Anodic oxidation of methylene blue at Ti/Pt electrode

H. Lebik[1,2*], H. Ait-Amar[2] , R. Elhadi[3], F. Madjene[1], D. Tassalit[1]

[1]Unité de Développement des Equipements Solaires, UDES, Centre de Développement des Energies Renouvelables, CDER, 42004, Tipaza, Algérie
[2]Laboratoire des Sciences du Génie des Procédés Industriels (LSGPI), Faculté de Génie Mécanique et de Génie des Procédés, USTHB, BP 32, El-Alia 16112 Bab-Ezzouar, Algérie
[3]Centre de Recherche Scientifique et Technique en Analyses Physico – Chimiques BP 384, Zone Industrielle Bou-Ismail RP 42004 Tipaza, Algérie

*Corresponding author: lebik.hafida@udes.dz; Tel.: +21324 30 07 18; Fax: +21324 30 07 17

ARTICLE INFO

ABSTRACT/RESUME

Abstract:The electrochemical behaviour of methylene blue (MB) was studied in a single compartment cell with Ti/Pt anode. Experiments were carried out to investigate the influence of: current intensity (0.05 - 0.4 A), MB concentration (5 - 20 mg/L), initial pH (4 - 11) as well as electrolyte concentration (0.025 - 0.1 M NaCl) on the kinetic of MB degradation over a Ti/Pt electrochemical process. The results show that the removal rate is favoured in acidic medium and at increased both electrolyte concentrations and current densities. A complete colour removal of 10 mg/L MB solution is achieved within 35 min at optimal current intensity of 0.4 A with 0.1 M NaCl electrolyte solution at inherent pH. The decomposition follows a pseudo-first order kinetic where the removal rate is independent of MB initial concentration.

I. Introduction

Contamination of water by organics generated by industrial activity is a problem of a great concern. Among these organics, synthetic dyes commonly used in a wide range of industries such as food, textile, pulp and paper, cosmetics and pharmaceutical, represent a major class of pollutant. More than 100,000 commercially available dyes are produced annually, entering in the composition of over $7 \cdot 10^5$ MT (million tonnes) of dye-stuff, mainly used in textile industry, where about 12% of synthetic dyes are lost during manufacturing processes [1–3].

The large use of these chemicals combined with their recalcitrant nature, resulted in several negative impacts not only on environmental aspects but also on human health. Indeed, the toxic effect of dyes has been proved in several studies where evidence of their genotoxic/carcinogenic potential is demonstrated [4–6]. Moreover, the toxicity of dyes towards several aquatic organisms including fish, algae, and shellfish is reported [7].

Furthermore, owing to their complex chemical structure, dyes are poorly biodegradable, therefore, they cannot be completely removed by means of conventional biological wastewater treatment systems [8–10]. Also, due to their high solubility in water, dyes remain after passage through chemical/physical treatment processes and persist in environment for a longer time [4].

For these reasons, several strategies have been developed for the removal of such recalcitrant and toxic pollutants, including Electrochemical Advanced Oxidation Processes (EAOPs), which present the advantage of being a degradative not separative methods [11]. EAOPs offer a great alternatives for dye removal and most of the studies dealing with dyes removal from contaminated water reported a complete degradation [12–17]. Among EAOPs, the anodic oxidation (AO) is the most studied electrochemical process due to its versatility and ease automation [18].

AO involves the generation of hydroxyl radicals ($^\bullet OH$) formed as intermediates from water electrolytic discharge, according to Eq.(1), at high O_2 overvoltage anode [19]. Thus, the efficiency of the process is highly affected by the nature of the electrode material as well as the operating conditions [17].

$$H_2O + M \rightarrow M[^\cdot OH] + H^+ + e^- \qquad \textbf{(1)}$$
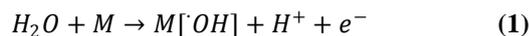
In this study, Ti/Pt anode was used in the AO of a synthetic solution of methylene blue dye (MB). MB, also called Basic Blue 9, is an aniline-based dye that was synthesized in 1876 originally, for the textile industry [20]. It was used later in microscopy stains, in clinical therapy as an antiseptic [21]. MB was also tested as an antimalarial drug at the end of the nineteenth century [22].

The AO of MB has been already investigated by Panizza [23] where a total mineralization was achieved over a BDD (Boron-Doped Diamond) anode. On the other hand, Indu [24] obtained an overall COD removal of 62% in synthetic MB solution with lead acid battery anode.

With this study, we aimed to gain a better understanding of the AO of MB on a Ti/Pt anode. The evaluation of the influence of initial pH, MB concentration, electrolyte concentration as well as current intensities on the degradation kinetics of MB is discussed.

II. Materials and methods

Synthetic polluted water was obtained by dissolving an appropriate amount of MB ($C_{16}H_{18}N_3SCl$) stock solution in ultrapure water (produced by Milli-Q system). All other reagents used in the study were analytical grade purchased from Sigma Aldrich. pH was adjusted with 0.1 M NaOH or 0.1 M H_2SO_4 solutions. NaCl was used as the supporting electrolyte.

The electrochemical oxidation experiments were conducted in an open undivided cell of a 200 mL capacity, where the solution was stirred at 250 rpm using a magnetic stirrer to ensure a uniform distribution of current-potential in the system. Experiments were conducted at a constant current provided by a digital power supply. Titanium-supported Platinum (Ti/Pt) was used as the anode while a stainless steel (SS) was used as the cathode. Both electrodes were plates parallel of 12.5 cm². A 7 cm inter-electrodes distance was kept during electrolysis.

Samples of 1.5 mL, taken at regular intervals, are passed through 0.45 µm microfilter prior to analysis.

The MB concentration in the solution was determined by UV-Vis spectrophotometer (Shimadzu) at 664 nm using the calibration curve. The latter was established for MB concentrations up to 20 mg/L. A good linearity was observed ($R^2 \geq$ 99.98%).pH analysis were performed using a TOLEDO multi parameter.

The MB removal rate R (%) was calculated as follows:

$$R\ (\%) = \frac{(C_0 - C)}{C_0} * 100 \qquad \textbf{(2)}$$

Where C_0 is the initial MB concentration and C is the MB concentration in the solution after t (a specific electrolysis time).

III. Results and discussion

III.1. Effectof MB initial concentration

The effect of the initial concentration of MB on the oxidation process was studied for MB concentrations in the range of 5 to 20 mg/L using [NaCl] = 0.1 M as a supporting electrolyte, under a current intensity of 0.4 A at an inherent pH = 4 ± 0.05. According to the results, represented in Figure 1, the removal rate increases slightly as the initial concentration of MB decreases. However, up to 35 min the dye colour is completely removed from the solution independently of the initial MB concentration and with almost the same trend. Similar findings were observed in the case of MB on lead anodic oxidation [24] as well as ethyl-paraben oxidation on BDD anode [25]. This highlights the fact that anodic oxidation can be used as for dye removal regardless of its initial concentration.
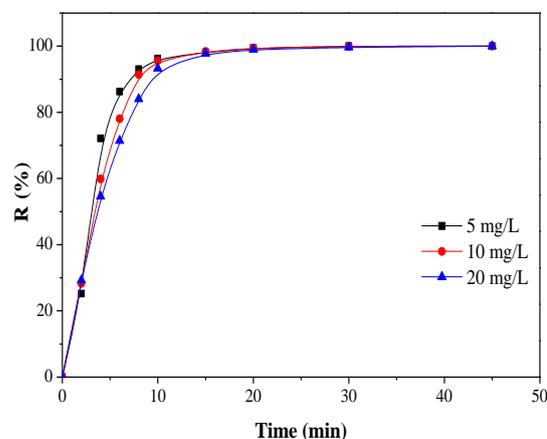

Figure 1.*Effect Effect of the initial MB concentration on the removal rate, [NaCl] = 0.1M, I = 0.4 A, inherent pH*

On the other hand, the electrochemical oxidation of MB can be described by a first order kinetic model:

$$r = \frac{dC}{dt} = k_{app}\ C \leftrightarrow ln\frac{C_0}{C} + k_{app}\ t \qquad \textbf{(3)}$$

Where r is the rate of degradation, k_{app} is the pseudo-first order rate constant.

Plotting $ln(C_0/C)$ as function of electrolysis time (t) results in a perfect fitting with a linear regression

(R² > 0.97), as shown in figure 2, which confirms a first order kinetic.

Besides, calculating the k_{app} for the three concentrations (represented by the slope as explained by Eq. (3)), confirms that the removal kinetic is independent of the initial concentration, since k_{app} is almost constant ($k_{app} = 0.23 \pm 0.05$ min^{-1}) in the range of the studied MB concentration (5 – 20 mg/L).

This behaviour maybe attribute to the occurrence of parasitic reactions like oxygen evolution, which compete with the oxidation of pollutant in the solution and became more concomitant when low concentrations of organic depolarizer are attained [26].
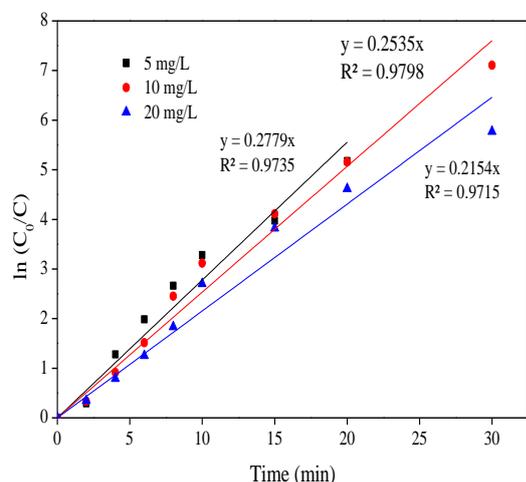

Figure 2. *Variation of $ln(C_0/C)$ as function of time for different MB concentrations*

III.2. Effect of current intensity

The applied current intensity is an important parameter in the anodic oxidation process, since it controls the production of hydroxyl radicals ($^{\bullet}$OH) [27].

Tests were carried out at a current intensity varying in the range of (0.05 - 0.4 A) using a solution of 10 mg/L MB at inherent pH and 0.1 M NaCl as a supporting electrolyte. As it can be observed in figure 3, increasing the current intensity from 0.05, 0.2 to 0.4 A resulted in increasing the removal rate from 59.88, 98.64 to 100%, respectively.

Likewise, Tavares [26] reported similar results in the electrochemical oxidation of methyl red, and the authors suggested that the oxidation process occurs by both direct (adsorption to electrode surface) and

mediated oxidation (by means of electrogenerated hydroxyl radicals).

On the other hand, increasing current intensity means generating more hydroxyl radicals in the solution which contribute to a faster MB colour removal.
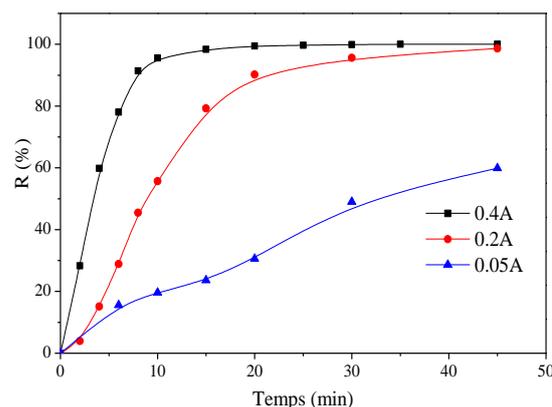

Figure 3. *The influence of current intensity on the removal rate, [MB] = 10 mg/L, [NaCl] = 0.1M, inherent pH.*

The kinetic apparent rate constant k_{app} calculated by the Eq.(3), confirmed the above findings. Indeed, the MB colour removal rate is faster with higher intensities. For instance, k_{app} increased from 0.02 to 0.25 min^{-1}, when current intensity increased from 0.05 to 0.4 A, respectively.
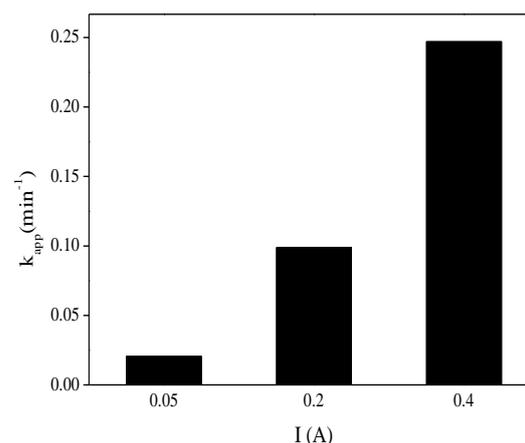

Figure 4. *Effect of current intensity on k_{app}*

III.3. Effect of electrolyte concentration

Sodium chloride (NaCl) with different initial concentrations up to 0.1 M was tested as a supporting electrolyte for the degradation of 10 mg/L MB under I = 0.4 A at inherent pH.

Figure 5 shows that the colour removal of MB increases from 84 to 99 and 100 % when increasing electrolyte concentration from 0.025 to 0.05 and 0.1 M, respectively.

Moreover, this phenomenon is much more obvious regarding to the apparent rate constant which six fold increases when increasing the electrolyte concentration from 0.025 to 0.1 M. This is probably due to the nature of electrolyte which generate strong oxidants as chlorate, that may contribute to indirect dye removal [26 , 28].
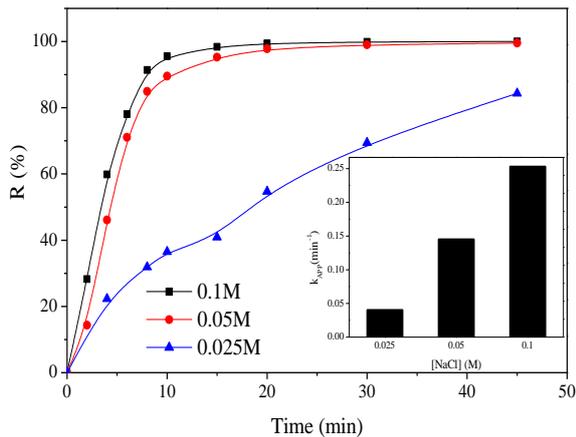

Figure 5.*The influence of supporting electrolyte on the removal rate, [MB] = 10 mg/L, I = 0.4 A, inherent pH. The inset graph shows the corresponding apparent kinetic constants as a function of supporting electrolyte.*

III.4. Effectof initial pH

Herein, the influence of initial pH solution on dye colour removal was investigated for three pH solutions: 4, 7 and 11; in the presence of 10 mg/L MB, and 0.1 M NaCl as a supporting electrolyte under 0.4 A current density. Regardless of the initial pH, almost a complete MB colour removal was observed after 45 min of electro-oxidation.
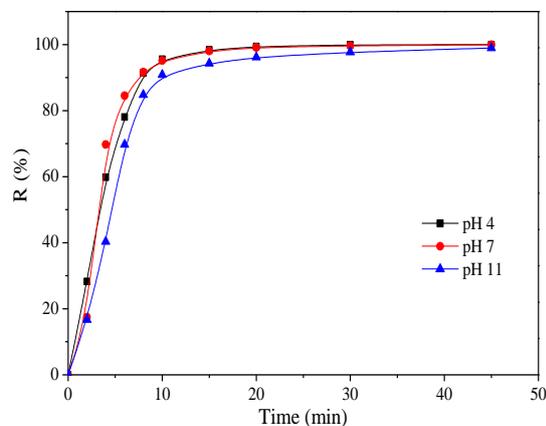

Figure 6.*The influence of initial pH on the removal rate, [MB] = 10 mg/L, I = 0.4 A, [NaCl] = 0.1 M.*

However, the apparent rate constant was, 0.25, 0.19 and 0.13 min^{-1} at pH values of 4, 7 and 11, respectively. It can be conclude that the oxidation process is favourable in an acidic pH more than in an alkaline medium and neutral pH, This could be attribute to the contribution of active chlorine species, present in the solution from the oxidation of the electrolyte NaCl, since the mediated oxidation of dyes by these species is expected to be faster in acidic conditions compared to alkaline medium [26].

Moreover, in acidic pH there is also an evidence of the participation of other reactive species in the oxidation process [29].
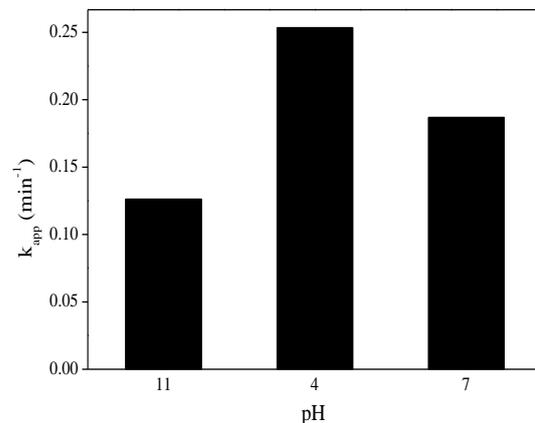

Figure 7.*Effect of initial pH on the apparent kinetic constants*

IV. Conclusion

In this paper, we have demonstrated that a Ti/Pt anode can be successfully used for the oxidation of MB solution which resulted in a complete colour removal in optimal conditions (for 10 mg/L MB: I = 0.4 A, [NaCl] = 0.1 M at inherent pH). In addition, results showed that the effectiveness of AO process depends directly on the operating parameters. Indeed, increasing the supporting electrolyte concentration enhanced the MB colour removal probably due to the mediation of electrogenerated active chlorine. The latter, is also responsible of the good performance of the system at acidic pH. On the other hand, increasing the current intensity promote the oxidation process, whereas the initial MB concentration didn't have any influence on the removal rate. The kinetic study shows that MB removal obey to a first order kinetic where the apparent rate constant is independent of the initial MB concentration.

V. References

1. Bhunia, B.; Mondal, A.; Bandyopadhyay, T. K.; Sasmal, S.; Mahata, N. and U. S. P. Uday. Dyes Contamination in the Environment: Ecotoxicological Effects, Health Hazards, and Biodegradation and Bioremediation Mechanisms for Environmental Cleanup. *Environmental*

Pollutants and their Bioremediation A roaches (2017) 127–176.

2. Tan, I. A. W.; Hameed, B. H. and Ahmad, A. L. Equilibrium and kinetic studies on basic dye adsorption by oil palm fibre activated carbon. *Chemical Engineering Journal*. 127 (2007) 111–119.

3. Hassaan, M. A.; El Nemr, A. Health and Environmental Impacts of Dyes. *American Journal of Environmental Science and Engineering*. 1(2017) 64–67.

4. Rawat, D.; Mishra, V.; Sharma, R. S. Detoxification of azo dyes in the context of environmental processes. Chemosphere. 155 (2016) 591–605.

5. Nohynek, G. J.; Fautz, R.; Benech-Kieffer, F.; Toutain, H. Toxicityand human healthriskofhairdyes. *Food and Chemical Toxicology*. 42 (2004) 517–543.

6. Bhatnagar, V. K.; Talaska, G. Carcinogen exposure and effect biomarkers. *Toxicology Letters*. 108 (1999) 107–116.

7. Bafana, A.; Devi, S. S. and Chakrabarti, T. Azo dyes: past, present and the future. *Environmental Reviews*. 19 (2011) 350–371.

8. Popa, N. and Visa, M. The synthesis, activation and characterization of charcoal powder for the removal of methylene blue and cadmium from wastewater. *Advanced Powder Technology*. 28 (2017) 1866–1876.

9. Mouni, L. *et al.* Removal of Methylene Blue from aqueous solutions by adsorption on Kaolin: Kinetic and equilibrium studies. *Applied Clay Science*. 153 (2018) 38–45

10. Mahmoud, M. S.; Farah, J. Y. and Farrag, T. E. Enhanced removal of Methylene Blue by electrocoagulation using iron electrodes. *Egyptian Journal of Petroleum*. 22 (2013) 211–216.

11. Nidheesh, P. V.; Zhou, M.; Oturan, M. A. An overview on the removal of synthetic dyes from water by electrochemical advanced oxidation processes. *Chemosphere*. 197 (2018) 210–227.

12. Faouzi, A. M.; Nasr, B.; Abdellatif, G. Electrochemical degradation of anthraquinone dye Alizarin Red S by anodic oxidation on boron-doped diamond. *Dyes and Pigments*.73 (2007) 86–89.

13. Zhao, G. *et al.* Electrochemical incineration of high concentration azo dye wastewater on the in situ activated platinum electrode with sustained microwave radiation. *Chemosphere*. 77(2009) 188–193

14. Martínez-Huitle, C. A. *et al.*Applicability of diamond electrode/anode to the electrochemical treatment of a real textile effluent. *Journal of Electroanalytical Chemistry*. 674 (2012) 103–107.

15. Nidheesh, P. V; Gandhimathi, R. Removal of Rhodamine B from aqueous solution using graphite–graphite electro-Fenton system. *Desalination and Water Treatment*. 52 (2014) 1872–1877.

16. Salazar, R.; Ureta-Zañartu, M. S. Degradation of acid violet 7 and reactive black 5 in water by electro-Fenton and photo electro-Fenton. *Journal of the Chilean Chemical Society*. 57(2012). 999-1003.

17. Martínez-Huitle, C. A.; Panizza, M. Electrochemical oxidation of organic pollutants for wastewater treatment. *Current Opinion in Electrochemistry*. 11 (2018) 62-71

18. Panizza, M. and Cerisola, G. Direct and Mediated Anodic Oxidation of Organic Pollutants. *Chemical Reviews*. 109 (2009) 6541–6569.

19. Comninellis, C.;Kapalka, A.; Malato, S.; Parsons, S. A.; Poulios, I. andMantzavinos, D. Advanced oxidation processes for water treatment: advances and trends for R&D. *Journal of Chemical Technology and Biotechnology*. 83 (2008) 769–776.

20. Berneth, H. Cationic Dyes. *Ullmann'sEncyclopedia of Industrial Chemistry* (2008).

21. Oz, M. ;Lorke, D. E. ; Hasan, M. ; Petroianu, G. A. Cellular and molecular actions of methylene blue in the nervous system. *Medicinal research reviews*. 31 (2011) 93–117.

22. Shanks, G. D. Chapter Six - Control and Elimination of Plasmodium vivax, in Hay, S. I.; Price, R.; Baird, J. K. B. T.-A. (eds). *Advances in Parasitology*. 80(2012) 301–341.

23. Panizza, M.; Barbucci, A.; Ricotti, R.; Cerisola, G.Electrochemical degradation of methylene blue. *Separation and Purification Technology*. 54 (2007) 382–387.

24. Indu, M. S.; Gupta, A. K. and Sahoo, C. Electrochemical Oxidation of Methylene Blue Using Lead Acid Battery Anode. *APCBEE Procedia*. 9 (2014) 70-74.

25. Frontistis, Z.; Antonopoulou, M.; Yazirdagi, M.; Kilinc, Z.; Konstantinou, I.; Katsaounis, A.; Mantzavinos, D. Boron-doped diamond electrooxidation of ethyl paraben: The effect of electrolyte on by-products distribution and mechanisms. *Journal of Environmental Management*. 195 (2017)148–156.

26. Tavares, M. G.; da Silva, L. V. A.; SalesSolano, A. M.; Tonholo, J.; Martínez-Huitle, C. A.; andZanta, C. L. P. S. Electrochemicaloxidationof Methyl RedusingTi/Ru$_{0.3}$Ti$_{0.7}$O$_2$andTi/Pt anodes. *Chemical Engineering Journal*. 204–206 (2012) 141–150.

27. Rabaaoui, N.; Saad, M. E. K. ; Moussaoui, Y. ; Allagui, M. S. ; Bedoui, A. ; andElaloui, E. Anodic oxidation of o-nitrophenol on BDD electrode: Variable effects and mechanisms of degradation. *Journal of Hazardous Materials*, 250–251(2013) 447–453.

28. Moreira, F. C.; Boaventura, R. A. R.; Brillas, E.; andVilar, V. J. P. Electrochemical advanced oxidation processes: A review on their application to synthetic and real wastewaters. *Applied Catalysis B: Environmental*. 202 (2017) 217-261

29. Akrout, H.; Jellali, S. ;and Bousselmi, L. Enhancement of methylene blue removal by anodic oxidation using BDD electrode combined with adsorption onto sawdust. *ComptesRendusChimie*. 18(2015)110–120.