Anodic oxidation of methylene blue at Ti/Pt electrode

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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.

Key Words: Methylene blue; Electrochemical oxidation; Ti/Pt electrode; Kinetic.

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 10^7 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 ('OH) formed as intermediates from water electrolytic discharge, according to Eq.(1), at high O₂ 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].
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 (C₁₆H₁₈N₃SCl) 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 H₂SO₄ 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 (R² ≥ 99.98%). pH analysis were performed using a TOLEDO multi parameter.

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

\[ R(\%) = \frac{(C_0 - C)}{C_0} \times 100 \]  

Where C₀ 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. Effect of 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 ethylparaben oxidation on BDD anode [25]. This highlights the fact that anodic oxidation can be used as dye removal regardless of its initial concentration.

Figure 1. 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:

\[ r = \frac{dC}{dt} = k_{app} C \leftrightarrow \ln \frac{C_0}{C} + k_{app} t \]

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 ± 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 become more concomitant when low concentrations of organic depolarizer are attained [26].

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.

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

The applied current intensity is an important parameter in the anodic oxidation process, since it controls the production of hydroxyl radicals (’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).

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].

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 evidence of the participation of other reactive species in the oxidation process [29].

III.4. Effect of 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.

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.

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