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Research article

Modelling and experimental checking of the influence of substrate concentration on the first order kinetic constant in photo-processes

M. Gómez [a, *], M.D. Murcia [a], E. Gómez [a], S. Ortega [a], A. Sánchez [a], O. Thaikovskaya [b], N. Briantceva [b]

[a] Chemical Engineering Department, University of Murcia, 30071, Murcia, Spain
[b] Innovative Technology Department, Tomsk State University, Russia

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ABSTRACT

Most photoprocesses follow a pseudo first order kinetic law and, commonly, the kinetic parameter depends on the initial concentration of the substrate. In this work, a kinetic model, which explains this dependence on the substrate concentration and on the other operational variables, has been developed. In the model, mass transfer of substrate from the bulk solution to the wall of the photoreactor was assumed as the step determining the rate of the process. To check the model, methylene blue (MB) has been used as model substrate and photodegradation experiments have been carried out in an exciplex KrCl flow-through photoreactor, It was observed that the methylene blue conversion improved with a decrease in its initial concentration, in good agreement with the model. Also, by fitting the experimental data to the model, high correlation coefficients and a high degree of agreement between experimental and calculated conversion was obtained, which validates the model.

1. Introduction

In most of the photodegradation processes the progress curves can be successfully fitted to a pseudo first order kinetics and, commonly, the first order kinetic parameter is not constant and shows a dependence on the initial concentration of substrate, which is not the expected behaviour for a true first order kinetics. In this work, a kinetic model, which explains this dependence on the substrate concentration and the influence of other operational variables, has been developed. To check the model, methylene blue (MB) has been used as model substrate and experiments have been carried out in an exciplex KrCl flow-through photoreactor, both in the presence of H_2O_2 and Fenton reagent.

Methylene blue (MB) has been chosen as model substrate in this work because this cationic dye has not only been used in the textile industry, but also in numerous therapeutic applications, from microbiology to psychiatry (Bruchey and González-Lima, 2008; Gonzalez-Lima and Bruchey, 2004; Poteet et al., 2012; Wainwright and Crossley, 2002).

Nowadays, more than 10,000 different types of dyes and commercial pigments are available (Tan et al., 2007) and more than 700,000 tons are produced worldwide (Fassold et al., 1999; Kannan and Meenakshisundaram, 2002). Industrial dyes are known to be among the main water contaminants due to the strong colour of their wastewater, which, once discharged in the receiving water bodies, diminishes water oxygenation capacity and blocks light absorption, avoiding plants photosynthesis and damaging biological activity (Eyvaz et al., 2009; Pearcea et al., 2003). The main risk for human health derived from dyes is the fact that most of them are formed from aromatic amines, which after the metabolic oxidation of dyes can lead to reaction products that covalently bond with the DNA nucleic acids (Gerulis, 1985). As a result, many dyes are carcinogenic, teratogenic or mutagenic to both aquatic and human life (Adam et al., 2013).

Moreover, as the required characteristics for industrial dyes are resistance to light, temperature, wash and microbial attack, these substances are highly recalcitrant, which, in addition to their complex structure, makes their treatment more complicated, especially when using conventional biological treatments (Frijters et al., 2006; Seshadri et al., 1994). Enzymatic treatments have shown better results, although their high cost remains as the main disadvantage (Ferreira-Leitão et al., 2003; Ferreira-Leitão et al.,

* Corresponding author.
E-mail address: maria.gomez@um.es (M. Gómez).

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2007). Adsorption has proven to be a simple physical method successfully used to remove methylene blue, among other dyes (Shi et al., 2013; Suteu and Malutan, 2013).

Among the chemical methods used to degrade dyes and other organic pollutants, Advanced Oxidation Processes (AOPs) have been able to achieve complete mineralization of the most recalcitrant contaminants due to their high oxidant power (Benitez et al., 2000; Lachheb et al., 2002). The main characteristic of these systems is the generation of very reactive and oxidizing free radicals, especially hydroxyl radicals produced by combining ozone, hydrogen peroxide, UV radiation and Fenton reagent (Ledakowicz et al., 2001; Liu et al., 2013; Pera-Titus et al., 2004).

Photodegradation techniques are a significant part of the AOPs and, recently, excimer lamps or excilamps have been developed, as new UV sources based on transitions of exciplex (rare gas halides) or excimer molecules (rare gas or halogen dimmers). They have important advantages such as the emission in a narrow-band UV radiation, nearly monochromatic and matching the dissociation energies of the main organic compounds bonds, the absence of toxic mercury and long lifetime, among others (Lomaev et al., 2006; Sosnin et al., 2006).

Excilamps have been successfully used in the removal of different organic pollutants, mainly phenolic compounds (Gómez et al., 2010a, 2010b; Matafonova et al., 2008; Tchaikovskaya et al., 2012), although recently some preliminary studies on their application for the removal of dyes have been performed. In this way, degradation of methyl green and congo red was tested in discontinuous reactors using KrCl, XeBr and Cl_2 excilamps (Gómez et al., 2011; Murcia et al., 2011), obtaining the best results with the KrCl excilamp for both dyes. In addition, a pseudo first order kinetic model was proposed and validated, but some of the results obtained in the fitting of the model to the experimental data, such as the presence of a residual concentration of substrate in the kinetic law, initially justified by the shielding effect, and the dependence of the pseudo-first order kinetic parameter on the initial concentration, were not well supported by the model. Several authors have also proposed a pseudo-first order kinetic for the photodegradation of methylene blue (Banat et al., 2005; Zhang et al., 2013). However, the influence of the dye initial concentration remains unclear and does not agree with the mentioned kinetic.

In the present work, and based on the good results previously obtained with the KrCl excilamp, the same excimer molecules have been used but with a different reactor configuration: a flow-through photoreactor, previously tested for 4-chlorophenol degradation (Gomez et al., 2012), which allows the treatment of higher sample volumes as a first step towards continuous processes. Also, a new and more detailed kinetic model has been developed. The model assumes mass transfer of methylene blue from the bulk solution to the wall of the photoreactor as the step determining the rate of the photodegradation process, which explains the existence of a limit concentration of MB not degraded after long time of phototreatment. Also, a density of the radiation intensity per mass unit is defined in the model, which explains the dependence of the kinetic parameter on initial substrate concentration. Methylene blue has been selected as a model dye both to study the experimental conditions leading to efficient degradation and to check the proposed kinetic model.

2. Materials and methods

2.1. Reagents and materials

The main chemicals and reagents, methylene blue (95%) and hydrogen peroxide (35%), were obtained from Sigma–Aldrich. $FeSO_4$ was purchased from Probus. Other chemicals were of analytical grade and were used without further purification.

All experiments have been carried out using a KrCl photoreactor, purchased from the Institute of High Current Electronics of Tomsk (Russia). The lamp has a wavelength of maximum emission at 222 nm and an average radiation intensity of 2.38 mW cm^{-2}, as previously described (Batalova et al., 2003; Gomez et al., 2012).

An ultraviolet/visible Shimadzu spectrophotometer, model UV-160, was used to measure the decreasing of methylene blue concentration along time. In addition, COD was also analyzed with specific equipment consisting of reactor and photometer, model HI 938800 and model 83,099, respectively, from HANNA Instruments.

2.2. Experimental and analytical methods

Methylene blue was pumped from a stirred feed tank to the photoreactor and the effluent was continuously recycled to the tank, so that the system acts as a discontinuous batch reactor (flow-through reactor). In the UV/H_2O_2 and photo-Fenton assays hydrogen peroxide and $FeSO_4$ were added to the feed tank together with the dye at the required initial concentration.

All the experiments were done at room temperature (23–25 °C), with an operational time of 120 min (except for the last experimental series, of 60 min). Samples were taken at different reaction times (0, 2.5, 5, 10, 20, 40, 60, 90 and 120 min) from the feed tank. Fig. 1 shows a scheme of the system, including the main components and the nomenclature used in the present work. Duplicate experiments were carried out and average values were obtained. Standard deviation calculated for the whole set of data was 1.95%.

The following operational variables were studied: H_2O_2:MB mass ratio; flow rate (with the variation of the rotational speed of the pump, flow rate (ml/min) = 2.3039 × rotational speed (rpm), $R^2 = 0.9975$); initial MB concentration; sample volume and Fe^{2+} concentration.

Samples were analyzed by spectrophotometry at the wavelength of maximum absorption of the dye, 660 nm. The corresponding calibration curve was done, being the obtained equation: [MB] (mg/l) = Absorbance/0.1996 ($R^2 = 0.9917$). Additionally, COD determination was done for several assays corresponding to the first experimental series.

3. Kinetic model

In the development of a kinetic model for the photodegradation process, the configuration of the reaction system shown in Fig. 1 as well as the following experimental behaviour observed in the photodegradation of the substrate type used, MB, have been taken into account:

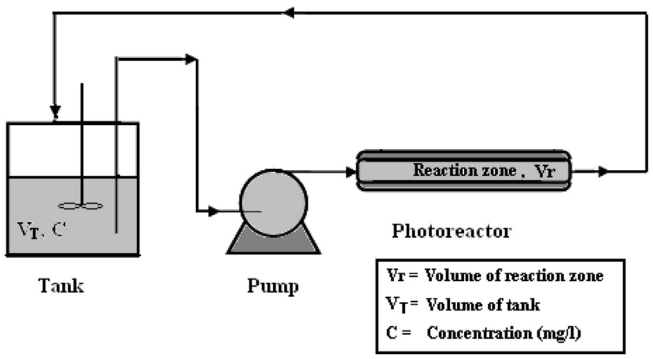

Fig. 1. Scheme of the experimental reaction system.

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a) The degradation progress curves of MB can be fitted, with a good degree of agreement, to a pseudo-first order kinetic model and the fitting improves by taking the reaction rate proportional not to the current MB concentration, C, but to the difference between this concentration and a residual one, C_{Lim}, which can be assumed constant in each experiment.
b) The apparent pseudo-first order kinetic constant depends on the experimental conditions, increasing with the hydrogen peroxide:MB mass ratio and feed flow and decreasing with initial MB concentrations and sample volume. This is not the typical behaviour for a kinetic constant of a true first order reaction, where the kinetic parameter is not dependent on experimental conditions and only depends on temperature.

3.1. Model hypotheses

1 The volume of the reaction zone, V_r, is continuously recycled and mixed with the tank volume, V_T. Their sum gives the total sample volume, V. The flow rate through the photoreactor is high enough to consider that the methylene blue concentration, C, is practically the same both in the tank and inside the photoreactor and only varies with time.
2 In previous assays it has been observed that direct photolysis is negligible, which makes the presence of hydrogen peroxide necessary. Additionally, the presence of ferrous salts (Fenton reagent) improves the rate of the process.
3 Photodegradation of methylene blue involves several consecutive steps, from the initial compound to different intermediates and final products. The global reaction can be formulated as follows:

$$MB + n\ H_2O_2 \rightarrow \text{Final products} \quad (1)$$

In the presence of the stoichiometric amount of hydrogen peroxide, total conversion to CO_2 and H_2O can be achieved.

4 At any time of the photodegradation process, if C (mg/l) is the concentration of non-degraded MB and C_i (mg/l) the concentration of each one of the n photoproducts generated during the process, taken into account the discontinuous and closed nature of the experimental system and according to the mass conservation law it must be verified:

$$C + \sum_{i=1}^{n} C_i = C_0 \quad (2)$$

where C_0 is the MB initial concentration (mg/l).

5 In the photoreactor, the intensity, I, of the radiation delivered to the sample is constant and uniformly distributed on the sample. A density of the radiation intensity per total mass unit can be defined as:

$$I_m = \frac{I}{C_0} \quad (3)$$

As a consequence, for a concentration C of MB at time t, the fraction of total radiation received by MB is equal to the product of the above defined density of radiation intensity by the concentration of MB, being proportional to the mass fraction of MB in the sample.

6 On the other hand, the penetration power of the radiation is limited, so it can be considered that the photodegradation reaction takes place only in a thin area close to the tube wall and directly exposed to the radiation. This assumption implies two regions with different MB concentrations: the one close to the tube wall, with a concentration C_{Lim}, and the inner tube, where the concentration is C, which determines a transport of methylene blue from the centre of the tube to the wall, being the driving force the concentration gradient $C - C_{lim}$. This behaviour is shown in Fig. 2.
7. The photodegradation rate of methylene blue near the tube wall is much faster than the mass transfer rate from the centre of the tube to the wall, being the last one the step determining the overall rate of the photodegradation process.

3.2. Model equations

3.2.1. Global mass balance of methylene blue in the system

If r_{MB} is the degradation rate of methylene blue in the photoreactor, and taking into account that the amount of MB degraded in the photoreactor must be equal to the decrease of MB in the tank, the following equation can be obtained:

$$V_T \frac{dC}{dt} = -V_r r_{MB} \quad (4)$$

3.2.2. Mass transfer rate and photodegradation rate

According to the hypothesis number 6, if k_La is the volumetric transport coefficient, the mass transfer rate, r_{dif}, of methylene blue from the centre of the tube to the walls is given by:

$$r_{dif} = k_La(C - C_{Lim}) \quad (5)$$

From the total mass of MB transported, given by Eq. (5), only the fraction activated by the radiation can react. Considering the hypothesis 5, the fraction of radiant energy received by the mass of

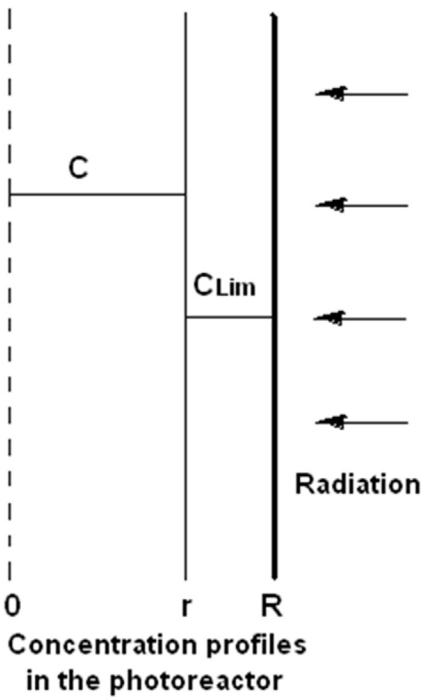

Fig. 2. Methylene blue concentration profile in the photoreactor.

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methylene blue that arrives to the tube wall from the centre must be proportional to its mass fraction. If k_E is the proportionality constant between the mass fraction and the energy received and ε the quantum yield of the process, the photodegradation rate of MB is given by:

$$r_{MB} = \varepsilon k_E I \;\; k_L a \frac{(C - C_{Lim})}{C_0} \tag{6}$$

By defining a new constant, k, as:

$$k = \varepsilon k_E I \;\; k_L a \tag{7}$$

The photodegradation rate of MB can now be expressed as:

$$r_{MB} = k \frac{(C - C_{Lim})}{C_0} \tag{8}$$

And by replacing Eq. (8) in Eq. (4), the following expression for the methylene blue mass balance equation is obtained:

$$V_T \frac{dC}{dt} = -kV_r \frac{(C - C_{Lim})}{C_0} \tag{9}$$

Finally, an apparent overall reaction constant can be defined as follows:

$$k_r = \frac{kV_r}{V_T C_0} \tag{10}$$

And Eq. (9) can be rearranged to obtain the differential equation for the variation of the methylene blue concentration with time in the system:

$$\frac{dC}{dt} = -k_r (C - C_{Lim}) \tag{11}$$

With the initial condition:

$$t = 0, \;\; C = C_0 \tag{12}$$

3.2.3. Model integration: reaction progress curves

From Eqs. (11) and (12) it can be obtained:

$$\ln\left(\frac{C - C_{Lim}}{C_0 - C_{Lim}}\right) = -k_r t \tag{13}$$

And, from the previous equation:

$$C = C_{Lim} + (C_0 - C_{Lim}) e^{-k_r t} \tag{14}$$

Given the following definitions of MB conversion, X, and limit conversion, X_{Lim}:

$$X = \frac{C_0 - C}{C_0} \tag{15}$$

$$X_{Lim} = \frac{C_0 - C_{Lim}}{C_0} \tag{16}$$

It is easy to obtain the following equation for the methylene blue conversion with time:

$$X = X_{Lim}\left(1 - e^{-k_r t}\right) \tag{17}$$

The previous equation gives the theoretical reaction progress curves with time.

For the fitting of the experimental data, the software Sigma Plot V8.0 has been used, with Eq. (17) modified as follows:

$$X = a\left(1 - e^{-bt}\right) \tag{18}$$

Where: $a = X_{Lim}$; $b = k_r$

3.3. Checking the model

3.3.1. Experimental results

Fig. 3 shows the experimental progress curves and the results of the fitting of the experimental conversions of methylene blue to Eq. (18), for all the experimental series. In these figures, the points correspond with the experimental conversion values and the continuous lines with the calculated ones using the model.

From Fig. 3A, it can be seen that an increase in the mass ratio H_2O_2:MB has a positive effect on the reaction, being the presence of H_2O_2 a determining factor to reach high conversion values. However, there is no significant improvement for ratios higher that 5:1, which is related with the stoichiometric one as it can be considering that, for stoichiometric amounts of MB and H_2O_2, the total oxidation of MB by H_2O_2 is given by the following molar relationship:

$$51\ H_2O_2 + C_{16}H_{18}N_3SCl \rightarrow 16\ CO_2 + 57\ H_2O + HCl + 3\ HNO_3 + H_2SO_4$$

And, taking into account the molecular mass of MB (319.5 g/mol) and H_2O_2 (34 g/mol), the above molar relationship 51:1 corresponds, practically, with the mass ratio 5:1 (exactly 5.4:1). Additionally, as shown in Fig. 4, COD considerably increases above this stoichiometric ratio, due to an excess of hydrogen peroxide. So the ratio 5:1 was selected for the rest of the experimental series.

In Fig. 3B, corresponding to the series of flow rate variation, it can be observed that the increase in the flow rate increases the turbulence, which improves the mass transport from the centre of the quartz tube to its wall, where the MB is irradiated. This improves the efficiency of the photoprocess. Also, this series validates hypothesis 7 of the proposed kinetic model, confirming that mass transfer is the step determining the rate of the photodegradation process. However, the improvement in the photodegradation efficiency is more remarkable from 10 to 20 rpm than from 20 to 30 rpm, which is why the flow rate corresponding to 20 rpm was selected as the optimum value.

The influence of methylene blue initial concentration is shown in Fig. 3C. Conversion values increase when the initial dye concentration decreases, which agrees with hypothesis 5: with lower initial concentrations of MB, lower is the total mass irradiated (the sum of the residual MB and the different photoproducts), higher is the density of radiation per mass unit and higher is the fraction of the total radiation received by the MB.

In Fig. 3D it can be observed that, for the same reaction time, conversion increases with a decrease in the sample volume, since the total mass to degrade diminishes as well.

Finally, in Fig. 3E, it can be seen that conversion increases with an increase in the Fenton reagent concentration. This is due to a faster production of hydroxyl radicals involved in the photoprocess, which diminishes the limit concentration, C_{Lim}, increasing the driven force of the mass transfer, C-C_{Lim}, which also increases the mass transfer of MB from the bulk solution to the wall of the quartz tube.

Nearly total degradation of methylene blue was achieved for almost all the assays (except in the absence of hydrogen peroxide) at different reaction times, depending on the experimental conditions. Using the optimum mass ratio H_2O_2:MB and flow rate, 5:1

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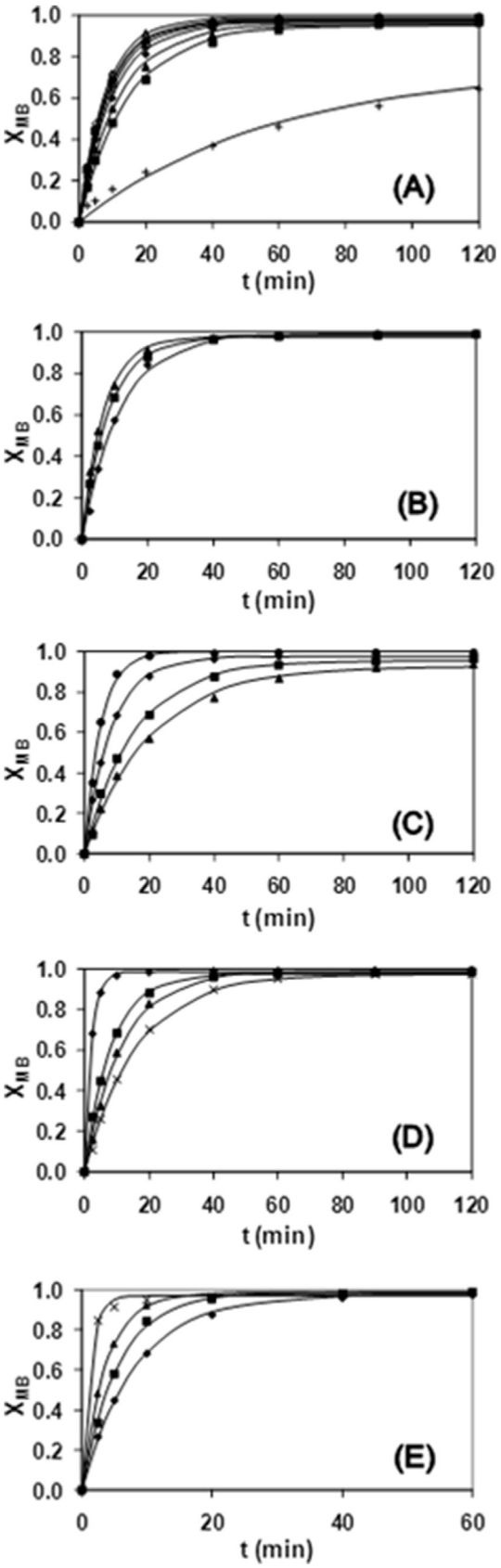

Fig. 3. Methylene blue conversion versus time, experimental and calculated values. **(A)** Variation of mass ratio $[H_2O_2]_0$:$[MB]_0$. 20 rpm, $[MB]_0$ = 25 mg/l, V = 250 ml, $[Fe^{2+}]_0$ = 0 mg/l. Mass ratio $[H_2O_2]_0$:$[MB]_0$: +0:1, ■ 1:1, ▲ 2:1, ◆ 3:1, * 4:1, ● 5:1, □ 6:1, ◊ 7:1, Δ 8:1. **(B)** Flow rate variation. Mass ratio $[H_2O_2]_0$:$[MB]_0$ = 5:1, $[MB]_0$ = 25 mg/l, V = 250 ml, $[Fe^{2+}]_0$ = 0 mg/l rpm: ◆ 10, ■ 20, ▲ 30. **(C)** Variation of methylene blue initial concentration. Mass ratio $[H_2O_2]_0$:$[MB]_0$ = 5:1, 20 rpm, V = 250 ml, $[Fe^{2+}]_0$ = 0 mg/l $[MB]_0$ (mg/l): ● 12.5, ◆ 25, ■ 50, ▲ 75. **(D)** Sample volume variation. Mass ratio $[H_2O_2]_0$:$[MB]_0$ = 5:1, 20 rpm, $[MB]_0$ = 25 mg/l, $[Fe^{2+}]_0$ = 0 mg/l. V (ml): ◆ 125, ■ 250, ▲ 375, x 500. **(E)** Variation of ferrous cation Fe^{2+} initial concentration. Mass ratio $[H_2O_2]_0$:$[MB]_0$ = 5:1, 20 rpm, $[MB]_0$ = 25 mg/l, V = 250 ml $[Fe^{2+}]_0$ (mg/l): ◆ 0, ■ 0.5, ▲ 1, x 2.

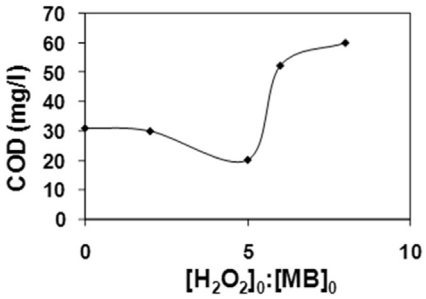

Fig. 4. Chemical oxygen demand (COD) at the end of the treatment versus mass ratio $[H_2O_2]_0$:$[MB]_0$.

corresponding with 20 rpmand the higher Fe^{2+} concentration, 2 mg/l, respectively, the dye was totally degraded within 10 min reaction time.

3.3.2. *Model fitting: kinetic parameters*

As it can be seen in Fig. 3A–E a good agreement between experimental and calculated conversion data was obtained in all series.

Also, for each assay, the kinetic parameters *a* and *b* (from Eq. (18)), corresponding to the limit conversion X_{Lim} and the apparent reaction constant k_r (from Eq. (17)) were obtained. The influence of the different parameters from Eq. (10) on the apparent reaction constant k_r has been analyzed and is shown in Fig. 5A–E.

From Fig. 5A, corresponding to the first experimental series, it is observed that k_r increases until reaching the maximum value for the H_2O_2:MB mass ratio 5:1, corresponding to the stoichiometric ratio. Above this ratio, methylene blue becomes the limited reagent and the hydrogen peroxide excess does not significantly enhance the process. This improvement in the apparent reaction constant up to the stoichiometric ratio can only be due to the increase of the parameter *k*, since the other parameters of Eq. (10), V_r, V_T and C_0, had fixed values in this series. The established relation between the reaction rate and the mass ratio H_2O_2:MB can only be explained by an improvement in some of the different parameters that appears in Eq. (7), where the *k* parameter was defined. In this way, the improvement of parameter *k* must be attributed, basically, to the volumetric transport coefficient k_La (see Eq. (7)), which depends not only on the flow rate, constant in this series, but also on the chemical composition of solution, which varies with the mass ratio H_2O_2:MB.

In Fig. 5B, it is shown that *kr* increases when higher flow rates are used, which agrees with the experimental behaviour of the conversion and supports once again the model hypothesis that considers the mass transfer as the rate determining step. As it has been explain above, this improvement in the value of k_r is due to an increase in the value of the volumetric coefficient k_La.

In Fig. 5C, the kinetic parameter k_r increases when there is a decrease in the methylene blue initial concentration (third experimental series), in good agreement with Eq. (10). This indicates that the reaction will be faster for lower MB concentrations because, when the dye concentration increases, there is a subsequent decrease in the amount of radiation received per mass unit of MB.

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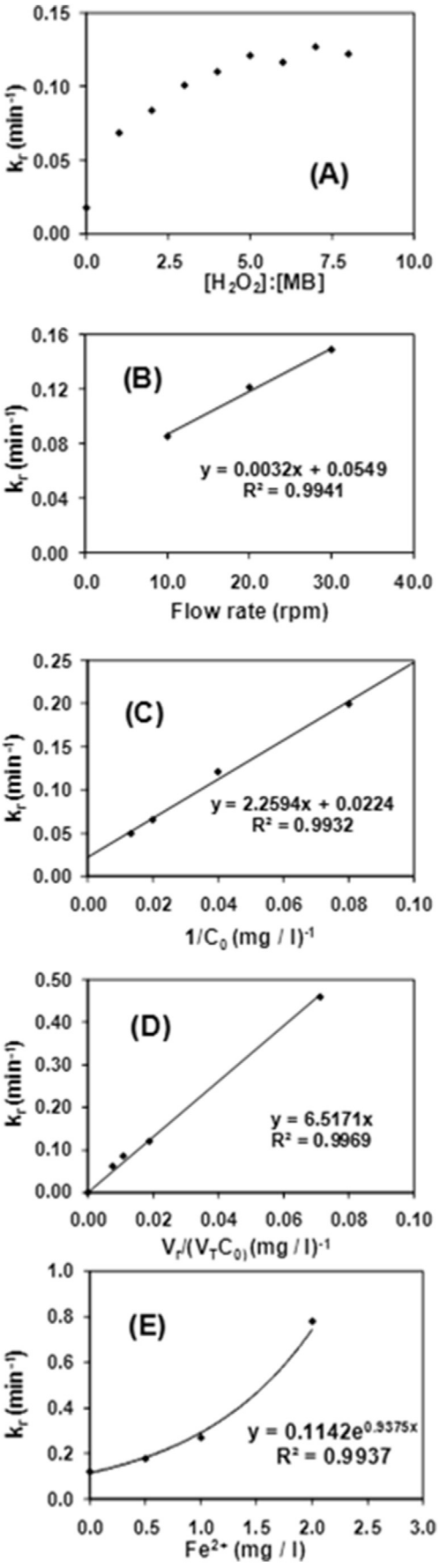

The influence of the ratio V_r/V_T (reaction volume: tank volume, whose sum gives the sample volume, V) on k_r is depicted in Fig. 5D. Taking into account that the reaction volume is constant, because it is the volume of the quartz tube, the mentioned ratio decreases when increasing the sample volume (fourth experimental series), which also decreases the value of k_r, as predicted by Eq. (10).

Finally, in Fig. 5E, corresponding to the last experimental series where Fenton reagent was added, it can be observed that there is an exponential relationship between the kinetic parameter k_r and the concentration of the ferrous cation Fe^{2+}, considerably improving the reaction rate with a slight increase of the catalyst concentration. In this case, being the values of V_r, V_T and C_0 constant, the improvement of k_r can only be due to the increase of k, which is empirically given by:

$$k = k_0 e^{0{,}94Fe^{2+}} \tag{19}$$

being $k = k_0$ in the experimental series where no Fenton reagent was added.

From the fitting shown in Fig. 5E, a new equation for the apparent kinetic constant is obtained:

$$k_r = \frac{V_r}{V_T C_o} \cdot k_0 e^{0{,}94Fe^{2+}} \tag{20}$$

A value of k_0 can be estimated as follows. For the last experimental series it is verified that (see Fig. 5E):

$$\frac{V_r}{V_T C_o} \cdot k_0 = 0,1142 \ \text{min}^{-1}$$

where the following values are also known:

$V_r = 80$ ml
$V_T = V - V_r = 250{-}80 = 170$ ml
$C_0 = 25$ mg/l

From where the final value of k_0 was obtained:

$k_0 = 6.067$ mg l^{-1}min^{-1}

And, by replacing in Eq. (17) the new value of k_r obtained in Eq. (20), a new more general equation for the MB conversion is obtained:

$$X = X_{Lim}\left(1 - e^{-\frac{V_r}{V_T C_0} k_0 \cdot e^{0{,}94Fe^{2+}} t}\right) \tag{21}$$

By defining a new independent variable as:

$$z = \frac{V_r e^{0{,}94Fe^{2+}}}{V_T C_0} t \tag{22}$$

Eq. (21) can be reformulated in the software Sigma Plot V8.0 as follows:

$$X = a\left(1 - e^{-bz}\right) \tag{23}$$

And, this time, $a = X_{Lim}$ and $b = k_0$

This new equation was used to fit the experimental conversion

Fig. 5. **(A)** Influence of the mass ratio $[H_2O_2]_0$:$[MB]_0$ on the kinetic parameter k_r. **(B)** Influence of the flow rate on the kinetic parameter k_r. **(C)** Influence of the initial concentration of methylene blue on the kinetic parameter k_r. **(D)** Influence of the sample volume on the kinetic parameter k_r. **(E)** Influence of the initial concentration of ferrous cation Fe^{2+} on the kinetic parameter k_r.

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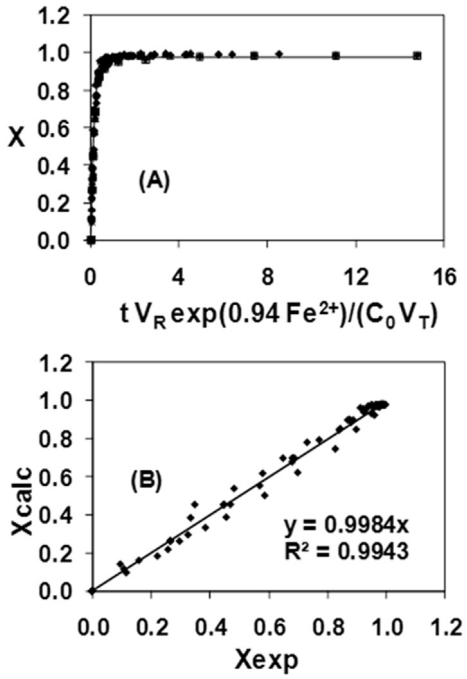

Fig. 6. **(A)** Fitting to Eq. (23) for experimental series 3, 4 and 5. $[MB]_0$ (mg/l): ▲ 12.5, x 25, * 50, ● 75. V (ml): +125, ◆ 250, - 375, ○ 500. $[Fe^{2+}]_0$ (mg/l): ■ 0, Δ 0.5, ◊ 1, □ 2. **(B)** Experimental versus calculated conversions for series 3, 4 and 5.

values from series 3, 4 and 5, with the results shown in Fig. 6A. From the fitting ($R^2 = 0.9971$), parameters a ($= X_{Lim}$) and b ($= k_0$) from Eq. (23) were obtained, with values of 0.978 and 6.628 mg l^{-1} min^{-1}, respectively. It can be observed that the value obtained for k_0 using all experimental data is very close to the one previously estimated with the data of the last experimental series.

Finally, for the series 3, 4 and 5, experimental versus calculated conversion values have been plotted in Fig. 6B, with an excellent fitting to the diagonal and a high determination coefficient ($R^2 = 0.9943$), confirming the validity of the proposed model.

4. Conclusions

Methylene blue (MB) was efficiently degraded with a KrCl flow-through photoreactor in the presence of hydrogen peroxide and Fenton reagent. With the optimum values of mass ratio H_2O_2:MB and flow rate, 5:1 and 20 rpm, respectively, and the higher Fe^{2+} concentration tested, 2 mg/l, the dye was completely degraded within 10 min reaction time.

It was also found that higher initial methylene blue concentrations led to lower conversion values, as expected, since the same amount of UV radiation is available although the amount of dye to be degraded is increased. Also, with higher sample volumes there is a decrease in the conversion values.

A pseudo-first order kinetic model that contemplates all the singularities observed in previous studies, where it has been assumed that the step determining the rate of the photodegradation process is the transfer rate of methylene blue and the driving force the concentration gradient $C - C_{lim}$, was validated with the experimental data. An excellent degree of agreement between calculated and experimental conversion data was obtained ($R^2 = 0.9943$). The main kinetic parameters were determined, with the values of the apparent reaction constant, k_r, supporting the experimental results.

Based on the promising results obtained in the present work for the degradation of methylene blue with excimer technology, together with a deeper knowledge of the process after validating the kinetic model, further research using continuous or semi-continuous systems and different dyes can be undertaken in the future.

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