Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2014.891079

54 (2015) 1862–1871
May

Taylor & Francis
Taylor & Francis Group

Photodegradation of 2-methyl-4-chlorophenol in a KrCl exciplex flow-through photoreactor: a kinetic study

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Received 9 September 2013; Accepted 31 January 2014

ABSTRACT

The removal of 2-methyl-4-chlorophenol (MC), the main photoproduct from 4-chloro-2-methylphenoxyacetic acid oxidation, has been studied with an advanced oxidation treatment and, for this purpose, a KrCl exciplex flow-through photoreactor was tested. Preliminary results show that the use of UV treatment leads to practically total MC degradation in 10, 60 or 90 min for the initial concentrations of 0.2, 1.0 or 2.0 mM, respectively. However, to attain higher elimination of the main photoproducts, 2-MH and 2-MB, addition of an oxidizing agent, such as hydrogen peroxide, is necessary. With molar ratios H_2O_2/MC/1 or higher, smaller concentrations of photoproducts are obtained after the treatment. Additional chemical analysis, such as chemical oxygen demand (COD) suggests that although COD is smaller after the treatment than before, for the highest H_2O_2 concentrations an excess of H_2O_2 remains in the medium, which increases this parameter, being required longer treatment times. Total phenols, pH, and residual chlorine also confirm these results. Besides, a photodegradation mechanism, based on the formation of an unstable intermediate compound that quickly degrades to the photoproducts, was also proposed. A kinetic model was developed and the good level of approximation between experimental and theoretical conversion values for all the experiments confirms the validity of the model.

Keywords: 2-Methyl-4-chlorophenol; Photodegradation; UV; Excilamp; KrCl photoreactor

1. Introduction

2-Methyl-4-chlorophenol (MC) has been identified as the main photoproduct initially formed when an aqueous solution containing 4-chloro-2-methylphenoxyacetic acid (MCPA) is irradiated at 290 nM [1]. In a second step, MC is photolysed into two main photoproducts: methylhydroquinone (MH) and methylbenzoquinone (MB).

MC is used in the industry as an intermediate in the synthesis of other phenoxy herbicides such as 4-chloro-2-methylphenoxy butyric acid or 2-(4-chloro-2-methylphenoxy)-propionic acid [2]. Consequently, MC can be found in the environment from the industrial production, processing and formulation of

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phenoxy herbicides. These herbicides and their derivatives are widely used throughout the world to control weeds and it cannot be presented in ground waters over the maximum levels permitted [3,4]. Besides, MC is a high production chemical figuring in the priority list EEC/793/33 [5].

Among the different methods for the removal of toxic compounds, direct photolysis of pesticides was typically done with high- and middle-pressure conditions of mercury lamps [1,6,7]. Lately, the systems based on the generation of very reactive and oxidizing free radicals, especially hydroxyl radicals have aroused increasing interest due to their high oxidant power. Such systems are commonly named advanced oxidation processes (AOPs) and they have been efficiently applied to the treatment of waters contaminated with chloroaromatic compounds for which biodegradation is generally difficult.

Some of these processes which include application of technologies, such as O_3, O_3/UV, H_2O_2/UV, Fenton, Fenton/UV [8] or UV/TiO_2 [2], have been applied to the oxidation of MC. It has been described [5] that the main primary photoproducts after irradiated MC in aqueous solutions are MB and MH.

Recently, new UV sources called excimer lamps or excilamps have been developed and efficiently used alone [9–11] or in combination with hydrogen peroxide [12,13].

These lamps are based on transitions of exciplex (rare gas halides) or excimer molecules (rare gas or halogen dimmers) and their main advantages are the emission in a narrow-band UV radiation, as well as the absence of toxic mercury and the long lifetime, among others [14,15]. However, the main problem with these new technologies until now is that their use has been limited to laboratory scale, discontinuous systems and small reaction volumes. Optimum conditions for a scaling-up need to be determined and a proper kinetic study and system simulation can be very useful in order to do so.

These kinds of lamps have been applied for the 4-chlorophenol oxidation [10,12,16] and recently the effect of UV radiation of discontinuous KrCl and XeBr photodegradation of 4-chlorophenol-2-methylphenoxyacetic acid was studied [17].

But as far as we know there is no study about the oxidation of MC with these lamps, for that, in the present work, a KrCl flow-through photoreactor (previously applied [18] for 4-chlorophenol removal) has been used for the removal of MC and UV/H_2O_2 treatment has been tested with the aim of optimizing the experimental conditions for higher reaction volumes. Additionally, important reaction parameters, such as pH, chlorine ion, COD and total phenol concentrations, have been monitorized.

2. Materials and methods

2.1. Reagents

The following chemicals and reagents were obtained from Sigma-Aldrich Co: MC (97%), MB (98%), MH (98%) and hydrogen peroxide (35%). Other chemicals were of analytical grade and were used without further purification.

2.2. Photodegradation treatment and samples analysis

A KrCl photoreactor, purchased from the Institute of High Current Electronics of Tomsk (Russia), has been used in all assays. The lamp has a wavelength of maximum emission at 222 nM and an irradiation zone length of 30 cm. Fig. 1(a) shows a scheme of the photoreactor.

The MC initial solution at the required concentration was pumped from a stirred feed tank to the photoreactor (Fig. 1(b)). In the UV/H_2O_2 assays, the corresponding volumes of hydrogen peroxide were added to the feed tank together with the MC. The photodegradation process takes place only along the length of the irradiation zone of the lamp and the effluent of photoreactor was recycled to the feed tank, so that the system acts as a batch reactor (flow-through reactor). All the experiments were done at room temperature (23–25°C), flow rate of 46 mL min^{-1}, with an operational time of 120 min and with a total volume of 500 mL. Duplicates experiments were carried out and average values were obtained. Standard deviation calculated for the whole set of data was 2.27%.

Samples were taken at different reaction times (0, 2, 4, 8, 15, 30, 45, 60, 90 and 120 min) from the feed tank, being this one constantly stirred to assure homogenization. The samples were taken to 2 mL vials and the MC remaining after treatment, as well as the major photoproducts of the photodegradation process, MB and MH, were determined by HPLC analysis using a Waters chromatograph with a 2996 diode array detector and a C18 reverse-phase column. The mobile phase was a mixture of methanol and 4 mM sulphuric acid (50:50 v/v) with a flow rate of 1 mL min^{-1} [19]. Table 1 shows the different retention times and wavelengths used in the analysis of MC and the two main photoproducts, MB and MH. In the determination of calibration curves, for MC and each one of two main photoproducts, standard samples, in the concentration range from 0.005 to 0.5 mM, were used.

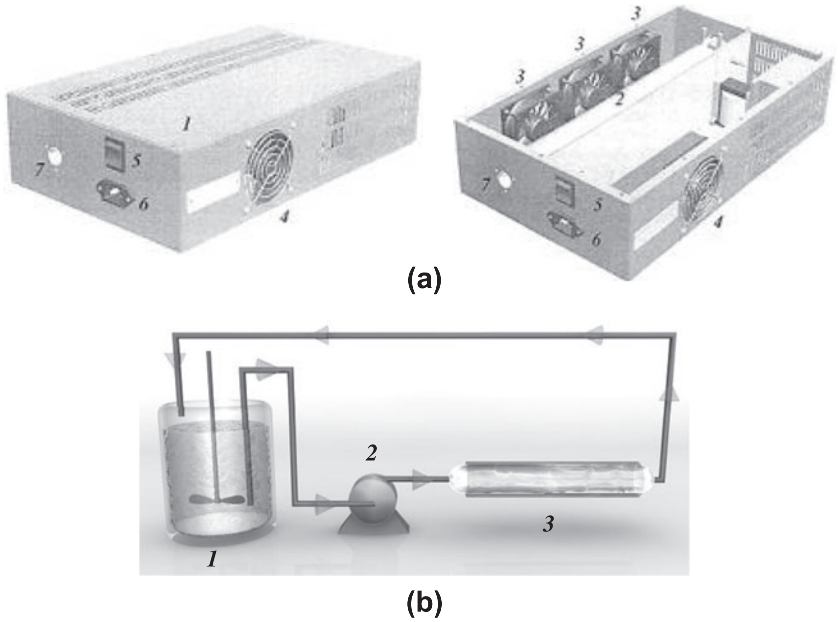

Fig. 1. (a) Scheme of the KrCl flow-through photoreactor: (1) box; (2) lamp bulb; (3) fans for bulb cooling; (4) fan for power supply cooling; (5) switcher; (6) connecting cable slot; (7) hole for quartz tube. (b) Scheme of experimental system: (1) feed tank, (2) peristaltic pump, (3) excimer lamp.

Table 1
Retention time and wavelength for the 2-methyl-4-chlorophenol and the different photoproducts

Compound	Retention time (min)	Wavelength (nm)
2-Methyl-4-chlorophenol	15.2	225
Methylbenzoquinone	3.1	248
Methylhydroquinone	2.4	290

By this, 0.005 mM can be established as a reliable method detection limit (MDL) for the different compounds. For the analysis of more concentrated samples, dilution was made.

2.3. Total phenol, hydrogen peroxide, COD and chlorine concentration determination

Total phenol concentration in solution was estimated from the blue colour produced with Folin–Ciocalteu's reagent. About 0.5 mL of reagent and 2.0 mL of (10%, wt/vol) sodium carbonate solution were added to 1.0 mL of test solution. After 10 min, 1 mL of the solution was diluted to 5 mL with water, and the absorbance at 620 nM was recorded [20].

To determine hydrogen peroxide concentration, 5 mL of H_2SO_4 (1:4) and 1 g KI were added to 10 mL of solution with hydrogen peroxide and was left for 30 min, after that titrometric determination with $Na_2S_2O_3$ (0.1 m) was done. Concentration of H_2O_2 was calculated according to the formula m (H_2O_2)=V ($Na_2S_2O_3$) x0.001701 [21].

COD was measured using commercial vials of mid range (0–1,500 mg L^{-1}) and low range (0–150 mg L^{-1}) and a HI 83099 COD and multiparameter direct reading spectrophotometer. Chlorine ion was determined by ionic chromatography.

3. Theoretical analysis: kinetic model

3.1. Proposed mechanism

Fig. 2 shows a scheme of the mechanism proposed for the photodegradation of MC, which is similar to the one previously proposed [18] for studying 4-chlorophenol photodegradation with this photoreactor. This mechanism is based on the formation of an intermediate compound that quickly degrade to the identified primary photoproducts, mainly MB and MH, which will degrade further to produce other photoproducts that will finally degrade to CO_2 and H_2O. From this mechanism, the mass balance equations for MC, the intermediate (I) and the different primary photoproducts (MB and MH) can be formulated and the corresponding equations of concentrations change vs. time can be obtained, as described below.

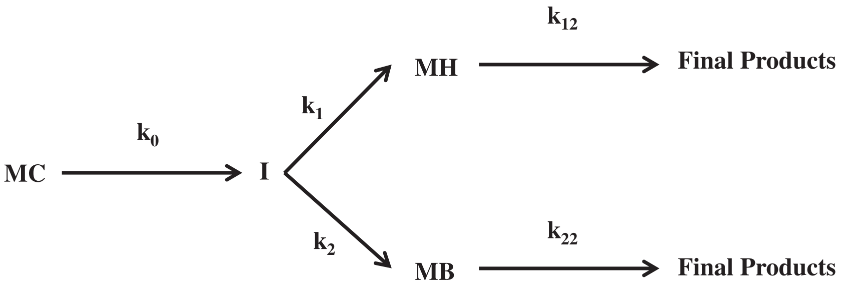

Fig. 2. Proposed photodegradation mechanism for MC.

3.2. *Variation of 2-methyl-4-chlorophenol concentration with time*

From the proposed mechanism, and taking into account the behaviour of experimental data, a first-order kinetic has been assumed for the degradation of MC, which leads to:

$$[\mathrm{MC}] = [\mathrm{MC}]_0 \, e^{-k_0 t} \tag{1}$$

where $[\mathrm{MC}]_0$ is the initial concentration of MC and [MC] the one at time t, being k_0 the first-order kinetic constant.

3.3. *Intermediate compound I*

In the mechanism, an intermediate and very unstable compound, I, is postulated. It is formed from the MC and during the photodegradation process it leads to the primary photoproducts MB and MH.

For the concentration of the intermediate compound, [I], and by defining an overall constant, k_i, as:

$$k_I = \sum_{i=1}^{2} k_i \tag{2}$$

it is verified that,

$$\frac{d[I]}{dt} = k_0[\mathrm{MC}] - k_I[I] \tag{3}$$

with the initial condition,

$$t = 0;\ [I] = 0 \tag{4}$$

By integrating Eq. (4), the concentration of intermediate compound, *I*, is obtained

$$[I] = \frac{k_0[\mathrm{MC}]_0}{k_I - k_0}\left(e^{-k_0 t} - e^{-k_I t}\right) \tag{5}$$

3.4. *Primary photoproducts: methylbenzoquinone and methylhydroquinone*

For the concentrations of each one of the primary photoproducts, $[P_i]$ (= [MH] and [MB], respectively), formed form the intermediate compound *I*, it is verified that:

$$\frac{d[P_i]}{dt} = k_i[I] - k_{i2}[P_i] \tag{6}$$

with the initial condition,

$$t = 0;\ [P_i] = 0 \tag{7}$$

This is a linear differential equation with constant coefficients where the intermediate concentration, [*I*], is given by Eq. (5), so it can be solved with the following result:

$$[P_i] = \frac{k_i k_0 [\mathrm{MC}]_0}{k_I - k_0}\left(\frac{1}{k_{i2} - k_0}\left(e^{-k_0 t} - e^{-k_{i2} t}\right) \times \frac{1}{(k_{i2} - k_I)}\left(e^{-k_I t} - e^{-k_{i2} t}\right)\right) \tag{8}$$

In this equation, the values 1 or 2 for subscript i correspond with MB and MH, respectively.

3.5. *Model fitting: general procedure*

The fitting of the proposed model to the experimental results has been done using the software Sigma Plot V8.2. For the fitting of experimental progress curves of MC, Eq. (1) has been used. However, some modifications have been introduced in Eq. (8) to make it suitable to be used in the previously mentioned software. So, Eq. (8) can be rearranged as follows:

$$[P_i] = \frac{k_i k_0 [\mathrm{MC}]_0}{(k_I - k_0)(k_{i2} - k_I)} \times \left(e^{-k_{i2}t} - \frac{k_{i2} - k_0}{k_I - k_0} e^{-k_I t} + \frac{k_{i2} - k_I}{k_I - k_0} e^{-k_0 t} \right) \tag{9}$$

And, according to the nomenclature used by this software for the different parameters, this equation must be rewritten as:

$$[P_i] = a\left(e^{-bt} + ce^{-dt} - (1 + c)e^{-ft}\right) \tag{10}$$

Being,

$$a = \frac{k_i k_0 [\mathrm{MC}]_0}{(k_{i2} - k_0)(k_{i2} - k_I)};\ b = k_{i2};$$
$$c = \frac{k_{i2} - k_0}{k_0 - k_I};\ d = k_I \text{ and } f = K_0 \tag{11}$$

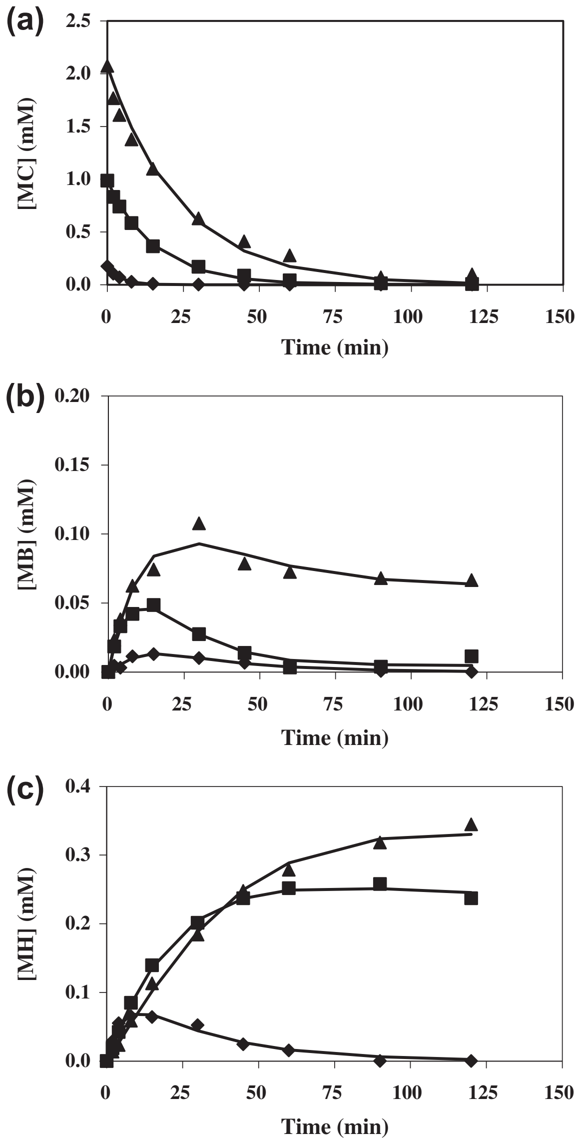

Fig. 3. Experimental and theoretical concentrations of substrate and photoproducts vs. time at different initial MC concentrations: (▲) 2 mM, (■) 1 mM and (♦) 0.2 mM and (−) model. (a) MC, (b) MB and (c) MH.

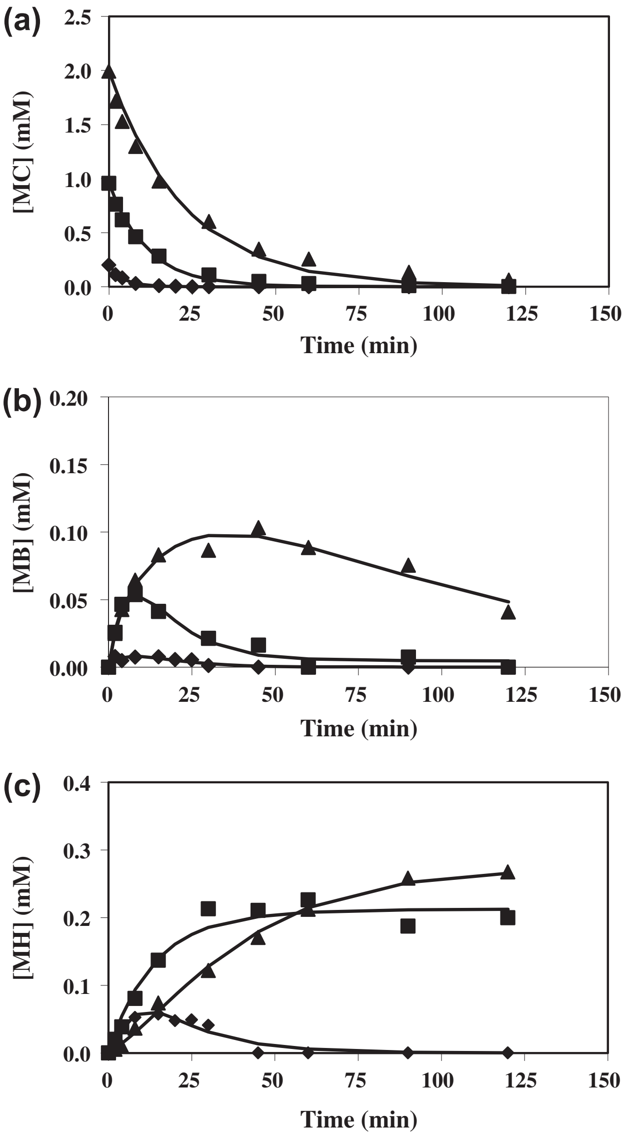

Fig. 4. Experimental and theoretical concentrations of substrate and photoproducts vs. time at different initial hydrogen peroxide and MC concentrations and molar ratio 1:1: (▲) 2 mM, (■) 1 mM, (♦) 0.2 mM and (−) model. (a) MC, (b) MB and (c) MH.

4. Experimental results: influence of operational conditions

4.1. Variation of initial 2-methyl-4-chlorophenol concentration

In the first experimental series, in the absence of hydrogen peroxide, three initial MC concentrations were tested: 0.2, 1.0 and 2.0 mM. Experimental results are shown in Fig. 3 with dots, where it can be observed that although at the end of the treatment all the substrate is removed in 10, 60 or 90 min depending on the initial MC concentration, high MB concentrations still remain after the 120 min of treatment with the highest MC concentration (2.0 mM). And high concentrations of MH remain in the medium after the treatment, except for the lowest MC concentration tested. These results improve the ones obtained in a previous work [8], where the degradation of MC using only a UV mercury lamp, which emits its maximum radiation at 365 nM, was not effective in degrading the compound and the use of various oxidants are proposed.

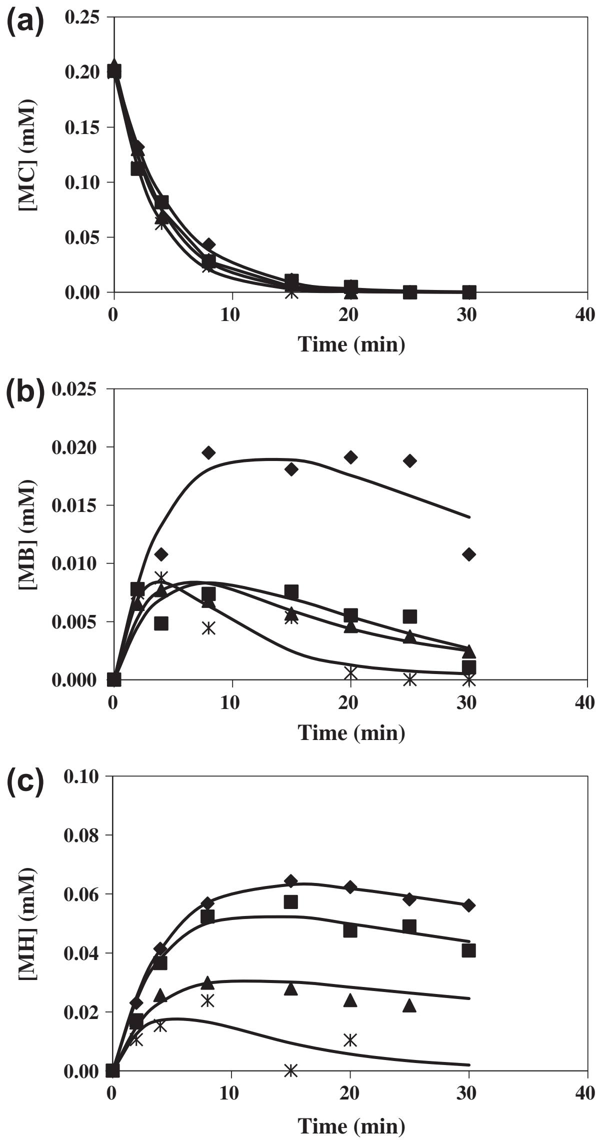

Fig. 5. Experimental and theoretical concentrations of substrate and photoproducts vs. time at initial MC concentration of 0.2 mM and different H_2O_2:MC molar ratios: (*) 10:1, (▲) 5:1, (■) 1:1, (♦) 0:1 and (−) model. (a) MC, (b) MB and (c) MH.

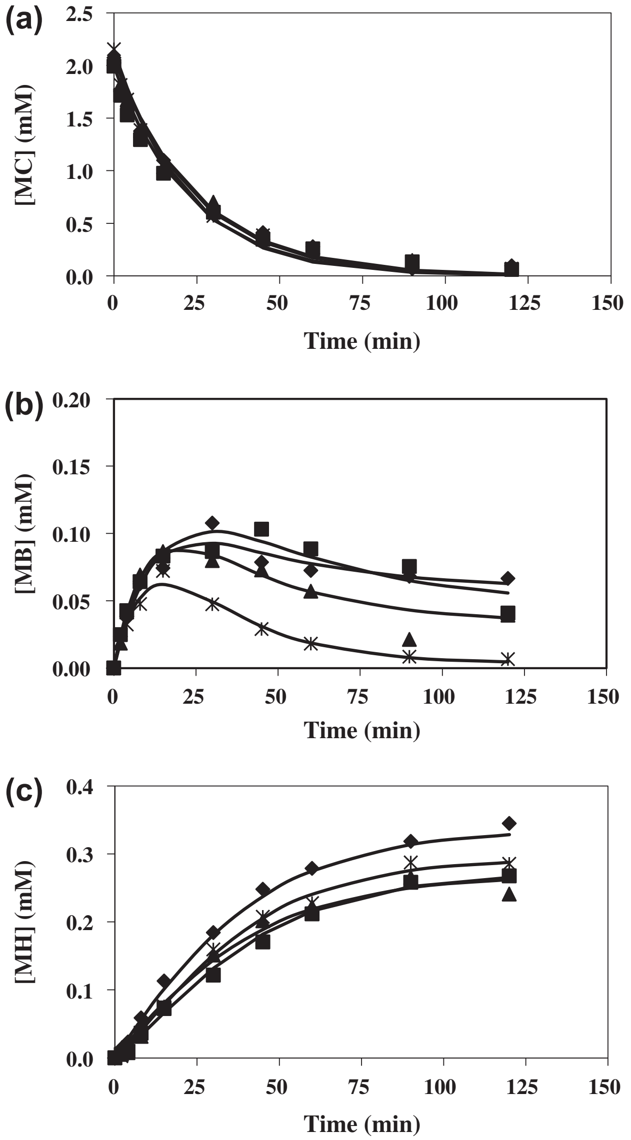

Fig. 6. Experimental and theoretical concentrations of substrate and photoproducts vs. time at initial MC concentration of 2 mM and different H_2O_2:MC molar ratios: (*) 10:1, (▲) 5:1, (■) 1:1, (♦) 0:1 and (−) model. (a) MC, (b) MB and (c) MH.

To attain higher elimination degree of MB and MH, more photodegradation time or the addition of an oxidizing agent is necessary, such as the hydrogen peroxide.

4.2. Variation of 2-methyl-4-chlorophenol and H_2O_2 concentrations with molar ratio 1:1

In the second experimental series, experiments were carried out with variable concentrations of MC and hydrogen peroxide (2.0, 1.0 and 0.2 mM) at molar ratio of 1:1. Results are depicted in Fig. 4.

From Fig. 4(a), it is observed that MC concentration variation over time is similar to the obtained in the absence of hydrogen peroxide (Fig. 3(a)). However, Figs. 4 (b) and (c) compared with Figs. 3(b) and (c) show that in the presence of hydrogen peroxide, despite no total elimination is attained, MB and MC concentrations after the treatment are smaller than without this oxidizing agent.

4.3. Variation of H_2O_2: 2-methyl-4-chlorophenol molar ratio

To improve the removal degree of the photoproducts, a third series of experiments were developed by varying the molar ratio H_2O_2:/MC from 0:1 to 10:1, and for MC initial concentrations of 0.2 and 2.0 mM, results are shown in Figs. 5 and 6, respectively.

Figs. 5 and 6 show that the H_2O_2/ MC molar ratio has not a significant influence on MC, while the removal of the photoproducts, especially MB, is enhanced with the highest molar ratios tested. Fig. 6(c) shows how MH degradation decreases when the highest molar ratio H_2O_2/MC is used. This behaviour agrees with the one previously reported [8], where an optimum H_2O_2 dosage was described.

4.4. Chemical analysis

In Table 2, the results obtained from different chemical assays are summarized, such as total phenols and hydrogen peroxide concentration, pH and COD values before and after the treatment and residual chlorine concentration after the treatment.

In this table, it can be observed that COD after the treatment is still high, although some reduction is achieved with the treatment. Besides, total phenol concentration after the treatment is slightly smaller with hydrogen peroxide than without it for the same MC initial concentrations. Results also show that the increase of Cl^{-} is consistent with the MC degradation, being pH smaller with the higher ion chlorine concentrations, which agrees with a previous study [17].

5. Model fitting: results and discussion

Figs. 3–6 show the results obtained in the fitting of the experimental concentrations of MC and the primary photoproducts to Eqs. (3) and (10). In these figures, the points correspond to the experimental values of concentration and the continuous lines with the calculated ones using the model. In all cases an excellent degree of agreement is achieved.

Table 2
COD values before and after treatment for all the experiments done

$[MC]_0$ (mM)	$[H_2O_2]_0$ (mM)	COD (b.t.)	COD (a.t.)	[Total phenols] (b.t.)	[Total phenols] (a.t.)	$[H_2O_2]$ (mM) (a.t.)	pH (b.t.)	pH (a.t.)	Cl^{-1} (ppm) (a.t.)
0.2	0.0	50	43	0.2	0.14	0.00	5.87	3.51	6.59
1.0	0.0	266	213	1.0	0.97	0.00	5.85	2.85	34.87
2.0	0.0	507	329	2.0	1.60	0.00	5.76	2.66	55.57
0.2	0.2	76	28	0.2	0.13	0.10	5.85	3.47	7.58
1.0	1.0	252	218	1.0	0.88	0.35	5.86	2.79	35.00
2.0	2.0	580	391	2.0	1.52	0.65	5.82	2.73	59.99
0.2	0.0	50	43	0.2	0.14	0.00	5.87	3.51	6.59
0.2	0.2	76	28	0.2	0.13	0.10	5.85	3.47	7.58
0.2	1.0	91	59	0.2	0.09	0.35	6.06	3.42	7.34
0.2	2.0	102	68	0.2	0.08	0.70	5.75	3.35	8.78
2.0	0.0	507	329	2.0	1.60	0.00	5.76	2.66	55.57
2.0	2.0	580	391	2.0	1.52	0.65	5.82	2.73	59.99
2.0	10.0	660	517	2.0	1.54	3.20	5.46	2.66	53.88
2.0	20.0	886	782	2.0	1.26	6.07	5.58	2.67	59.61

b.t.: before treatment; a.t. : after treatment.

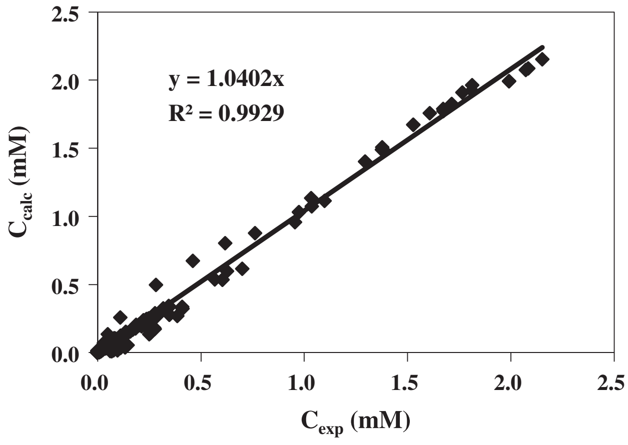

Fig. 7. Calculated vs. experimental concentrations.

To validate the model, for all the experimental data, experimental values of concentration were plotted vs. calculated ones. Fig. 7 shows the results where high proximity to the diagonal ($[C_{calc}] = 1.0402[C_{exp}]$, $R^2 = 0.9929$) confirms the validity of the model.

Otherwise, the kinetic parameters *d* and *f*, corresponding to the values of the intermediate compound and MC degradation rate constants, respectively, are shown in Table 3.

From Table 3, it can be observed that the values of the parameters *d* and *f* increase when lower MC is used. This confirms that initial MC concentration has a significant influence on the kinetic parameters. The same behaviour was observed in a previous work [16].

The same tendency is observed in the series of variation of MC and hydrogen peroxide concentrations with molar ratio 1:1, where the values of the parameters *d* and *f* increase when MC concentration decrease.

In the series where molar ratio H_2O_2: MC was varied for two initial MC concentrations of 0.2 and 2.0 mM (see Table 3) kinetic parameter *f* slightly increase ($[MC]_0 = 0.2$ mM) or practically keep constant ($[MC]_0 = 2.0$ mM) when higher molar ratio H_2O_2: MC was used. Whereas parameter *d* clearly increase with the highest molar ratio H_2O_2: MC used. This behaviour can also be appreciated in Figs. 5 and 6, where it can be observed that although molar ratio H_2O_2: MC has no a significant influence on MC degradation, it improves the removal of photoproducts.

6. Conclusions

Practically complete degradation of both MC and its photoproducts was attained using a KrCl flow-through photoreactor in combination with hydrogen peroxide, for a substrate concentration of 0.2 mM and under the following experimental conditions: 500 mL reaction volume, flow rate of 46 mL min^{-1}, molar ratio H_2O_2/MC of 10/1. Although total removal, until the method determination limit, of MC is obtained without hydrogen peroxide, the presence of this oxidizing agent improved the photoproducts degradation.

Chemical analysis showed that COD is smaller after the treatment than before in all cases. However, for the treatment times tested, high values of COD still remain in the medium after the treatment due to the presence of residual concentrations of photoproducts and an excess of hydrogen peroxide. Also, total phenols concentration after the treatment is smaller in the presence of hydrogen peroxide and pH values decrease with the increasing of ion chlorine concentration.

The proposed photodegradation mechanism, based on the formation of an unstable intermediate compound that quickly degrades to the photoproducts, as well as its kinetic model, were validated with

Table 3
Model parameters for the different series: series 1, variation of MC concentration; series 2, variation of MC and hydrogen peroxide concentrations with molar ratio 1:1; series 3, variation of H_2O_2:MC molar ratios with initial MC concentration of 0.2 mM; series 4, variation of H_2O_2:MC molar ratios with initial MC concentration of 2 mM

	2 mM		1 mM		0.2 mM	
Series	d (min^{-1})	f (min^{-1})	d (min^{-1})	f (min^{-1})	d (min^{-1})	f (min^{-1})
1	0.0000	0.0415	0.0000	0.0643	0.0692	0.2395
2	0.0562	0.0439	0.0753	0.0888	0.1291	0.2472

	10:1		5:1		1:1		0:1	
	d (min^{-1})	f (min^{-1})	d (min^{-1})	f (min^{-1})	d (min^{-1})	f (min^{-1})	d (min^{-1})	f (min^{-1})
3	0.1565	0.2839	0.0521	0.2533	0.0324	0.2472	0.0151	0.2207
4	0.0032	0.0464	0.0022	0.0407	0.0018	0.0439	0.0012	0.0415

an excellent degree of agreement between experimental and calculated concentration data ($[C_{\mathrm{calc}}] = 1.0402[C_{\mathrm{exp}}]$, $R^2 = 0.9929$). The main kinetic parameters, *d* and *f* (corresponding to the values of the degradation rate constants for the intermediate compound and MC, respectively) were determined with their values also supporting the experimental results.

Acknowledgements

This work is a result of the 08683/PI/08 research project, financed by the Foundation Séneca, Agency of Science and Technology of the Region of Murcia (Spain), in the II PCTRM 2007-2010, by Tomsk State University (The Priority Direction of Development No. 1, the activities No. 3). M.D. Murcia was beneficiary of Juan de la Cierva scholarship from MICINN.

Nomenclature

MB — methylbenzoquinone
MC — 2-methyl-4-chlorophenol
MCPA — 4-chloro-2-methylphenoxyacetic acid
MH — methylhydroquinone
[MB] — concentration of methylbenzoquinone at a time *t*, (mM)
[MC] — concentration of 2-methyl-4-chlorophenol at a time *t*, (mM)
[MH] — concentration of methylhydroquinone at a time *t*, (mM)
$[\mathrm{MB}]_0$ — initial concentration of methylbenzoquinone, (mM)
$[\mathrm{MC}]_0$ — initial concentration of 2-methyl-4-chlorophenol, (mM)
$[\mathrm{MH}]_0$ — initial concentration of methylhydroquinone, (mM)
a — parameter defined in Eq. (11) (dimensionless)
b — parameter defined in Eq. (11) (min^{-1})
c — parameter defined in Eq. (11) (dimensionless)
d — parameter defined in Eq. (11) (min^{-1})
f — parameter defined in Eq. (11) (min^{-1})
I — intermediate compound formed from 2-methyl-4-chlorophenol
[I] — concentration of intermediate compound I at a time *t*, (mM)
k_0 — first-order kinetic constant for 2-methyl-4-chlorophenol, (min^{-1})
k_I — consumption constant of intermediate compound I, (min^{-1})
k_i — formation constant of primary photoproducts, (min^{-1})
k_{i2} — consumption constant of primary photoproducts, (min^{-1})
$[P_i]$ — concentration of primary photoproducts at a time *t*, (mM)
t — time (min)

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