Comparative efficiencies of the decolourisation of Methylene Blue using Fenton's and photo-Fenton's reactions

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Comparative efficiencies of the decolourisation of Methylene Blue using Fenton's and photo-Fenton's reactions†

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The decolourisation and mineralization of Methylene Blue azo dye (MB) under Fenton's and photo-Fenton's conditions have been studied. Some parameters, such as initial concentrations of iron (Fe^{2+}) and fixed hydrogen peroxide (H_2O_2), were evaluated to find the optimal conditions for the efficient degradation of azo dye. The experimental assays showed better efficiency for the photo-Fenton's system. Pseudo-first order degradation rate constants were obtained from batch experimental set up. It is suggested that photo-Fenton's reactions are viable processes for treatment of azo dye MB, according to the high levels of colour (UV_{665}) and total organic carbon (TOC) removal.

Introduction

In order to obtain a useful final product, the textile industry uses many unit operations, which generate along the way large quantities of effluents with significant concentrations of organic compounds. These organics are directly discharged to wastewater, in most of the cases into the rivers and other water courses.[1,2] Dyes have a great variety of organic structures, characterized by the presence of unsaturated groups, basically chromophores, such as –C=C–, –N=N– and –C≡N–, which originate the dye colour, and functional groups responsible for their fixation to fibres, for example, $-NH_2$, $-OH$, $-COOH$, $-SO_3H^3$. The most common chromophore group present in the textile industry wastewater is the azo dyes class (–N=N–).[3,4] In order to meet the regulations imposed by the current legislation and the demand of the society, these discharges are commonly treated by physicochemical, oxidative or active sludge biochemical treatments,[4] but in many cases colour removal is not effectively obtained. In this context, it is necessary to promote new alternatives for wastewater treatment. Advanced oxidation processes (AOPs) have been developed, operating at or near room temperature and pressure and based on the promotion of highly reactive species, the free hydroxyl radicals ($^{\cdot}OH$, $E° = 2.8V$ *vs* NHE).[5,6] Hydroxyl radicals produced by the AOPs do not selectively attack the organic compounds.[7] In 1990, Carey[8] described a common pathway for the degradation of organic compounds by free $^{\cdot}OH$ as follows:[9]

$$^{\cdot}OH + RH \rightarrow H_2O + R^{\cdot} \tag{1}$$

$$R^{\cdot} + H_2O_2 \rightarrow ROH + {}^{\cdot}OH \tag{2}$$

$$R^{\cdot} + O_2 \rightarrow ROO^{\cdot} \tag{3}$$

$$ROO^{\cdot} + RH \rightarrow ROOH + R^{\cdot} \tag{4}$$

Among them, Fenton's and photo-Fenton's systems are very promising treatments for organic compounds, because they promote high reaction yields at low process treatment cost.[10] These kinds of AOPs have been applied successfully to treat many azo dyes compounds for textile wastewater.[11–19]

Fenton's and photo-Fenton's chemistry

In the Fenton's reagent, a mixture of hydrogen peroxide and ferrous salt react[20] to generate the free $^{\cdot}OH$, as described in the next equation:[10]

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\cdot}OH + HO^- \tag{5}$$

Then, Fe^{3+} can be reduced by reaction with H_2O_2 excess to form again Fe^{2+} and produce more free $^{\cdot}OH$.

The rate of pollutant oxidation in solutions containing the Fenton's reagent is substantially increased when the system is irradiated with UV light, based on previous observations.[21–24] This approach, commonly known as the photo-Fenton's or photo-assisted Fenton's process, is based on ferric ion generation as a by-product of the reaction between Fe^{2+} and H_2O_2, and then photochemically transformed back into ferrous ions as shown by eqn (6),[25]

$$Fe^{3+} + H_2O \xrightarrow{h\nu} Fe^2 + H^+ + {}^{\cdot}OH \tag{6}$$

This closed cycle maintains a continuous generation of hydroxyl radicals in the solution.

The Fenton's and photo-Fenton's systems offer successful azo dye degradation with relative low treatment cost, avoiding secondary expenses, such as sludge.

In this work, we studied Fenton's system with and without the use of irradiation, to carry out effectively the decolourisation and degradation of a common synthetic azo dye solution, Methylene Blue (MB). The aim of this study is to evaluate in detail the role of a selected set parameters (initial concentration of Fe^{2+} and the effect of the H_2O_2 concentration). Special attention was taken in the determination of kinetic parameters like rate constant and half life time for the oxidation MB.

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Materials and methods

Synthetic dye solution

A commercial azo dye Methylene Blue (MB), empirical formula $C_{16}H_{18}ClN_3S\cdot3H_2O$, was supplied by Merck and used as received without any purification. The chemical structure of the dye is shown in Fig. 1. The initial concentration of MB for all experiments was 50 mg L^{-1}, a typical dye concentration in real-world textile effluents. The pH was adjustment between 2.8 to 3 with chlorhydric acid 1 N, preparing for Fenton's and photo-Fenton's operation conditions.
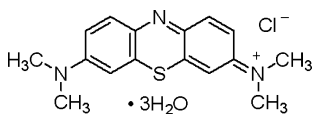
Fig. 1 Structure of azo dye Methylene Blue.

Fenton's and photo-Fenton's oxidation reagent

The free hydroxyl radicals $\cdot$OH, was generated *in situ* by addition of the following regents in aqueous solution: hydrogen peroxide (H_2O_2) 30% w/v and ferrous sulfate $FeSO_4\cdot7H_2O$, 99.5%, both by Merck.

Setup and light sources

The experiments were performed in 0.5 L glass cell. The reaction mixture inside the cell consists of 500 mL of the dye sample (50 mg L^{-1}) and a precise amount of Fenton's reagent under constant stirring with a magnetic bar, carrying out the experiments at room temperature and pressure. A 75 mW UVA lamp supplied by UVP, which basically emits 365 nm, was used as artificial light source when working under photo-Fenton's conditions.

Chemical assays

The UV-vis absorption spectra were recorded by using a UV Perkin Elmer Lambda 12 spectrophotometer in the 200–700 nm range. As can see in Fig. 2, the absorption spectra of the Methylene Blue is characterised by three main bands, one in the visible region ($\lambda_{max} = 665$ nm), and two in the UV region ($\lambda_{max} = 300$ nm and
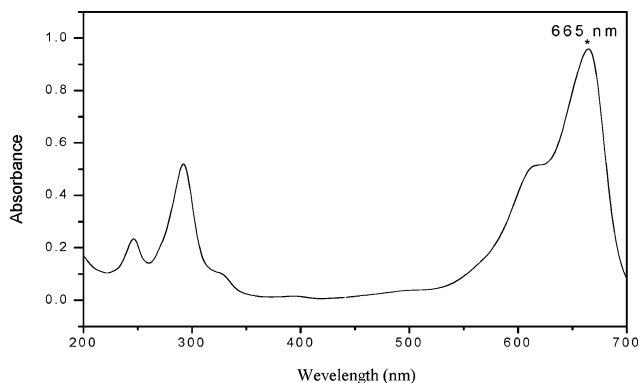
$\lambda_{max} = 250$ nm). In our case, the most important band is at 665 nm (azo dye content).

Total organic carbon (TOC) in the solution was measured by Direct Method LR (0.1–20 mg L^{-1} of carbon) based on Hatch Water Analysis Handbook.

Results and discussion

Colour removal efficiency and kinetic parameters

The colour removal efficiency (η) is defined as:

$$\eta(\%) = (C_0 - C)/C_0 \times 100 \qquad (7)$$

where C_0 and C are MB concentration at initial time and given time t, respectively.[26]

The kinetics of Fenton's reaction can be fitted using apparent first-order kinetics. We follow the rate of decolourization of MB ($\lambda_{max} = 665$ nm) as shown in the next equation:

$$\ln(C_0/C) = k_1 t \qquad (8)$$

where k_1 is the apparent first-order reaction rate constant, t is the reaction time and C_0 and C are the initial and final concentration values of the dye solution, respectively. As indicated by several researchers,[10] decolourisation and aromatic content removal kinetics of most azo dyes, can be fitted using a first-order rate equation. The parameter we selected to evaluate the optimal conditions to carry out the decolourization and degradation of the MB was Fe^{2+} concentration. The pH in the initial test was 3, since it has been reported that Fenton's system occurs efficiently at pH in a range between 2.8 and 3.[2,27,28]

For a fixed H_2O_2 concentration 8.0×10^{-3} M, the following Fe^{2+} concentrations were tested: 5.0×10^{-4}, 1.0×10^{-3}, 1.5×10^{-3}, 2.0×10^{-3} M. Fig. 3 depicts the results obtained when we use Fenton's treatment under the precise established conditions.

Fig. 3 Colour removal efficiency for dissolution of 0.5 L containing 50 mg L^{-1} of MB, fixed H_2O_2 concentration (8.0×10^{-3} M) and different Fe^{2+} concentrations in the Fenton's system.

Under these conditions, for Methylene Blue azo dye content removal, the best Fe^{2+} concentration is 2.0×10^{-3} M. At these conditions, the colour removal efficiency is close to 98.6% in the first 10 min of treatment. This value is two percent higher than with the lower concentration (5.0×10^{-4}). It is important to mention that

Fig. 2 Absorption spectra of Methylene Blue (50 mg L^{-1}) before treatment.

Table 1 TOC determinations for Fenton's system

t/min	TOC_t/TOC_0 0.5×10^{-4} M Fe^{2+}	TOC_t/TOC_0 1.0×10^{-3} M Fe^{2+}	TOC_t/TOC_0 1.5×10^{-3} M Fe^{2+}	TOC_t/TOC_0 2.0×10^{-3} M Fe^{2+}
0	1	1	1	1
30	0.52	0.37	0.74	0.5
60	0.5	0.22	0	0

the colour removal efficiency between the four Fe^{2+} concentrations tested is not significant, because the η is similar in all cases.

Results obtained for the removal of total organic carbon applying Fenton's system are shown in Table 1.

It is shown the best conditions to reduce TOC load is when we supply 2.0×10^{-3} M of Fe^{2+}, achieving the total mineralization of MB azo dye after 60 min of treatment. The main reason for the quick azo dye decomposition is the well known behaviour of ferrous ions reacting rapidly with H_2O_2 ($k = 53$ mol^{-1} dm^{-3} s^{-1}) to generate great quantities of free $^{\bullet}OH$ (eqn (5)), which in turn react rapidly with the azo dye molecules to degrade them.

However, when we carry out assays with the photo-Fenton's system, the degradation rate of organic compounds is increased (eqn (6)). It is well known that UV radiation improves the free $^{\bullet}OH$ generation thus increasing dye decomposition. The results for these experiments are shown in Fig. 4.

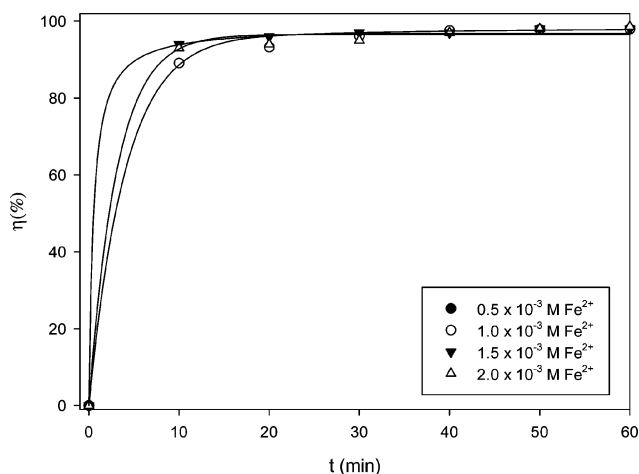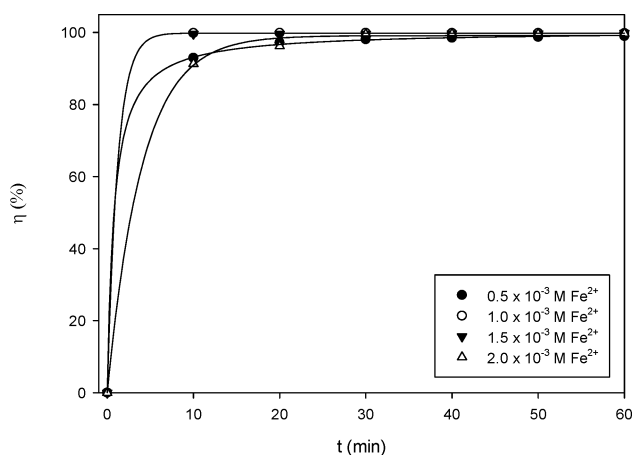**Fig. 4** Colour removal efficiency for dissolution of 0.5 L containing 50 mg L^{-1} of MB, fixed H_2O_2 concentration (8.0×10^{-3} M) and with different Fe^{2+} concentrations in the photo-Fenton's system ($\lambda = 365$ nm).

As can be observed, the colour removal effiency is close to 100% in all the cases tested after 20 min of reaction.

The results for the reduction of total organic carbon applying photo-Fenton's system are shown in the Table 2.

As can be seen, the remaining TOC concentration is zero after 30 min of photo-Fenton's treatment when we add to the solution 2.0×10^{-3} M of Fe^{2+}, improving the result obtained by Fenton's system close to 50%. This demonstrates the well known effi-

Table 3 Comparison Fenton's and photo-Fenton's systems

Fenton's system

Fe^{2+}/M	k_1/min^{-1}	$t_{1/2}/min$
0.5×10^{-3}	3.0×10^{-3}	23.10
1.0×10^{-3}	1.4×10^{-3}	49.51
1.5×10^{-3}	2.3×10^{-3}	30.13
2.0×10^{-3}	3.5×10^{-3}	19.80

Photo-Fenton's system

Fe^{2+}/M	k_1/min^{-1}	$t_{1/2}/min$
0.5×10^{-3}	3.6×10^{-3}	19.25
1.0×10^{-3}	4.1×10^{-3}	16.90
1.5×10^{-3}	2.0×10^{-3}	38.50
2.0×10^{-3}	7.2×10^{-3}	9.62

ciency of Advanced Oxidation Process in the decolourisation/degradation of azo dye organic compounds, as reported by several authors.[1,10,29]

Comparison of different Fenton's and photo-Fenton's system

Lastly, the comparison between Fenton's and photo-Fenton's systems was carried out based on kinetic parameters, using colour removal values, such as apparent first-order reaction rate constant (k_1) and half life time ($t_{1/2}$). The results are presented in the Table 3.

From this table, the best conditions for the azo dye Methylene Blue treatment in both processes is the addition of 2.0×10^{-3} M of Fe^{2+} and maintaining the initial H_2O_2 concentration at 8.0×10^{-3} M. The Fenton's process is achieved with a rate constant of 3.5×10^{-3} min^{-1} and $t_{\frac{1}{2}} = 19.80$ min; photo-Fenton's process acts faster than Fenton's system, since the rate constant is 7.2×10^{-3} min^{-1} (>2 times), and $t_{1/2} = 9.62$ min (twice as fast), with respect to Fenton's treatment. Is important to mention that the intermediate concentrations of Fe^{2+} (1.0×10^{-3} M and 1.5×10^{-3} M) the azo dye degradation is slow, because hydrogen peroxide in excess acts as $^{\bullet}OH$ scavenger as shown by the following equation:[10]

$$^{\bullet}OH + H_2O_2 \rightarrow H_2O + HO_2^{\bullet} \qquad (9)$$

Additionally, another reasonable reaction could take place:

$$2^{\bullet}OH \rightarrow H_2O_2 \qquad (10)$$

Table 2 TOC determinations for photo-Fenton's system

t/min	TOC_t/TOC_0 0.5×10^{-4} M Fe^{2+}	TOC_t/TOC_0 1.0×10^{-3} M Fe^{2+}	TOC_t/TOC_0 1.5×10^{-3} M Fe^{2+}	TOC_t/TOC_0 2.0×10^{-3} M Fe^{2+}
0	1	1	1	1
30	0.72	0.56	0.05	0
60	0.05	0.05	0	0

Conclusions

The Fenton's process for azo dye Methylene Blue was found to follow pseudo-first order kinetics under the operating conditions studied. For azo dye compound decolorisation and removal, the best Fenton's reagent conditions were: initial $[H_2O_2] = 8.0 \times 10^{-3}$ M, $[Fe^{2+}] = 2.0 \times 10^{-3}$ M, achieving 100% TOC reduction after 60 min. Under photo-assisted conditions ($\lambda = 365$ nm), the time to reduce half the initial azo bond content (UV_{665}) of the dye was $t_{1/2} = 9.62$ min with a rate constant $k = 7.2 \times 10^{-3}$ min^{-1}. Moreover, the TOC reduction was always greater under the presence of a source of light, since the 100% TOC removal was obtained in 30 min of treatment.

Acknowledgements

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