

Application of electro-Fenton process for the treatment of Methylene Blue

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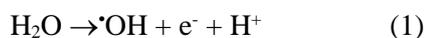
The electrochemical removal of an aqueous solution containing 0.25 mM of methylene blue (MB), one of the most important thiazine dye, has been investigated by electro-Fenton process using a graphite-felt cathode to electrogenerate in situ hydrogen peroxide and regenerate ferrous ions as catalyst. The effect of operating conditions such as applied current, catalyst concentration, and initial dye content on MB degradation has been studied. MB removal and mineralization were monitored during the electrolysis by UV-Vis analysis and TOC measurements. The experimental results showed that MB was completely removed by the reaction with •OH radicals generated from electrochemically assisted Fenton's reaction, and in any conditions the decay kinetic always follows a pseudo-first-order reaction. The faster MB oxidation rate was obtained applying a current of 300 mA, with 0.3 mM Fe²⁺ at T=35 °C. In these conditions, 0.25 mM MB was completely removed in 45 min and the initial TOC was removed in 90 min of electrolysis, meaning the almost complete mineralization of the organic content of the treated solution.

Keywords: Methylene Blue, electro-Fenton, graphite felt, dye oxidation.

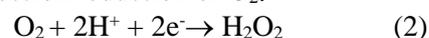
INTRODUCTION

Synthetic dyes usually contain aromatic rings and consequently they are toxic and bio-recalcitrant and cause serious environmental problems. Therefore, there is a widespread consideration on the development of efficient and cost effective methods for the removal of such hazardous pollutants from industrial effluents. Conventional methods for the removal of synthetic dyes, such as coagulation and filtration generate large volume of sludge to be disposed and/or need the regularly regeneration of adsorbent materials, resulting in an increase in the operational costs [1-3]. Many papers reported that Advanced Oxidation Processes (AOPs) such as Fenton's reagent, ozonation and photochemical oxidation provide effective colour removal and complete destruction of dyes molecules avoiding the potential formation of wastes [4-6].

Among the AOPs, the Electrochemical Advanced Oxidation Processes (EAOPs) are a promising alternative because they are environmentally clean and can produce large amount of hydroxyl radicals (•OH) on demand, under control of applied current [7-12]. In these processes, heterogeneous •OH generated by anodic oxidation (AO) of water using high O₂ overvoltage anodes such as boron-doped diamond (BDD) [13-21] or PbO₂ [22-27] anodes:



Recently, a new EAOP was proposed for synthetic dye removal and it is based on the production of homogeneous •OH in solution bulk through electrochemically assisted Fenton's reaction (EF), where hydrogen peroxide is generated in situ from the two-electron reduction of O₂:



These reactions occur with high yield and satisfactory rate only at gas diffusion cathodes (GDE) [28-32] and three-dimensional carbon-based cathodes, such as RVC [33] and graphite felt [34-38].

Reaction (3) is propagated thorough the continuous regeneration of ferrous iron at the cathode (reaction 4) thus avoiding Fe³⁺ accumulation in the medium and consequently eliminating the production of iron sludge:



In this study we report a detailed discussion on the degradation of methylene blue (MB), a thiazine dye selected as model compound, by electro-Fenton process using commercial graphite-felt as cathode for the production in situ of hydrogen peroxide.

EXPERIMENTAL

Chemicals and analytical procedures

The synthetic solution was prepared by dissolving 0.25 mM of MB (C₁₆H₁₈ClN₃S, inset of Figure 1 (a)) (Carlo Erba reagents, 92% purity) used

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without further purification, in bi-distilled water, in 50 mM Na₂SO₄ (Sigma Aldrich). Analytical grade H₂SO₄ (Sigma Aldrich) were used to adjust the initial pH of the solution at the value of 3 using a Schott Gerate CG822 pH-meter. This value of pH was chosen because many literature studies reported to be the optimum for electro-Fenton process [39].

A JascoV-570 UV/VIS spectrophotometer using silica cells of path length 1 cm was used for the determination of MB concentration. A Lambert–Beer diagram was established to correlate the absorbance at 664 nm to MB concentration.

The evolution of TOC was analyzed by using a Hach-Lange reagent Set and the spectrophotometer Dr. Lange LASA50.

Electrochemical system

The experiments were performed using an undivided cell with a volume of 300 mL, supplied with a heat exchanger and a magnetic stirrer under galvanostatic conditions using an AMEL 2055 potentiostat/galvanostat. The cathode was a 70 cm² (10 cm x 7 cm) carbon-felt piece (Carbone Loraine) with a thickness of 0.5 cm, and the anode was a 4.5 cm height cylindrical grid (i.d = 3.1 cm). The anode was a Ti/RuO₂ net centered in the electrolytic cell, surrounded by the cathode, which covered the inner wall of the cell. The distance between the electrodes was 1.6 cm. H₂O₂ was produced from reduction of O₂ dissolved in the solution, from reaction (2). Continuous saturation of the solution by O₂ at atmospheric pressure was ensured by bubbling of compressed air having passed through a frit at about 1 dm³ min⁻¹, starting 10 min before electrolysis. Solutions were vigorously stirred using a cylindrical with a magnetic bar (length: 25 mm, diameter: 6 mm) with a rotation rate of about 700 rpm to allow mass transfer.

RESULTS AND DISCUSSIONS

For each experiment, the removal of MB and the effectiveness of electro-Fenton process has been followed using UV-vis spectrophotometry. The absorption spectra of MB at room temperature present two absorption bands at about 664 and 611 nm which are directly related to the colour of the solution. The more well-defined peak at 611 nm was chosen for the determination of the concentration of MB using Lambert–Beer correlation. Figure 1(a) shows an example of UV-spectra evolution for 0.25 mM MB during electrolysis with an applied current of 200 mA and iron concentration of 0.3 mM. During the electrolysis the absorbance bands decrease continuously until disappearing meaning that the MB is almost completely removed by the reaction with •OH radicals electrogenerated (Eq. 3). Figure

1(b) shows that 98% of MB was removed in 90 min and its oxidation can be satisfactorily described by a pseudo-first order reaction kinetic.

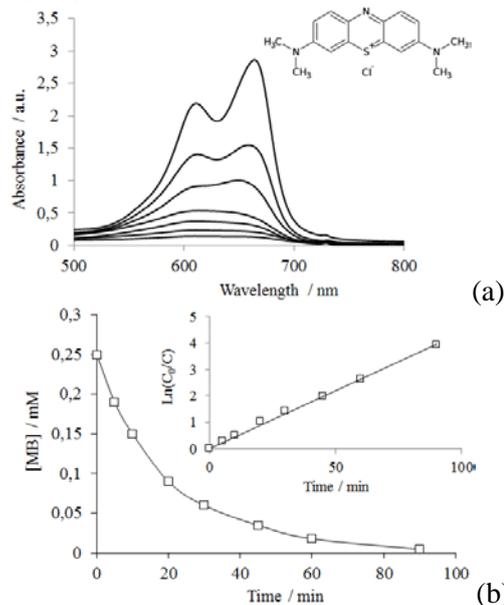


Fig.1. Evolution of (a) UV–visible spectra; (b) MB concentration and corresponding kinetic analysis (inset) as a function of time during electrolysis of 0.25 mM MB. Experimental conditions: [Fe²⁺] = 0.3 mM, I = 200 mA, T = 20 °C, pH = 3.

The effect of several operational parameters including applied current, initial iron concentration and temperature on MB removal was studied during the electro-Fenton treatment of 0.25 mM of MB at pH=3. In the electro-Fenton process the applied current is an important parameter that has to be optimized because both the production rate of H₂O₂ and the regeneration of Fe²⁺ is affected by the applied current [40, 41]. The effect of this parameter on the decay kinetics of MB was investigated performing electrolysis at different current values, i.e., 100, 200, and 300 mA in the presence of 0.3 mM of Fe²⁺ as catalyst and the results are reported in Figure 2.

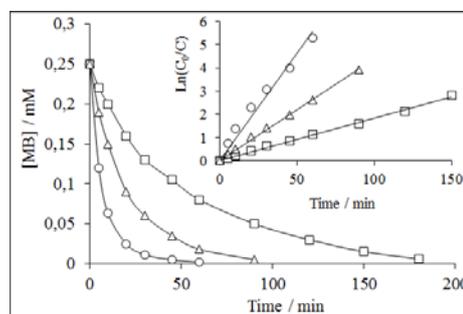


Fig. 2. Effect of applied current on the evolution of MB concentration during the electrolysis of 0.25 MB solution at applied current of: (□) 100 mA; (Δ) 200 mA; and (○) 300 mA. Conditions: pH = 3; T = 20 °C; [Fe²⁺] = 0.2 mM. The inset presents the corresponding kinetics analysis assuming a pseudo first-order reaction.

As can be seen, an increase of the applied current resulted in a higher oxidation rate and in less time required for the complete oxidation of MB. In fact, the time necessary for 96% removal of MB was 180, 90 and 60 minutes at a current of 100, 200 and 300 mA, respectively.

This enhancement of the oxidation rate with the applied current can be related to a greater production of H₂O₂ (Eq. 2) and regeneration of Fe²⁺ (Eq. 4) leading to the generation of higher amount of hydroxyl radicals from Fenton's reaction (Eq. 3).

It can be also seen from Figure 2 that the concentration of MB decreases exponentially for all current values and it can be satisfactorily described by a pseudo-first order reaction kinetic (inset of Figure 2). Apparent rate constants for oxidative degradation of MB, obtained from the slope of straight lines of the inset of Fig. 1 were reported in Table 1. The values of the apparent rate constant increased almost linearly with the applied current.

The Fe²⁺ concentration is another important parameter in the electro-Fenton process. In an attempt to optimise reaction conditions on the EF system, degradation of 0.25 mM MB was investigated in the presence of different Fe²⁺ concentrations at pH 3 applying a constant current of 300 mA. The effect of Fe²⁺ concentration on the degradation of MB was shown in Figure 3.

The MB removal rate increases with increasing Fe²⁺ concentration from 0.1 to 0.3 mM, and after this value the degradation rate decreases by increasing Fe²⁺ concentration. The negative effect of the higher catalyst concentration on the degradation kinetic can be explained by increase of the rate of the waste reaction occurring between the hydroxyl radicals and the excess of ferrous ions [39, 42-44]:

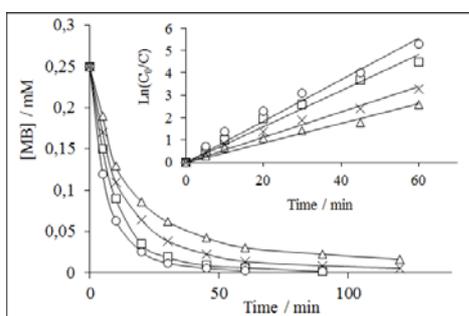
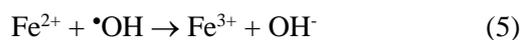


Fig. 3. Effect of Fe²⁺ concentration on the oxidation kinetics of MB during its degradation electro-Fenton treatment. Conditions: pH = 3; T = 20 °C; applied current = 300 mA; [Fe²⁺] = (□) 0.1 mM, (○) 0.3 mM, (×) 0.5 mM, (Δ) 1.0 mM, the inset presents the corresponding kinetics analysis assuming a pseudo first-order reaction.

The inset of the panel of Figure 3 presents the excellent correlation decay considering a pseudo-first-order reaction rate. The values of the apparent rate constants obtained from the kinetic analyses of the plots in Figure 4 are reported in Table 1.

Table 1. Effect of applied current on the of the relative pseudo-first-order rate constant under conditions given in Figs 2-6

Run	I (mA)	[Fe ²⁺] (mmol dm ⁻³)	T (°C)	k _{app} (min ⁻¹)
1	100	0.3	20	0.0184
2	200	0.3	20	0.0441
3	300	0.3	20	0.0928
4	300	0.1	20	0.0568
5	300	0.5	20	0.0823
6	300	1.0	20	0.0436
7	300	0.3	35	0.1177

Figure 4 reports the effect of temperature on the removal of MB in the range 20 – 35 °C. As can be observed, there are no significant differences between the two temperatures, but higher oxidation rate was obtained at higher temperature because the reaction of hydroxyl radicals oxidizing the dye molecules could be accelerated by increasing the temperature, according to Arrhenius law. Temperature above 35 °C was not considered because it is not convenient, from economic point of view, to further heat the solution.

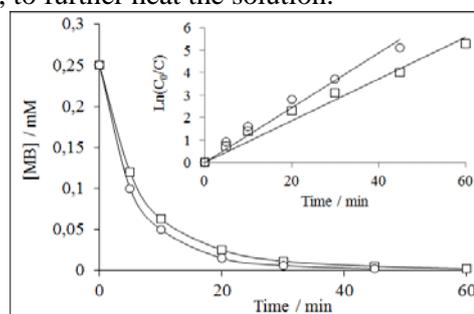


Fig. 4. Effect of temperature on the evolution of MB concentration during the electrolysis of 0.25 mM MB solution. Conditions: pH = 3; applied current 300 mA; [Fe²⁺] = 0.2 mM, T = (□) 20 °C; (○) 35 °C. The inset presents the corresponding kinetics analysis assuming a pseudo first-order reaction.

The complete oxidation of MB is not an indication that all the organic compounds presents in the solution oxidation have been degraded because of formation of oxidation reaction intermediates. Thus, the mineralization of MB was monitored measuring the TOC of the solution during the electrolysis under best conditions found previously (i.e. applied current 300 mA and Fe²⁺ concentration 0.3 mM and temperature of 35 °C) and the results are presented in Figure 5.

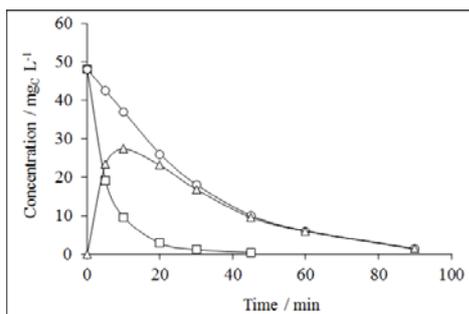


Fig. 5. Evolution of the (o) TOC, (\square) MB concentration and (Δ) intermediates expressed as mg/L of carbon, during electro-Fenton treatment of MB aqueous solution. Experimental conditions: pH = 3; applied current 300 mA; $[\text{Fe}^{2+}] = 0.2 \text{ mM}$, $T = 35 \text{ }^\circ\text{C}$; $[\text{MB}] = 0.25 \text{ mM}$

After 90 min of treatment, more than 96% of TOC was removed, meaning that almost all the organic compounds (i.e. MB and its oxidation intermediates) are completely mineralised to CO_2 and water. However, the faster decrease of MB concentration (expressed in term of mg dm^{-3} carbon) compared to the removal of TOC indicates that some intermediates are produced during the oxidation. The concentration of this intermediates, obtained by difference between TOC and MB concentration, increased in the first 10 min and then it progressively decreased up to zero.

CONCLUSIONS

The oxidative degradation of MB, one of the most important thiazine dye, by electro-Fenton process has been studied under different experimental conditions. Results show that it is possible to attain a complete removal of the dye and the TOC. This fact is due to the generation of hydroxyl radicals, from Fenton's reagent, that attack to the organic matter present in wastewater, favoring its complete degradation.

In any applied conditions the decay kinetic of MB follows a pseudo-first-order reaction and the oxidation rate largely depends on applied current, Fe^{2+} concentration, while temperature has only a slightly effect. With our cell design the higher oxidation rate was obtained for applied current of 300 mA, catalyst (Fe^{2+}) concentration of 0.3 mM and $T = 35 \text{ }^\circ\text{C}$.

In these conditions, 0.25 mM MB was completely removed in 45 min and the initial TOC was removed in 90 min of electrolysis, meaning the almost complete mineralization of the organic content of the treated solution.

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ПРИЛОЖЕНИЕ НА ЕЛЕКТРО-FENTON ПРОЦЕСА ЗА ТРЕТИРАНЕ НА МЕТИЛЕНОВО СИНЬО

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(Резюме)

Електрохимичното отстраняване на метиленово синьо (МВ) от воден разтвор, съдържащ 0.25 mM МВ, едно от най-важните тиазинови багрила, е изследвано чрез електро-Fenton процес, като се използва графитно кече за катод, за да се генерира *in situ* по електричен път водороден пероксид и да се регенерират железните йони като катализатор. Изследван е ефектът на условията на работа, като например приложен ток, концентрация на катализатора и първоначално съдържание върху разграждането на МВ. Отстраняването на МВ и минерализирането бяха наблюдавани по време на електролизата чрез UV-Vis анализ и ТОС измервания. Експерименталните резултати показват, че МВ е напълно отстранен чрез реакцията с •ОН радикали, генерирани от електрохимично подпомогната реакция на Fenton и при всички условия кинетиката на разпад винаги следва реакция от псевдо-първи ред. По-бързата скорост на окисление на МВ се получава при прилагане на ток от 300 mA с 0,3 mM Fe²⁺ при T = 35°C. При тези условия 0.25 mM МВ се отстранява напълно за 45 минути и първоначалният ТОС се отстранява за 90 минути електролиза, което означава почти пълната минерализация на органичното съдържание на третирания разтвор.

Ключови думи: метиленово синьо, електро-Fenton, графитово кече, окисляване на багрилото