METHYLENE BLUE MINERALISATION BY ELECTROCHEMICAL PROCESS MEDIATED BY COBALT CATALYST ON PLATINUM ELECTRODES

Abstract

In this study, the electrochemical decolorization of the Methylene Blue dye on Platinum electrodes was assessed. Direct oxidation results demonstrate a partial pollutant degradation reaching a maximum of 64 %. However, the addition of a small amount of a redox mediator Co2+/3+ is efficiently able to electrocatalyse the Methylene blue oxidation by shortening significantly the treatment time and enhancing clearly the dye decolorization rate. Nearly complete decolorization was achieved (92 % in 1h 45min). The most striking results achieved within the cyclic voltammetry study demonstrate undoubtedly the pollutant mineralisation. Electrochemical experiments were performed using the spectrophotometric method, which is very convenient, easy and allows monitoring the spectral changes as well as the determination of the dye concentration during the process. The kinetics data show a first-order indirect oxidation kinetics. A mechanism was proposed to explain the different phenomenon during the electrochemical process.

Keywords: *Decolorization, Methylene Blue, catalyst, Platinum electrode, mineralisation.*

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INTRODUCTION :

Methylene Blue (MB) is widely used in biology and chemistry for diverse applications such as; photosensitizer to generate Singlet oxygen, stain for fixed and living tissues, antidote to cyanide and nitrate poisoning (Parry, 1993). In food industry, it is used as optical oxygen sensors. Moreover, it's an organic dye, used to dye cotton, acrylic, silk and wood *(El hajj hassan and El jamal, 2012)*. Generally, dyes are used in various industries such as textile, paint, leather, paper and food *(Hameed and Lee, 2009)*. In the case of textile industry, up to 50 % of the synthetic dyes with different structural varieties such as; azo, diazo, quinine imine, thiazole and others *(Banat and Nigam, 1996)* are lost after the dyeing process and disposal out in the effluents *(Zollinger, 1991)*. Therefore, their elimination from wastewaters is an obligation to prevent the ecosystem destruction. Conventional wastewater treatment based on biological process is not suitably enough to remove recalcitrant dyes from effluents *(Shaul et al., 1991)*. Physical and chemical methods used for eliminating dyes (i.e. adsorption, incineration, electrocoagulation, photocatalysis, ozonation and others) are reasonably effective but relatively cost *(Zhu et al., 2000; Szpyrkowicz et al., 2001)*. That's why; it's necessary to find an effective wastewater method capable of degrading toxic organic compounds from industrial effluents. As alternative, the electrochemical oxidation process is a clean advanced oxidation technology because, the main reagent; the electron, is a clean one *(Jüttner et al., 2000)*. It was applied successfully and proved to be convenient and fruitful to destruct bio-refractory organic compounds due to its high effectiveness and environment well-suited. In the electrochemical oxidation under room temperature and atmospheric pressure, generally, researchers focus their particular interest on the anode oxidation process than the cathode reduction. The Electrochemical methods designed for wastewater treatment consist of direct and indirect oxidation. Mediated Electrochemical Oxidation (MEO) with a redox mediator is considered as one alternative to efficiently remove color from solutions of structurally different dyes. It is as well admitted through this indirect oxidation that a strong oxidative intermediates were generated in situ and consequently convert pollutants into less hazardous products *(Sanromán et al., 2004)*. In this context, we accomplish the MB electrochemical degradation in the presence of $Co^{2+/3+}$ selected as a redox mediator using Pt electrodes. Moreover, it is important to note the conductor behavior of MB, that's why, we achieved this study without any supporting electrolyte to test the feasibility of the MB electrochemical degradation. It should be noted as well that generally dyes are susceptible to undergo a photochemical degradation as they absorb in the visible part of the electromagnetic spectrum, that's why we have worked in the obscurity to avoid any probability of a possible photodegradation pathway. The aim of this work was to test the feasibility of the electrodegradation of MB in our particular conditions. The decolorization rate has been evaluated with and without the redox mediator and the mechanism of the process was suggested in both direct and indirect oxidation.

2. EXPERIMENTAL SECTION

2.1 Materials

Methylene blue (MB) was purchased from Labosi (for analysis) and used without further purification. The cobalt chloride ($CoCl_2$, 6 H_2O) used as redox mediator was purchased from Biochem. Solutions were prepared using distilled water.

2.2 Methods summary :

The electrochemical process was carried out using the spectrophotometric method to follow the dye decolorization. The study was conducted on aqueous solution of MB (3.125 μM), initial pH of 7.8, under atmospheric pressure, at room temperature and in the dark. Experiments were carried out in an electrochemical cell containing the amount of 25 ml of MB for each experiment and using electrodes placed in the cell centre with a distance of 2 cm separating them. The anode and cathode are Pt wire from Voltalab. The ratio electrode surface/volume of dye solution was 0.04 m^2. m^{-3} at laboratory scale. A constant voltage drop of 2 Volt was applied to the electrodes using Potentiostat (Alimentatore per electtroforsi el VI 16, Italy). The reaction vessel was placed on a magnetic stirrer for continuous stirring to ensure the solution homogeneity during the electrochemical process. The conductivity of the initial MB solution was equal to 14.5 μS/cm measured by a conduct-meter model (Inolab Cond 7110). According to this conductor behavior, we choose to perform our experiments without any electrolytes to test the feasibility of the MB degradation in this condition. During the electrochemical process, after each treatment time, we transfer the solution to the UV-visible spectrophotometer (Jenway 6505) to record the absorption spectra of the dye solution and to measure the absorbance at the maximum of MB absorbance (660 nm) using a matched pair of quartz flows cells (1 cm path length). The absorbance data were converted to the concentration using Beer-Lambert (Eq.1). $A = \varepsilon . C. L$ (1), where A and ε are respectively the absorbance and molar absorptivity coefficient values at 660 nm, C is the dye concentration at time t, l is the light path length. The value of ε at 660 nm is deduced from the MB calibration curve, it is equal to 38701 $M^{-1}.Cm^{-1}$. The assays were done twice; the experimental error was below 3 %. The decolorization rate of the dye (Dec %) was expressed as a percentage and calculated by the following (Eq.2). % dye decolorization = $[(C_0 - C_t) / C_0] \times 100$ (2), where C_0 and C_t are the dye concentrations at time 0 and time t respectively. The concentration of the dye was calculated from the absorbance value at 660 nm using a calibration curve. Voltammetric experiments were carried out with a potentiostat model Gamry (USA). The working electrode was a platinum electrode and a reference electrode was a saturated calomel electrode (SCE). All potentials were reported vs. the SCE. A platinum electrode was used as the counter electrode. The scan rate was 100 mV/ s. The experiments were achieved using a cell of 20 ml, we purged the dissolved oxygen by nitrogen bubbling during 25 minutes and we used as 0.1 M of KCl as supporting electrolyte.

3. RESULTS AND DISCUSSION

3.1 Direct oxidation of methylene blue MB

3.1.1 Decolorization rate

To assess the feasibility of the electrochemical process conducted on a solution of methylene blue (3.125 μM) at initial pH of 7.8, we experimentally followed the decolorization by measuring the dye absorbance at its maximum absorption (660 nm) as a function of the different electrochemical treatment time. The decolorization expressed in terms of percentage was calculated according to (Eq.1). The obtained results are shown in (Fig.1). It should be noted that no significant change was observed on the initial pH value of MB during the electrochemical process.
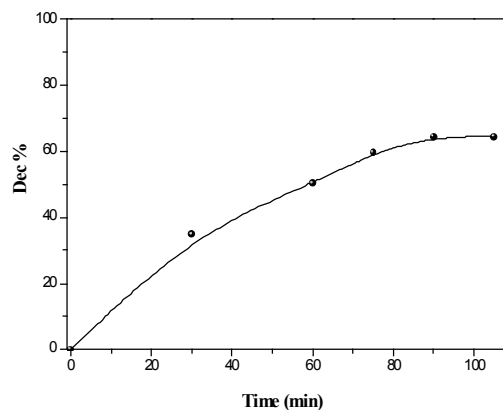

Fig.1. MB decolorization percentage (Dec %) versus the treatment time

Figure.1 indicates a progressive increase of the dye decolorization up to 90 minutes where this last reached a maximum of 64 %. Experiment reveals the gradual disappearance of the blue color which suggests the oxidation of the dye; furthermore, the reaction by-products are colorless. For a treatment time of 105 minutes, the decolorization percentage doesn't change; this leads us thinking about an inhibitory effect against the MB elimination.

3.1.2 Electro-degradation kinetics

To better understand the pollutant behavior, we converted the absorbance to the corresponding concentration and then plotted the pollutant disappearance kinetics (Fig.2).
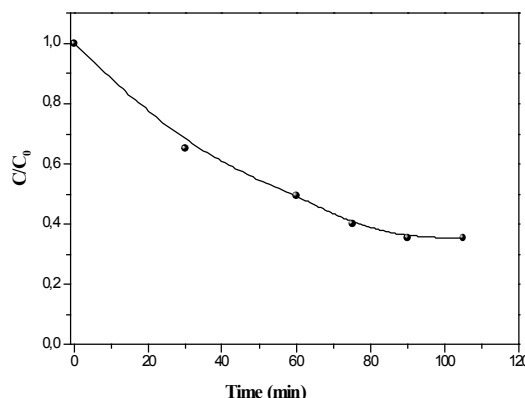

Fig.2. Electrochemical decolorization of Methylene blue (direct oxidation)

According to the plotted curve, it appears two different phases, the first one correspond to a treatment time between 0 and 90 minutes, the elimination rate is rapid at the beginning of the reaction (0,043 μ.mol.l^{-1}.min^{-1}) and the

half-life time is 60 minutes. During this time period, we can readily admit that the reaction proceeds most probably by a transfer of electrons. In other words, the pollutant undergoes anodic oxidation from one hand, since it is capable to give electrons, especially those of the lone doublets of sulfur and nitrogen atoms. On the other hand, we admit a cathodic reduction of water; this last lead to the formation of OH$^-$ anions with the release of H$_2$ according to the (reaction.1)

$$2\ H_2O + 2\ e^- \rightarrow 2\ OH^- + H_2 \quad (1)$$
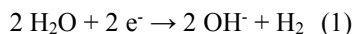
We can summarize the proposed mechanism of electro-degradation according to (scheme.1) *(where P and P$^+$ are respectively the pollutant and the oxidized pollutant).*
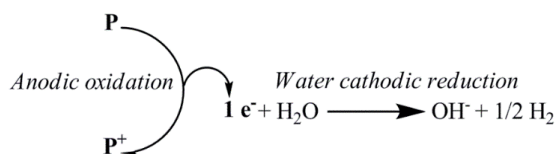
Scheme.1. MB direct oxidation mechanism

The second part of the curve is included between 90 and 105 minutes, we stopped at this end, because the electro-degradation rate no longer changes. This strongly suggests that the intermediates formed during the reaction can compete with the pollutant itself and thus inhibit its elimination. We can generally accept that reactions consuming electrons can limit the MB direct oxidation in solution. All this goes to prove that the direct electrochemical oxidation is only capable to partially oxidize the MB solution, that's why it's interesting to optimize this process to reach the dye total degradation.

3.2 Indirect oxidation :

It's well established that the redox mediators such as (Fe$^{2+/3+}$, Ce$^{3+/4+}$, Co$^{2+/3+}$) are able to generate electrochemically oxidizing species capable of inducing degradation of dyes (Bringman et al., 1995; Farmer et al., 1992). Therefore, it is interesting to consider the redox catalyst effect on MB oxidation. We started our experiment with Ce$^{3+/4+}$ catalyst, no significant change was observed in terms of dye disappearance, this is probably due to its moderate oxidation potential (1.72 V). The second attempt was performed using the couple Co$^{2+/3+}$ with a slightly higher oxidation potential (1.92 V). We tested its effect on MB electro-degradation.

3.2.1 Evolution of MB absorption spectra :

In terms of experimental conditions, the study was performed by adding a solution of CoCl$_2$ (10^{-7} M) to the initial MB solution (3.125 μM), (initial pH 7.8) using the same platinum electrodes. The monitoring of the absorption spectra evolution according to the treatment time between 0 and 105 minutes was accomplished using UV-visible spectrophotometric method. According to (Fig.3), we presented those recorded after 30 and 60 minutes. It clearly appears a decrease in the absorbance at MB maximum absorption (660 nm) in the visible region between (550-750 nm).
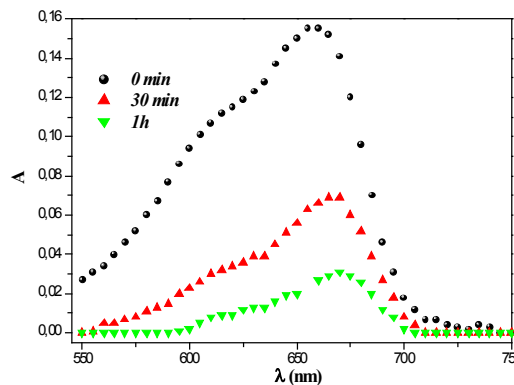
**Fig.3.** Evolution of the MB absorption spectra during the indirect oxidation

Figure 4 shows properly according to the treatment time, the evolution of the absorbance (A) at 660 nm, which reflects the effective disappearance of the dye and thus our process was significantly optimized by just adding a small quantity of a catalyst.
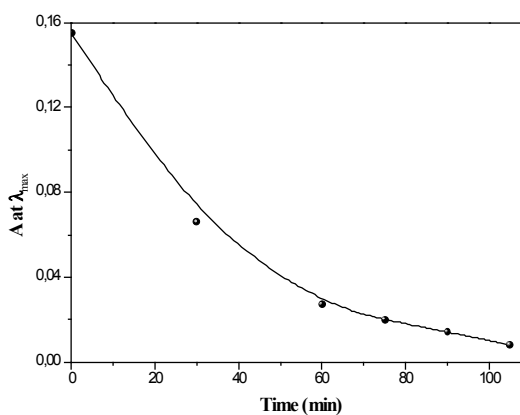
Fig.4. Absorbance evolution (at 660 nm) according to the treatment time

3.2.2 Decolorization rate :

Figure 5 shows the MB decolorization percentage according to the different treatment time during the indirect oxidation.
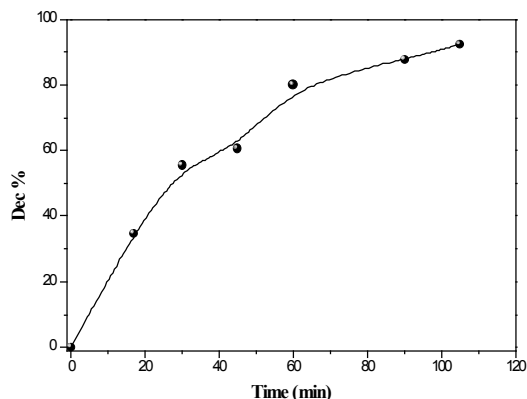
Fig.5. Methylene blue decolorization rate (Dec %) in the presence of Cobalt catalyst

The most important result shows a nearly complete decolorization of 92 % after 105 minutes against 64 % within the direct oxidation. *This reflects the substantial role played by the catalyst in the electrochemical process to increase the dye decolorization percentage.*

3.2.3 Electro-degradation kinetics :

To illustrate the catalyst effect within the indirect oxidation, we have calculated the concentrations from their corresponding absorbances and plotted the kinetics of MB disappearance (C/C_0 versus the treatment time t). (Fig.6)
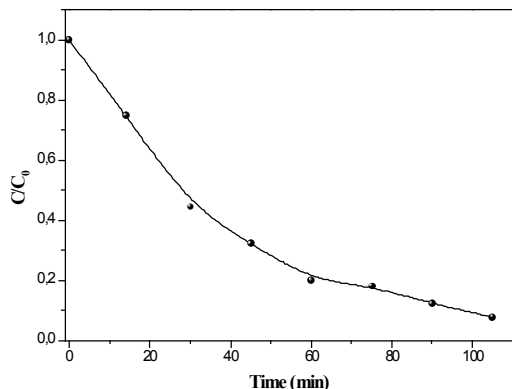

Fig.6. Methylene blue electrochemical decolorization (indirect oxidation)

Figure.6 shows explicitly the dye fast indirect oxidation, the initial rate of disappearance equal to (0.07 $\mu.mol.l^{-1}.min^{-1}$) is 1.62 times faster than the one of the direct oxidation. The half life time is only 28 minutes against 60 minutes in direct oxidation. In other words, the process with the cobalt redox mediator is able to electrocatalyse efficiently the oxidation of MB shortening significantly the treatment time. The superposition of the curves (with and without catalyst) clearly shows these finding (Fig.7).
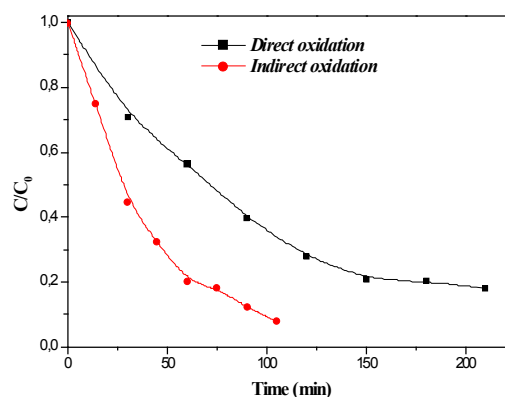

Fig.7. Comparison between the two MB disappearance kinetics (with and without catalyst).

These results demonstrate that the addition of a small amount of cobalt (10^{-7} M) is largely enough to effectively catalyze the MB electrochemical reaction. Furthermore, in terms of reaction kinetics, the indirect oxidation is a first order kinetics. The reaction rate constant is deduced from the curve representing (ln C_0/C versus time) (Fig.8). The plot is linear ($R^2 = 0.995$) and the rate constant value k is 0.024 min^{-1}.
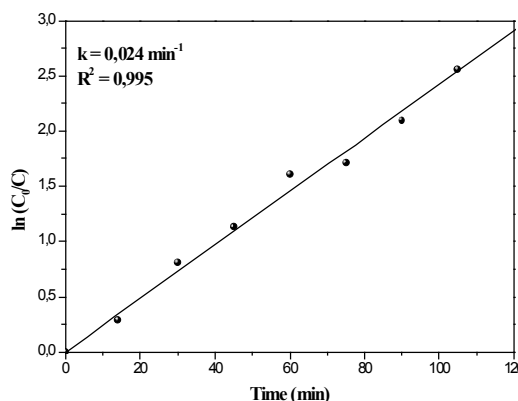
Fig.8. Determination of the rate constant of the MB indirect oxidation.

In this process, metal ions are oxidized anodically from a stable oxidation state to reactive species, which in turn, are capable of oxidizing organic substances to CO_2 (Bringmann et al., 1995). The electro-degradation mechanism is proposed by scheme.2.
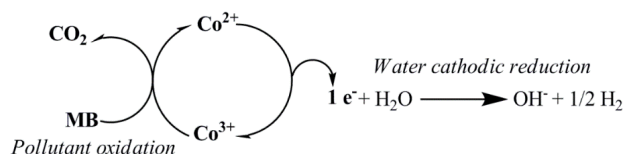
Scheme.2. MB indirect oxidation mechanism

3.2 Cyclic voltammetry :

The cyclic voltammograms (CV) of methylene blue at the potential range -0.8 V to 0.2 V are shown in (Fig.9). The curve (a) on the graph present free MB which yielded one reversible redox system, with the anodic peak potential (E_{ap}) at - 0,148 V, the cathodic peak potential (E_{cp}) at - 0,328 and the peak separation ΔE_p = 1.8 V. In the indirect oxidation, we reached 92 % of MB degradation after 1h 45 min. To guarantee a total MB degradation, we electrochemically treated the solution longer (2h 15 min). The (CV) of this solution was presented on the curve (b). Several conclusions can be deduced; first of all, it appears clearly the complete disappearance of the reversible system found with Free MB; in other words, a complete degradation of the product was observed. Added to this, after a precise search for the apparition of any anodic or cathodic peak, no one was found in the potential range [-2 V, +2 V]. These results provide evidence that all the products yielded from the MB transformation were degraded in their turn. With harmony to these results, we can confirm the mineralisation of the MB dye according to the following reaction: MB ($+ e^-$) $\rightarrow CO_2 + H_2O$. We searched the reduction peak of CO_2 situated at -2.15 V/ CSE according to the following reaction: $CO_2 + e^- \rightarrow CO_2^{\cdot -}$. This peak disappears in our conditions most likely because of the nitrogen bubbling in the solution during all the experiment.
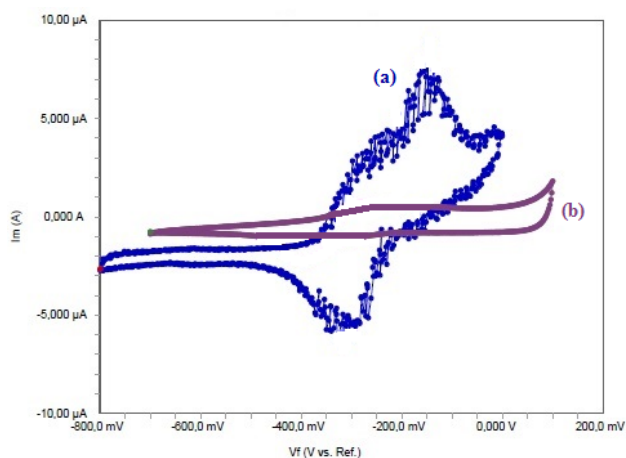
Fig.9. Methylene blue Cyclic Voltammograms, *(a): free MB, (b): MB with cobalt catalyst*

CONCLUSION

The spectrophotometric method was applied successfully on the decolorization of Methylene Blue from aqueous solution by electrochemical process. The results confirm the ability of the direct oxidation to partially oxidize the Methylene blue pollutant. However, a mineralization of the pollutant was obtained by adding a small amount of cobalt redox mediator which increases the decolorization rate and shortens the treatment time. It is noteworthy that the absence of a supporting electrolyte in this study didn't affect the efficiency of the electrochemical process. Added to this, cobalt is not consumed during the process, that's why it can be recovered from the effluent by precipitation or ionic exchange avoiding thus its discharge in the environment.

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