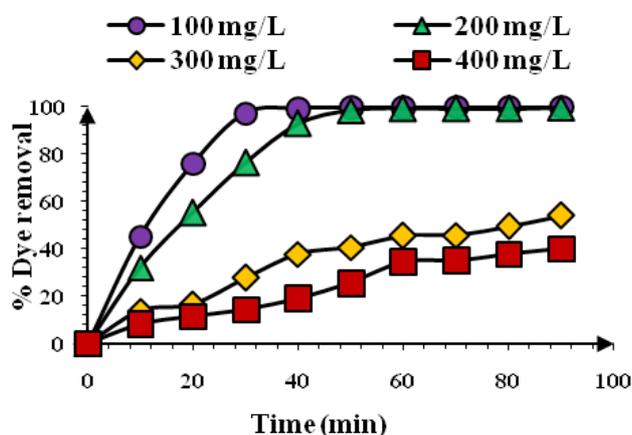


Fig. 6. Effect of initial concentration of MB on the percentage of removal color during electrolysis of the MB on the DSA anode (Conditions: [NaCl] = 0.08 mol L⁻¹, i = 0.08 A, pH = 3, T = 25°C and Flow-rate = 30 L h⁻¹).

to determine if the dye removal rate would be affected by the specific oxidizing chlorine species that are present in the solution, the curves obtained in Fig. 7 show that the rate of removal of MB is not greatly affected by the pH of the solution since no difference was observed in the proportion of MB molecules that were degraded. After changing the solution pH, the same performance was obtained in the different chosen pH values, this can be explained by the same oxidizing rate of the different species (Cl₂, HOCl, and ClO⁻) at different pH values. The color was removed obeying pseudo-first order kinetics in every pH value.

3.6. COD removal

Since this study aimed at the de-colorization of dye, the dye concentration was used to evaluate the treatment. The efficiency in terms of dye de-colorization under the optimized condition is above 99.9%. The optimal experimental conditions obtained leading to the highest MB removal (initial pH = 3, T = 25°C, i = 0.08 A, [NaCl] = 0.08 mol L⁻¹ and 100 mg L⁻¹ of MB) were followed by COD. As can be seen from Fig. 8, COD trend is getting increased under those conditions indicating that experimental conditions strongly affect the degradation rate, it can be concluded that methylene blue was oxidized initially to color less intermediates, and then to carbon dioxide.

For example, after 40 min of electrolysis, the COD removal was only 17%, in the contrary the color removal was completely eliminated. It is known that the color removal was due to the cleavage of chromophore bond in the dye molecule. However, the degradation of aromatic molecules takes more time and hence the elimination of COD is very low.

Energy consumption is an important parameter that should be taken into account in an electrochemical process; it is defined as the electrical energy in kWh m⁻³ necessary to degrade the contaminated water. Table 2 sheds a light on the energy consumption of the treated dye at different conditions. The amount of energy consumed in the degradation of MB increased with increasing the current density, the consumption increased from 2.03 to 3.45

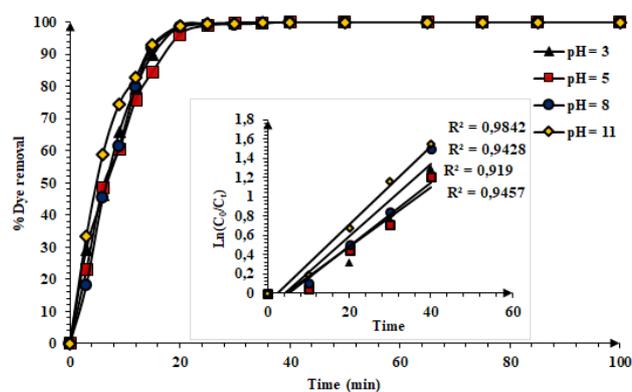


Fig. 7. The influence of the initial pH values on the color removal during the electrolysis of the MB on the DSA anode (Conditions: [NaCl] = 0.08 mol L⁻¹, [MB] = 100 mg L⁻¹, i = 0.08 A, pH = 3, T = 25°C and Flow-rate = 30 L h⁻¹).

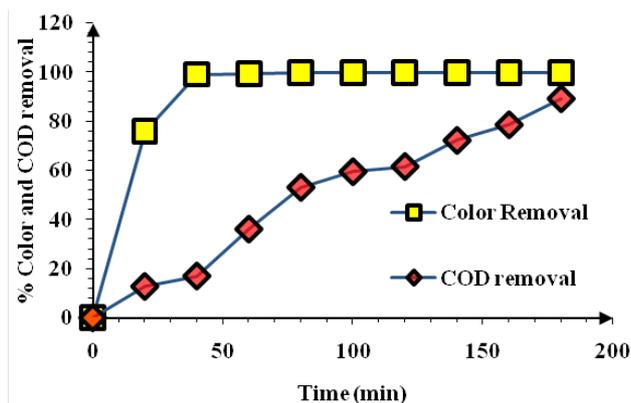


Fig. 8. Variation of % color removal and % COD during electrolyses of the MB on the DSA anode under the optimal experimental conditions (Conditions: $[\text{NaCl}] = 0.08 \text{ mol L}^{-1}$, $i = 0.08 \text{ A}$, $[\text{MB}] = 100 \text{ mg L}^{-1}$, $\text{pH} = 3$, $T = 25^\circ\text{C}$ and $\text{Flow-rate} = 30 \text{ L h}^{-1}$).

kWh m^{-3} of treated effluent when the current density was changed from 0.02 to 0.08 A. This latter value was chosen as the optimum since the other lower current densities, required longer reaction times to attain the required level of degradation.

Energy consumption values were obtained at different pH values as well, no big differences were observed as Table 2 presents. However, the decrease in charge requirements while rising temperature was confirmed. Contrariwise, it is observed that with the increase of NaCl concentration, the operating cell potential is increased and the energy consumption is higher. The process reported in Table 2 in order to show the viability of this process as a green alternative for the treatment of wastewaters.

4. Conclusion

Electrochemical degradation of an aqueous solution containing methylene blue (MB) dye was investigated using a commercial DSA electrode in the presence of chloride ions. The influence of current density, initial dye concentration, solution pH, supporting electrolyte and temperature on COD and color removal were followed and the following conclusions can be drawn:

- The addition of NaCl is very essential due to the formation of active chlorine and hypochlorite species, which are strong oxidizing agents that can lead to a rapid electrodegradation.
- High current densities have a significant effect leading to a good electrochemical performance.
- The electrochemical oxidation technology described herein could be an alternative option to treat effluents contaminated with MB.

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Conflict of interest

On behalf of all authors, the corresponding author states that there is no conflict of interest.

References

- [1] J.M. Aquino, K.N. Parra, D.W. Miwa, A.J. Motheo, Removal of phthalic acid from aqueous solution using a photo-assisted electrochemical method, *J. Environ. Chem. Eng.*, 3 (2015) 429–435.
- [2] A.P.H. Association, A.W.W. Association, W.P.C. Federation, and W.E. Federation, Standard Methods for the Examination of Water and Wastewater. Vol. 2, American Public Health Association, 1915.
- [3] A. Baddouh, G.G. Bessegato, M.M. Rguiti, B. El Ibrahim, L. Bazzi, M. Hilali, M.V.B. Zanoni, Electrochemical decolorization of Rhodamine B dye: Influence of anode material, chloride concentration and current density, *J. Environ. Chem. Eng.*, 6 (2018) 2041–2047.
- [4] A. Baddouh, M. Rguiti, E. Mohamed, B. El Ibrahim, L. Bazzi, M. Hilali, Electrochemical degradation of thiabendazole fungicide by anodic oxidation on the tin oxide electrode (SnO_2), *Appl. J. Environ. Eng. Sci.*, 3 (2017) 213–221.
- [5] E. Brillas, C.A. Martínez-Huitle, Decolorization of wastewaters containing synthetic organic dyes by electrochemical methods. An updated review, *Appl. Catal. B: Environ.*, 166 (2015) 603–643.
- [6] A. Buzzini, D. Miwa, A. Motheo, E. Pires, Use of electrochemical oxidation process as post-treatment for the effluents of a UASB reactor treating cellulose pulp mill wastewater, *Water Sci. Technol.*, 54 (2006) 207–213.
- [7] M. Catanho, G.R. Malpass, A.J. Motheo, Photoelectrochemical treatment of the dye reactive red 198 using DSA® electrodes, *Appl. Catal. B: Environ.*, 62 (2006) 193–200.
- [8] G. Chen, Electrochemical technologies in wastewater treatment, *Separ. Purif. Technol.*, 38 (2004) 11–41.
- [9] G.R. de Oliveira, N.S. Fernandes, J.V. de Melo, D.R. da Silva, C. Urghe, C. Martínez-Huitle, Electrocatalytic properties of Ti-supported Pt for decolorizing and removing dye from synthetic textile wastewaters, *Chem. Eng. J.*, 168 (2011) 208–214.
- [10] C.C. de Oliveira Morais, A.J.C. da Silva, M.B. Ferreira, D.M. de Araújo, C.L. Zanta, S.S.L. Castro, Electrochemical degradation of methyl red using $\text{Ti/Ru}_{0.3}\text{Ti}_{0.7}\text{O}_2$: fragmentation of azo group, *Electrocatalysis*, 4 (2013) 312–319.
- [11] E. Forgacs, T. Cserhati, G. Oros, Removal of synthetic dyes from wastewaters: a review, *Environ. Int.*, 30 (2004) 953–971.
- [12] L. Gomes, D.W. Miwa, G.R. Malpass, A.J. Motheo, Electrochemical degradation of the dye reactive orange 16 using electrochemical flow-cell, *J. Braz. Chem. Soc.*, 22 (2011) 1299–1306.
- [13] S. Hussain, S. Gul, J.R. Steter, D.W. Miwa, A.J. Motheo, Route of electrochemical oxidation of the antibiotic sulfamethoxazole on a mixed oxide anode, *Environ. Sci. Pollut. Res.*, 22 (2015) 15004–15015.
- [14] S. Hussain, J.R. Steter, S. Gul, A.J. Motheo, Photo-Assisted electrochemical degradation of sulfamethoxazole using a $\text{Ti/Ru}_{0.3}\text{Ti}_{0.7}\text{O}_2$ anode: mechanistic and kinetic features of the process, *J. Environ. Manage.*, 201 (2017) 153–162.
- [15] D. Jager, D. Kupka, M. Vaclavikova, L. Ivanicova, G. Gallios, Degradation of Reactive Black 5 by electrochemical oxidation, *Chemosphere*, 190 (2018) 405–416.
- [16] L. Krishtalik, Kinetics and mechanism of anodic chlorine and oxygen evolution reactions on transition metal oxide electrodes, *Electrochim. Acta*, 26 (1981) 329–337.
- [17] D. Krzemińska, E. Neczaj, G. Borowski, Advanced oxidation processes for food industrial wastewater decontamination, *J. Ecol. Eng.*, 16 (2015) 61–71.

- [18] G. Malpass, D. Miwa, A. Miwa, S. Machado, A. Motheo, Study of photo-assisted electrochemical degradation of carbaryl at dimensionally stable anodes (DSA®), *J. Hazard. Mater.*, 167 (2009) 224–229.
- [19] G. Malpass, D. Miwa, D. Mortari, S. Machado, A. Motheo, Decolorisation of real textile waste using electrochemical techniques: effect of the chloride concentration, *Water Res.*, 41 (2007) 2969–2977.
- [20] G.R. Malpass, A.J. Motheo, Screening process for activity determination of conductive oxide electrodes for organic oxidation, *J. Brazil. Chem. Soc.*, 19 (2008) 672–678.
- [21] C. Martinez-Huitle, S. Ferro, A. De Battisti, Electrochemical incineration in the presence of halides, *Electrochem. Solid-State Lett.*, 8 (2005) D35–D39.
- [22] C.A. Martinez-Huitle, S. Ferro, Electrochemical oxidation of organic pollutants for the wastewater treatment: direct and indirect processes, *Chem. Soc. Rev.*, 35 (2006) 1324–1340.
- [23] D. Miwa, G. Malpass, S. Machado, A. Motheo, Electrochemical degradation of carbaryl on oxide electrodes, *Water Res.*, 40 (2006) 3281–3289.
- [24] N. Mohan, N. Balasubramanian, C.A. Basha, Electrochemical oxidation of textile wastewater and its reuse, *J. Hazard. Mater.*, 147 (2007) 644–651.
- [25] N. Mohan, N. Balasubramanian, V. Subramanian, Electrochemical treatment of simulated textile effluent, *Chem. Eng. Technol.*, 24 (2001) 749–753.
- [26] S.A. Neto, A. De Andrade, Electrooxidation of glyphosate herbicide at different Dsa® compositions: pH, concentration and supporting electrolyte effect, *Electrochim. Acta*, 54 (2009) 2039–2045.
- [27] M. Panizza, A. Barbucci, R. Ricotti, G. Cerisola, Electrochemical degradation of methylene blue, *Separ. Purif. Technol.*, 54 (2007) 382–387.
- [28] M. Panizza, G. Cerisola, Electrocatalytic materials for the electrochemical oxidation of synthetic dyes, *Appl. Catal. B: Environ.*, 75 (2007) 95–101.
- [29] S. Parsons, *Advanced Oxidation Processes for Water and Wastewater Treatment*, IWA Publishing, 2004.
- [30] R. Pelegrini, P. Peralta-Zamora, A.R. de Andrade, J. Reyes, N. Duran, Electrochemically assisted photocatalytic degradation of reactive dyes, *Appl. Catal. B: Environ.*, 22 (1999) 83–90.
- [31] D. Pletcher, F.C. Walsh, *Industrial Electrochemistry*, Springer Science & Business Media, 2012.
- [32] S. Raghu, C.A. Basha, Electrochemical treatment of procion black 5b using cylindrical flow reactor—a pilot plant study, *J. Hazard. Mater.*, 139 (2007) 381–390.
- [33] D. Rajkumar, J.G. Kim, Oxidation of various reactive dyes with in situ electro-generated active chlorine for textile dyeing industry wastewater treatment, *J. Hazard. Mater.*, 136 (2006) 203–212.
- [34] D. Rajkumar, B.J. Song, J.G. Kim, Electrochemical degradation of reactive blue 19 in chloride medium for the treatment of textile dyeing wastewater with identification of intermediate compounds, *Dyes Pigm.*, 72 (2007) 1–7.
- [35] O. Scialdone, S. Randazzo, A. Galia, G. Silvestri, Electrochemical oxidation of organics in water: role of operative parameters in the absence and in the presence of NaCl, *Water Res.*, 43 (2009) 2260–2272.
- [36] A. Socha, E. Sochocka, R. Podsiadły, J. Sokołowska, Electrochemical and photoelectrochemical degradation of direct dyes, *Color. Technol.*, 122 (2006) 207–212.
- [37] A. Socha, E. Sochocka, R. Podsiadły, J. Sokołowska, Electrochemical and photoelectrochemical treatment of Ci acid violet 1, *Dyes Pigm.*, 73 (2007) 390–393.
- [38] M.G. Tavares, L.V. da Silva, A.M.S. Solano, J. Tonholo, C.A. Martinez-Huitle, C.L. Zanta, Electrochemical oxidation of methyl red using Ti/Ru_{0.3}Ti_{0.7}O₂ and Ti/Pt anodes, *Chem. Eng. J.*, 204 (2012) 141–150.
- [39] S. Trasatti, Electrocatalysis: understanding the success of DSA®, *Electrochim. Acta*, 45 (2000) 2377–2385.
- [40] S. Vahidhabanu, B. Ramesh Babu, Degradation of Ci reactive dyes (Yellow 17 and Blue 4) by electrooxidation, *J. Waste Resour.*, 5 (2015) 2.
- [41] K.M. Vieira, C.C. Nascentes, A.J. Motheo, R. Augusti, Electrochemical oxidation of ethinylestradiol on a commercial Ti/Ru_{0.3}Ti_{0.7}O₂ DSA electrode, *ISRN Environ. Chem.*, 2013.
- [42] J.L. Wang, L.J. Xu, Advanced oxidation processes for wastewater treatment: formation of hydroxyl radical and application, *Crit. Rev. Environ. Sci. Technol.*, 42 (2012) 251–325.
- [43] C.-H. Yang, C.-C. Lee, T.-C. Wen, Hypochlorite generation on Ru–Pt binary oxide for treatment of dye wastewater, *J. Appl. Electrochem.*, 30 (2000) 1043–1051.