Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2014.939864

55 (2015) 3646–3652
September

Taylor & Francis
Taylor & Francis Group

Modeling methylene blue oxidation by means of Fenton chemistry enhanced by UV irradiation at mild conditions

L. Jiménez-Lima[a], S. Silva-Martínez[b], J.A. Hernández[b], F.Z. Sierra[b], A. Alvarez-Gallegos[b,*]

[a]*Posgrado en Ingeniería y Ciencias Aplicadas FCQeI-CIICAp, Universidad Autónoma del Estado de Morelos, Av. Universidad 1001, Cuernavaca, Morelos 62209, México*
[b]*Centro de Investigación en Ingeniería y Ciencias Aplicadas, Universidad Autónoma del Estado de Morelos, Av. Universidad 1001, Cuernavaca, Morelos 62209, México, Tel./Fax: +52 777 329 7084, +52 329 777984; email: aalvarez@uaem.mx (A. Alvarez-Gallegos)*

Received 10 March 2014; Accepted 16 June 2014

ABSTRACT

Taking into account that Fenton chemistry can be enhanced under UV radiation, a systematic activation of different H_2O_2 concentrations (7–50 mM) in 0.05 M Na_2SO_4 (pH 2 adjusted with H_2O_4) was carried out, in the presence of UV/Fe^{2+} in a photochemical reactor. From the experimental results, a simple empirical correlation between the H_2O_2 activation velocity (AV) and its concentration was derived, as a result, a chemical model for the $OH^{\cdot}$ production was obtained. Considering that the attractiveness of the Fenton chemistry is its near-stoichiometric generation of a strong oxidant, it is possible to model the oxidation of organic matter under mild conditions. In this way, the fraction of H_2O_2 produced/consumed provides a measure of the efficiency of the oxidation process. The chemical model was tested in the photochemical reactor with several methylene blue (MB) concentrations (0.1–0.3 mM). Experimentally and theoretically, it was found that 0.1, 0.2, and 0.3 mM MB can be oxidized in 85, 90, and 100 min, respectively. The predictions of the theoretical model are based on 90% of Chemical Oxygen Demand (COD) abatement. Thus, the theoretical results (time for achieving 90% of COD removal, and the stoichiometric amount of H_2O_2 required for such COD achievement) obtained from the chemical model, agree within a range of 5–15% of relative error against the experimental results. Although Fenton chemistry is very complex, under this approach it is possible to predict the oxidation of the organic matter contained in synthetic industrial effluents by means of a simple chemical model.

Keywords: Photo Fenton; Modeling methylene blue oxidation; Wastewater treatment

1. Introduction

Although water is available in abundance in the world, either it is not always located where it is needed or it is contaminated. Aqueous industrial effluents are generated at manufacturing sites where synthetic dyes are produced or used. The negative impact of dye stuff in the environment is a common problem faced by most countries in the world. Dye pollutants

---

*Corresponding author.

Presented at the Conference on Desalination for the Environment: Clean Water and Energy
11–15 May 2014, Limassol, Cyprus

from industries are related to the following general social problems: health hazards, irreversible damage to the ecology, and they strongly limit the availability of clean water for the society [1]. Methylene blue (MB) is widely used as a paper dye, microscopy stain, medicinal agent, and cosmetic dye and therefore, its release in the environment through different streams is common. Although MB is not considered a dangerous pollutant, it has been frequently associated to harmful effects in humans. Among them, it can be mentioned cyanosis, quadriplegia, eye burns, mental confusion, methemoglobinemia, may cause nausea, increased heart rate, profuse sweating, and tissue necrosis [2–4]. Therefore, the removal of MB from effluents is plenty justified. Although MB is resistant to a biological degradation, it was demonstrated 20 years ago that it can be strongly adsorbed to the aquatic plant, *Hydrilla verticillata*. This aquatic plant was able to remove MB from aqueous solution rapidly; 0.27, 1.34, and 2.7 mM were 95, 95, and 42% absorbed, respectively, in 180 min using 0.5 g *Hydrilla* in 100 mL solution [5]. Since then, its physical property of adsorption was tested in several materials [6] and this method has been one of the most important wastewater treatment options to remove MB and other dyes from effluents [7,8]. Although the performance of the adsorption method is very good for organics removal and well documented [9,10]. The main drawbacks are the simple transfer of the dyes from one phase to another. However, the advanced chemical oxidation processes, based on the generation of extremely reactive hydroxyl radicals are among the promising techniques for the environmental destruction organic dyes, including MB, in aqueous solution. MB has been oxidized by the generation of hydroxyl radicals using different techniques, among them ultrasonic degradation [11–13] and sonophotocatalysis [14–17] can be mentioned.

In this paper, hydroxyl radicals ($OH^{\cdot}$) were generated by a mixture of H_2O_2 and Fe^{2+} and the resulting Fenton chemistry was enhanced under UV radiation in a photochemical reactor. Under these circumstances, different H_2O_2 concentrations (7–50 mM) in 0.05 M Na_2SO_4 (pH 2 adjusted with H_2O_4) were activated and a simple empirical correlation between the H_2O_2 AV and its concentration was derived. As a result, a chemical model for the $OH^{\cdot}$ production was obtained. The fraction of H_2O_2 activated ($OH^{\cdot}$ production) provides a measure of the efficiency of the oxidation process. Although Fenton chemistry is very complex, under this approach it is possible to predict the oxidation of the organic matter contained in synthetic industrial effluents by means of a simple chemical model.

2. Fenton chemistry

At first glance, Fenton chemistry seems to be very simple. The simple interactions of soluble iron cations (Fe^{II}/Fe^{III}) with H_2O_2 give a near-stoichiometric generation a strong oxidant that it is responsible for organic oxidation. In this way, the fraction of the organic conversion (or the fraction of the hydrogen peroxide activated) provides a measure of the efficiency of the oxidation process. However, it was needed more than one century to understand that the simple chemical interaction between H_2O_2 and Fe^{II}/Fe^{III} turns out, surprisingly, in a very complex chemistry and the identification of the strong intermediate oxidant is still controversial [18,19]. Although the existence of hydroxyl radical is not settled satisfactorily, it is accepted that the main hydroxyl radical production from chemical interaction between H_2O_2 and Fe^{II}/Fe^{III} could be explained according to the following mechanism [20–22]:

$$Fe^{2+} + H_2O_2 \rightarrow Fe(OH)^{2+} + OH^{\cdot} \tag{1}$$

If the reaction (1) is carried out in the presence of UV, the complex $Fe(OH)^{2+}$ can be reduced while the H_2O_2 can be activated simultaneously increasing the production of $OH^{\cdot}$ and regenerating the catalyst (Fe^{2+}) for the Eq. (1), according to the following reaction [20,23]:

$$Fe(OH)^{2+} \xrightarrow{h\nu} OH^{\cdot} + Fe^{2+} \tag{2}$$

$$H_2O_2 \xrightarrow{h\nu} 2OH^{\cdot} \tag{3}$$

Even if the radical mechanism cannot be explained solely by Eqs. (2) and (3) then it is clear that Fenton chemistry is enhanced under this approach. What is more, in a simplified mechanism the reduction of H_2O_2 can be visualized by means of the following reaction:

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \tag{4}$$

Eq. (4) is representing the H_2O_2 activated by the chemical mechanism described by Eqs. (1) and (2) or Eq. (3). In other words, by means of Eq. (4), it is possible to represent the near-stoichiometric oxidation of organic matter. This fact allows a theoretical assessment of the efficiency of the oxidation process.

3. Experimental

3.1. Solutions and chemicals

In order to give a more realistic approach, aqueous solutions were prepared using tap water and their chemical composition (major cations and anions) is shown in Table 1.

MB was supplied by Ciba Specialty Chemicals and it was used as obtained without further purification. The rest of chemicals used in this work were of reagent grade quality and were used as obtained from the supplier (Aldrich-Sigma or JT Baker) without further purification.

3.2. Photochemical reactor

The photochemical reactor was made of a UV lamp (44 cm long, 3 cm diameter, 15 W, $\lambda = 352$ nm, Cole Parmer) hosted 5 mm away from the internal walls of a Pyrex jacket, allowing a complete UV penetration in the working solution. The solution, containing a given concentration of H_2O_2 and/or MB in the presence of 1 mM Fe^{2+} in 0,05 M Na_2SO_4 medium (pH 2 adjusted with H_2SO_4), was recirculate (7 L min^{-1}) from a 300-mL reservoir through the photochemical reactor by means of a pump (see Fig. 1).

3.3. Procedures

The quantitative analysis of H_2O_2 was performed following the classical permanganate method [24]. The maximum absorption wavelength of MB was found at 663 nm. The absorbance measurements at 663 nm were employed to calculate the dye concentration from the calibration curve (absorbance vs. MB concentration) built at the corresponding pH of the aqueous solution. The pollution degree of dye solutions was assessed by means of Chemical Oxygen Demand (COD). The COD test was analyzed by a Hach procedure using a COD reactor and a spectrophotometer DR/4000 UV–Vis.

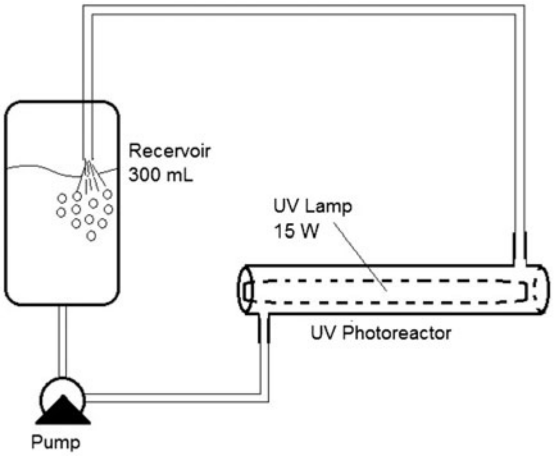

Fig. 1. Photochemical reactor. It is made of a UV lamp (44 cm long, 3 cm diameter, 15 W, $\lambda = 352$ nm) hosted 5 mm away from the internal walls of a Pyrex jacket, allowing a complete UV penetration in the working solution. The solution is pumped from a 300-mL reservoir through the photochemical reactor.

4. Results and discussion

4.1. H_2O_2 activation

300 mL of 14 mM H_2O_2 in a 0.05 M Na_2SO_4 medium (pH 2) was put in the photochemical reactor without UV irradiation. When the working solution was recirculating 1 mM Fe^{2+} was added and at this time the activation of H_2O_2 started. Under these circumstances, Fig. 2(a) presents the activation of H_2O_2 in the presence of Fe^{2+} (see Eq. (1)). It can be seen that the AV (0.036 mM min^{-1}) is constant during 180 min. During this time, the 46% (6.5 mM) of the H_2O_2 available was activated, the rest of it (7.5 mM) was remaining intact in the working solution. In order to assess the UV effect on the AV of H_2O_2, the experiment was repeated without Fe^{2+}. From Fig. 2(b) (Eq. (3)), it can be seen that AV of H_2O_2 by UV, increased (0.053 mM min^{-1}) almost 50% with respect to AV of H_2O_2 by Fe^{2+}. With the intention to test Eqs. (1) and (2), the experiment was again repeated in the presence of both: Fe^{2+} and UV irradiation. Fig. 2(c) shows the first 90 min of H_2O_2 activation. During this time, the 98% of the available H_2O_2 was activated. The 85% of the available H_2O_2 was activated in 60 min,

Table 1
Chemical composition of the tap water

Ion	Na^+	Mg^{2+}	Ca^{2+}	K^+	Cu^{2+}	Fe^{2+}	Cl^-	SO_4^{2-}	PO_4^{3-}	Total alkalinity as $CaCO_3$
ppm	130	5.5	3.2	2.6	<0.02	0.013	188	2.16	<0.001	65
pH	7.5									

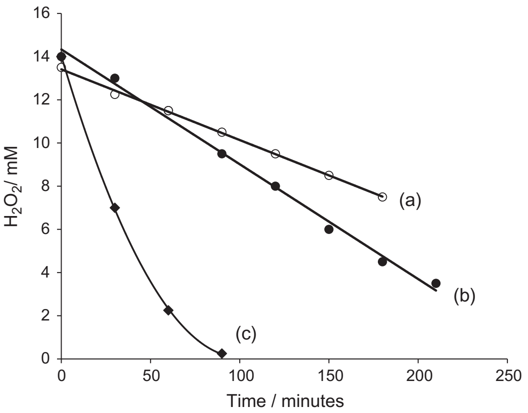

Fig. 2. Activation of 300 mL of 14 mM H_2O_2 in the photochemical reactor. (a) H_2O_2 + 1 mM Fe^{2+}. AV 0.036 mM min^{-1}; (b) H_2O_2 + UV. AV 0.053 mM min^{-1}; (c) H_2O_2 + 1 mM Fe^{2+} + UV. AV, 0.20 mM min^{-1}. Medium, 0.05 M Na_2SO_4 medium (pH 2).

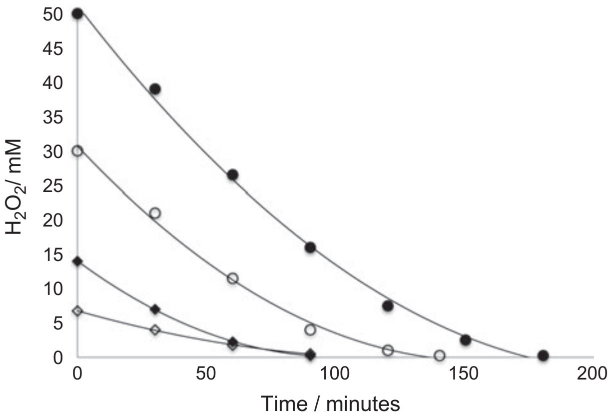

Fig. 3. Activation of H_2O_2 at different concentration, in the presence of 1 mM Fe^{2+} and UV irradiation in the photochemical reactor. (◇) 7 mM, AV: 0.07 mM min^{-1}; (♦) 14 mM, AV: 0.20 mM min^{-1}; (○) 30 mM, AV: 0.29 mM min^{-1}; (●) 50 mM, AV: 0.33 mM min^{-1}. Medium, 300 mL of 0.05 M Na_2SO_4 (pH 2).

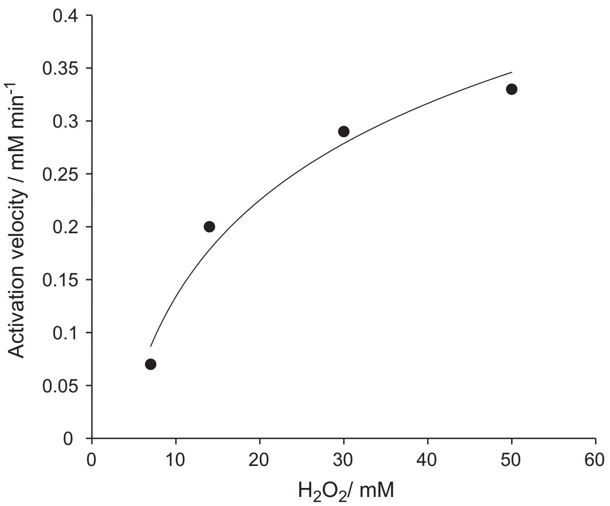

Fig. 4. H_2O_2 activation velocities as a function of its concentration. Medium, 300 mL of 0.05 M Na_2SO_4 (pH 2).

reaching a maximum AV of 0.20 mM min^{-1}. After 60 min, the AV starts to decrease slowly. As a result, the synergic effect of UV + Fe^{2+} on the AV of H_2O_2 enhances the $OH^{\cdot}$ production.

The synergic effect of UV + Fe^{2+} on the AV of H_2O_2 was further investigated with three more working solutions of 300 mL (0.05 M Na_2SO_4, pH 2), containing 7, 30, and 50 mM H_2O_2, each of them. In different experiments, each working solution was put in the photochemical reactor. As soon as the recirculation started, the UV irradiation was turned on and 1 mM Fe^{2+} was added to the solution. Fig. 3 shows the main results found. In general, it can be seen that for each H_2O_2 concentration: 7, 14, 30, and 50 mM H_2O_2, the 90% of the H_2O_2 is activated at the following constant AV's: 0.07, 0.20, 0.29, and 0.33 mM min^{-1}, respectively. In fact, Fig. 4 shows the AV of H_2O_2 as a function of its concentration. Although the AV follows a logarithmic behavior, the first three experimental points (the range in which the MB concentration was carried out), can be adjusted to a linear equation:

$$\mathrm{VA}\left(\mathrm{mM\ H_2O_2\ min^{-1}}\right) = 0.0077(\mathrm{mM\ H_2O_2}) + 0.0231;\quad R^2 = 1 \tag{5}$$

4.2. MB oxidation

The complete and theoretical oxidation of MB ($C_{16}H_{18}N_3SCl$) is a 78 electrons oxidation reaction, if chloride, sulfur, and nitrogen are transformed in hydrochloric and sulfuric acids, respectively. While nitrogen is transformed in ammonium, according to:

$$C_{16}H_{18}N_3SCl + 36H_2O - 78e^- \rightarrow 16CO_2 + 78H^+ + H_2SO_4 + 3NH_3 + HCl \tag{6}$$

Taking into account the latter hypothesis and the Eq. (4), the stoichiometric oxidation of MB by H_2O_2 is given by:

$$C_{16}H_{18}N_3SCl + 39H_2O_2 \rightarrow 16CO_2 + H_2SO_4 + 3NH_3 + HCl + 42H_2O \tag{7}$$

4.2.1. 0.2 mM MB

The experimental oxidation of 0.2 mM MB (COD_0 = 104 ppm) was investigated in the photochemical reactor, under the same experimental conditions described before. Fig. 5 reports spectra recorded at various stages during the 0.2 mM MB oxidation process in a working solution consisting of 7.8 mM H_2O_2 + UV + 1 mM Fe^{2+} + 0.05 M Na_2SO_4 and pH 2. The initial solution is bright blue and has to be diluted five times before a spectrum (dashed line) can be recorded. After 10 min, the solution is colorless (continuous line) and the MB concentration has dropped to 0.0018 mM (evaluated from its experimental absorbance and a calibration curve) indicating a 99% of MB concentration abatement. At 90 min, the oxidation process was considered to be complete, with 0.0004 mM MB (99.8% of concentration abatement) and $COD_F = 5$ ppm (95% of COD abatement).

4.2.2. 0.3 mM MB

The experimental oxidation of 0.3 mM MB ($COD_0 = 187$ ppm) was investigated in the photochemical reactor, under the same experimental conditions described before. Fig. 6 reports spectra recorded at various stages during the 0.3 mM MB oxidation process in a working solution consisting of 11.7 mM H_2O_2 + UV + 1 mM Fe^{2+} + 0.05 M Na_2SO_4 and pH 2. The initial solution is bright blue and has to be diluted 7.5 times before a spectrum (dashed line) can be recorded. After 10 min, the solution is colorless (continuous line) and the MB concentration has dropped to 0.009 mM (evaluated from its experimental absorbance and a calibration curve) indicating a 97% of MB concentration abatement. At 30 min, the MB concentration was 0.0043 mM (evaluated from the calibration curve), indicating a 98.6% of MB concentration abatement (dotted line). At 90 min, the oxidation process was considered to be complete. At this time, the MB concentration was practically constant, 0.0042 mM, evaluated from the calibration curve, (dashed and dotted line) with a final $COD_F = 15$ ppm (a 92% of COD abatement).

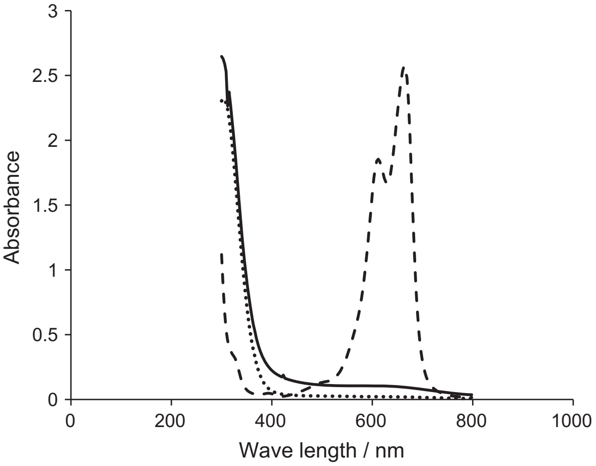

Fig. 5. Spectra recorded at various stages during the 0.2 mM MB ($COD_0 = 104$ ppm) oxidation and discoloration process in a working solution consisting of 7.8 mM H_2O_2 + UV + 1 mM Fe^{2+} + 0.05 M Na_2SO_4 and pH 2. (—): initial solution diluted five times. (——): After 10 min. (···): At the end of the oxidation, 90 min, $COD_F = 5$ ppm.

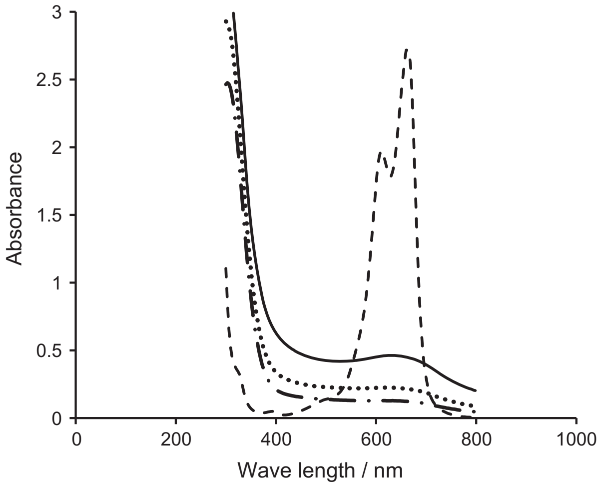

Fig. 6. Spectra recorded at various stages during the 0.3 mM MB ($COD_0 = 187$ ppm) oxidation and discoloration process in a working solution consisting of 11.7 mM H_2O_2 + UV + 1 mM Fe^{2+} + 0.05 M Na_2SO_4 and pH 2. (—): initial solution diluted 7.5 times. (——): After 10 min. (···): After 30 min. (–·–·–): At the end of the oxidation, 90 min, $COD_F = 15$ ppm.

4.3. Modeling MB oxidation

4.3.1. 0.2 mM MB

The conversion of 0.2 mM MB to CO_2 requires up to 7.8 mM H_2O_2, if Eqs. (4) and (7) are right and 100% efficient. According to Eq. (5), 7.8 mM H_2O_2 will be activated at 0.083 mM min^{-1}, hence, 94 min (4% more that the experimental time) are required to oxidize 0.2 mM MB according to Eqs. (4), (5), and (7). However, decolorizing 0.2 mM MB solution requires only a small amount of H_2O_2 (activation time in the photochemical reactor), because the color of the dyestuff is a function of the conjugated double bonds length in the aromatic molecule. The ring opening process should leads to discoloration early in the oxidation process. The theoretical required amount of H_2O_2 for 0.2 mM MB discoloration is not easy to find out. But it can be experimentally determined.

The required amount of H_2O_2 for the 99% of 0.2 mM MB concentration abatement (discoloration) can be found from Fig. 5. According to Eq. (5), in 10 min of the discoloration process 0.83 mM H_2O_2 was activated. As a result, this amount of H_2O_2 has abated 0.198 mM MB, see continuous line in Fig. 5. This fact allows us to describe the following stoichiometric MB discoloration by H_2O_2:

$$0.198\ \text{mM MB} + 0.83\ \text{mM}\ H_2O_2 \rightarrow 99\%\ \text{abatement of MB concentration} \tag{8}$$

Combining adequately Eqs. (4), (5), (7), and (8), it is possible to predict the discoloration rate and the time required for complete MB oxidation. In fact, the discoloration rate will follows a linear decay obeying Eqs. (5) and (8), see the theoretical prediction marked by a dashed line in Fig. 7 and experimental data symbolized by (○). Both theoretical processes, MB discoloration rate and the time required for complete MB oxidation, agree with experimental result.

4.3.2. 0.3 mM MB

The conversion of 0.3 mM MB to CO_2 requires up to 11.7 mM H_2O_2, if Eqs. (4) and (7) are right and 100% efficient. According to Eq. (5), the AV of such H_2O_2 concentration will be 0.113 mM min^{-1}. Therefore, 103 min (14% more than the experimental time found) will be enough to oxidize 0.3 mM MB, if Eqs. (4), (5), and (7) are right and 100% efficient.

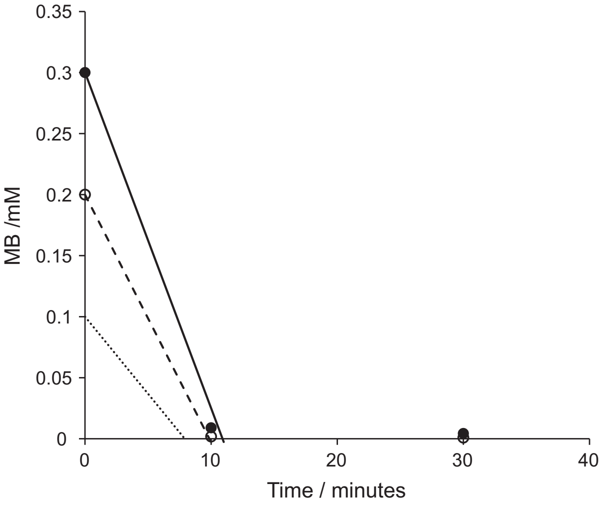

Fig. 7. Discoloration and oxidation process of three different concentrations of MB by means of H_2O_2, 1 mM Fe^{2+}, and UV, in the photochemical reactor. 0.3 mM MB + 11.7 mM H_2O_2 represented by experimental (●) and theoretical (——) results. 0.2 mM MB + 7.8 mM H_2O_2 represented by experimental (○) and theoretical (—) results. 0.1 mM MB + 3.9 mM H_2O_2 represented by theoretical (·····) results.

From Fig. 7, it can be seen that after 30 min the 98% of MB concentration was already abated (experimental data symbolized by ●). However, the MB discoloration process will take much less time. From Eq. (8), the 99% abatement of 0.3 mM MB concentration (0.297 mM MB) requires 1.25 mM H_2O_2, the 10.7% of the total H_2O_2 required for the complete MB oxidation. This amount of H_2O_2 will be activated in almost 11.1 min. During this time, 0.297 mM MB will be destroyed, following a constant oxidation velocity, numerically similar to the H_2O_2 AV. From Fig. 7, it can be seen that after 10 min the solution is colorless (experimental data symbolized by ●). The theoretical linear decrease of the MB concentration (and discoloration) is represented by a continuous line, in Fig. 7. At the end of 10 min, the theoretical MB concentration in the solution should be 0.025 mM (8% of the initial MB concentration), however, at this time, the experimental MB concentration (data symbolized by ●) was 0.012 mM (4% of the initial MB concentration). The differences can be explained by the fact that at lower MB concentration, the MB discoloration rate does not follows the H_2O_2 AV represented by Eq. (5). In fact, at lower MB concentration, the activated H_2O_2 (in reality, the strong oxidant $OH^{\bullet}$) will oxidize the abundant by-products of the earlier destroyed MB molecules. Once again, both theoretical processes, MB discoloration rate and the time required for complete MB oxidation agree with experimental result.

4.3.3. 0.1 mM MB

The conversion of 0.1 mM MB to CO_2 requires up to 3.9 mM H_2O_2, if Eqs. (4) and (7) are right and 100% efficient. The required amount of H_2O_2 for MB oxidation is not in the studied range of H_2O_2 AV (see Fig. 4). If Eq. (5) is still valid for such H_2O_2 concentration, therefore, the H_2O_2 AV would be 0.053 mM min^{-1}. Hence, 74 min will be enough to oxidize 0.1 mM MB, if Eqs. (4), (5**)**, and (7) are right and 100% efficient. Fig. 7 shows theoretical calculation for the discoloration rate (dotted line) of 0.1 mM MB.

5. Conclusions

For practical purposes (wastewater treatment), a simple chemical model, based on the Fenton Chemistry, is developed and successfully applied for the MB destruction. The chemical model is basically based on eight equations.

The H_2O_2 AV is a function of H_2O_2 concentration. In the range of 7–20 mM, the H_2O_2 AV increases linearly and the H_2O_2 AV can be described by a linear equation (see Eq. (5)). However, as the H_2O_2 concentration increases its AV decreases slowly.

In the MB concentration, range of 0.2–0.3 mM is feasible to derive an empirical and stoichiometric equation, for MB discoloration see Eq. (8).

Combining Eqs. (4), (5), (7), and (8), it is possible to predict the required time and H_2O_2 amount to convert a given MB concentration to CO_2. Moreover, the discoloration rate of MB in the range of 0.2–0.3 mM can be predicted as well.

This methodology was successfully applied for two concentrations: 0.2 and 0.3 mM. However, the methodology should be further tested before a developed and consistent technological procedure is applied for wastewater treatment.

References

[1] K.R. Ramakrishna, T. Viraraghavan, Dye removal using low cost adsorbents, Water Sci. Technol. 36(2–3) (1997) 189–196.

[2] J. Avom, J.K. Mbadcam, C. Noubactep, P. Germain, Adsorption of methylene blue from an aqueous solution on to activated carbons from palm-tree cobs, Carbon 35(3) (1997) 365–369.

[3] D. Ghosh, K.G. Bhattacharyya, Adsorption of methylene blue on kaolinite, Appl. Clay Sci. 20 (2002) 295–300.

[4] V. Vadivelan, K.K. Kumar, Equilibrium, kinetics, mechanism, and process design for the sorption of methylene blue onto rice husk, J. Colloid. Interface Sci. 286 (2005) 90–100.

[5] K.S. Low, C.K. Lee, L.L. Heng, Sorption of basic dyes by *Hydrilla verticillata*, Environ. Technol. 15(2) (1994) 115–124.

[6] N. Bhadusha, T. Ananthabaskaran, Adsorptive removal of methylene blue onto $ZnCl_2$ activated carbon from wood apple outer shell: Kinetics and equilibrium studies, E-J. Chem. 8(4) (2011) 1696–1707.

[7] S. Senthilkumaar, P.R. Varadarajan, K. Porkodi, C.V. Subbhuraam, Adsorption of methylene blue onto jute fiber carbon: Kinetics and equilibrium studies, J. Colloid Interf. Sci. 284 (2005) 78–82.

[8] B.H. Hameed, A.L. Ahmad, K.N.A. Latiff, Adsorption of basic dye (methylene blue) onto activated carbon prepared from rattan sawdust, Dyes Pigm. 75 (2007) 143–149.

[9] Y.S. Ho, G. McKay, The Kinetics of sorption of basic dyes from aqueous solution by sphagnum moss peat, Can. J. Chem. Eng. 76 (1998) 822.

[10] V.K. Gupta, I. Ali, M.D. Suhas, Equilibrium uptake and sorption dynamics for the removal of a basic dye (basic red) using low-cost adsorbents, J. Colloid Interface Sci. 265 (2003) 257.

[11] D. Kobayashi, Ch. Honma, A. Suzuki, T. Takahashi, H. Matsumoto, Ch. Kuroda, K. Otake, A. Shono, Comparison of ultrasonic degradation rates constants of methylene blue at 22.8 kHz, 127 kHz, and 490 kHz, Ultrason. Sonochem. 19 (2012) 745–749.

[12] Z.-D. Meng, W.-C. Oh, Sonocatalytic degradation and catalytic activities for MB solution of Fe treated fullerene/TiO_2 composite with different ultrasonic intensity, Ultrason. Sonochem. 18 (2011) 757.

[13] A.Z. Abdullah, P.Y. Ling, Heat treatment effects on the characteristics and sonocatalytic performance of TiO_2 in the degradation of organic dyes in aqueous solution, J. Hazard. Mater. 173 (2010) 159.

[14] L. Davydov, E.P. Reddy, P. France, P.G. Smirniotis, Sonophotocatalytic destruction of organic contaminants in aqueous systems on TiO_2 powders, Appl. Catal. B: Environ. 32 (2001) 95.

[15] S. Matsuzawa, J. Tanaka, S. Sato, T. Ibusuki, Photocatalytic oxidation of dibenzothiophenes in acetonitrile using TiO_2: Effect of hydrogen peroxide and ultrasound irradiation, J. Photochem. Photobiol. A: Chem. 149 (2002) 183.

[16] M. Mrowetz, C. Pirola, E. Selli, Degradation of organic water pollutants through sonophotocatalysis in the presence of TiO_2, Ultrason. Sonochem. 10 (2003) 247.

[17] A. González, S. Martínez, Study of the sonophotocatalytic degradation of basic blue 9 industrial textile dye over slurry titanium dioxide and influencing factors, Ultrason. Sonochem. 15 (2008) 1038–1042.

[18] S.H. Bossmann, E. Oliveros, S. Göb, S. Siegwart, E.P. Dahlen, L. Payawan, M. Straub, M. Wörner, A.M. Braun, New evidence against hydroxyl radicals as reactive intermediates in the thermal and photochemically enhanced fenton reactions, J. Phys. Chem. A. 102 (28) (1998) 5542–5550.

[19] M.L. Kremer, Mechanism of the Fenton reaction. Evidence for a new intermediate, Phys. Chem. Chem. Phys. 1 (1999) 3595–3605.

[20] J.J. Pignatello, Dark and photoassisted iron(3+)-catalyzed degradation of chlorophenoxy herbicides by hydrogen peroxide, Environ. Sci. Technol. 26 (1992) 944–951.

[21] O. Legrini, E. Oliveros, A.M. Braun, Photochemical processes for water treatment, Chem. Rev. 93 (1993) 671–698.

[22] J.J. Pignatello, G. Chapa, Degradation of PCBs by ferric ion, hydrogen peroxide and UV light, Environ. Toxicol. Chem. 13 (1994) 423–427.

[23] P.L. Huston, J.J. Pignatello, Degradation of selected pesticide active ingredients and commercial formulations in water by the photo-assisted Fenton reaction, Water Res. 33 (1999) 1238–1246.

[24] I.M. Kolthoff, R. Belcher, Volumetric Analysis, Titration, Methods: Oxidation Reduction Reaction, vol. III, Interscience Publishers Inc, New York, NY, 1957.