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Photodegradation of 4-chlorophenol using XeBr, KrCl and Cl_2 barrier-discharge excilamps: A comparative study

M. Gomez [a,b], M.D. Murcia [a,b], N. Christofi [a], E. Gomez [b], J.L. Gomez [b,*]

[a] *Pollution Research Unit, School of Life Sciences, Edinburgh Napier University, Merchiston Campus, Edinburgh EH10 5DT, Scotland, UK*
[b] *Department of Chemical Engineering, Murcia University, 30071 Murcia, Spain*

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ABSTRACT

A study on 4-chlorophenol (4CP) photodegradation has been carried out using UV radiation delivered from three different excimer lamps: XeBr, KrCl and Cl_2, with maximum emission wavelengths of 283, 222 and 259 nm, respectively. The influence of initial 4-chlorophenol concentration on the photodegradation process was examined with pollutant concentrations ranging from 50 to 500 mg L^{-1}, and degradation progress was followed by determining the residual 4-chlorophenol, as well as that of the main photoproducts, hydroquinone (HQ) and benzoquinone (BQ). All excilamps were able to degrade 4CP. XeBr and the KrCl excilamps achieved almost total 4-chlorophenol degradation, with the removal efficiency of the Cl_2 excilamp being considerably lower. The KrCl excilamp, in spite of requiring longer exposure times compared with the XeBr, needed a much lower UV dose and, consequently, a lower energy consumption for degradation and, as a result, has been considered the most effective and efficient in 4CP removal. Additionally, and by defining the limit of 4-chlorophenol degradation, a modified pseudo-first order kinetic model was used to fit the kinetics of the 4-chlorophenol degradation process where good agreement between experimental data and those predicted by the model was found. Shielding effects are considered to have an influence on 4-chlorophenol degradation as there is a decrease in the pseudo-first order rate constant with increasing 4-chlorophenol concentrations for the three excilamps. In addition, there is a noticeable decrease in the maximum removal of 4-chlorophenol for the Cl_2 excilamp due to the same effect.

1. Introduction

Chlorophenols (CPs) are commonly used in particular applications, as preservative agents for wood, paints and vegetable fibers or disinfectants. They are also generated by a range of industrial processes such as high-temperature coal conversion, petroleum refining and the manufacture of plastics, resins, textile, iron, steel and paper. They constitute a group of predominant environmental pollutants that can be extremely harmful to organisms at very low concentrations [1–3]. Their removal from waste streams includes the use of physical, chemical and biological methods, embracing incineration, adsorption onto activated carbon, chemical, enzymatic and photochemical oxidation, solvent extraction, microbial degradation and others [4–15]. Despite extensive research, convenient, robust and cost effective treatment technologies for the pollutants have still to be implemented, and, there is a continued need to develop effective systems.

In the removal of these toxic organic pollutants from wastewater, low- and medium-pressure UV mercury lamps have been widely used in the photolytic degradation of CPs [16,17]. More recently, the development of novel excimer lamps (excilamps) driven by dielectric barrier discharge [18], show promise because of the range of excimer molecules (rare gas or halogen dimers) and exciplex (rare gas halides) emitting radiation between 172 and 317 nm [19] providing wavelengths to match those of specific pollutant bonds where absorption facilitates break. This is the main distinction between the excilamps and traditional UV mercury lamps: with the use of excimer lamps, up to 80% of the total radiant flux or even more can be concentrated in a relatively narrow emission band of the corresponding molecule. Excilamps are advantageous in many other ways: they do not use elemental mercury, have a long lifetime, geometric freedom and high photon flux [20,21].

Excimer lamps have been proven to be of great interest in wastewater treatment [21,22], since the majority of components contained in water absorb radiation in the same range of the excilamp emissions. The UV radiation absorbed leads to excitation of the singlet electronic states of dissolved substances, and these excited states may then relax with formation of triplet states that will finally lead to bond homolysis or heterolysis. The values of disso-

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* Corresponding author. Tel.: +34 868887351; fax: +34 868884148.
E-mail address: carrasco@um.es (J.L. Gomez).

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Nomenclature

a	kinetic model parameter defined in Eq. (10) (dimensionless)
b	kinetic model parameter defined in Eq. (10) (min^{-1})
BQ	benzoquinone
4CP	4-chlorophenol
HQ	hydroquinone
k	pseudo-first order rate constant for 4-chlorophenol photodegradation (min^{-1})
t	reaction time (min)
X_{BQ}	benzoquinone conversion (dimensionless)
X_{4CP}	4-chlorophenol conversion (dimensionless)
X_{4CPmax}	maximum 4-chlorophenol conversion (dimensionless)
X_{HQ}	hydroquinone conversion (dimensionless)
[BQ]	concentration of benzoquinone at time t (mM)
[4CP]	concentration of 4-chlorophenol at time t (mM)
$[\text{4CP}]_{\text{Lim}}$	final non-degraded limit concentration of 4-chlorophenol (mM)
$[\text{4CP}]_0$	initial concentration of 4-chlorophenol (mM)
[HQ]	concentration of hydroquinone at time t (mM)

ciation energies of several chemical bonds, including the C–Cl and O–H bonds, and corresponding energies of UV photons of excimer and exciplex molecules can be found in reference [20]. This absorption of radiation and the subsequent breaking of chemical bonds lead to the initiation of photoinduced chemical reactions, with substrate oxidation and, finally, complete mineralization of the organic matter [23,24].

In the specific case of chlorophenolic pollutants, most authors agree that the breaking of the C–Cl bond is the first step of the photolytic reaction, when oxidative mechanisms which produce OH radicals are employed, leading to the formation of various intermediates [25]. Hydroquinone and benzoquinone are the main photoproducts that will degrade to other compounds of low molecular mass in further steps until complete mineralization is reached. According to some authors [25–27], a 4-hydroxyphenyl is the resultant radical or ionic intermediate form of the photodissociation of the C–Cl bond. In an aqueous environment this unstable product will react with oxygen atoms or water molecules leading to the formation of the mentioned mayor photoproducts, hydroquinone and 1,4-benzoquinone.

For process efficiency evaluation in wastewater treatment involving excimer lamps, attention must be focused not only on the pollutant removal efficiency, but also on energy consumption [23]. Ratios of substrate removal to energy consumption give more realistic information concerning the final aim of utilising the process at commercial scale.

Concerning the kinetics of the 4-chlorophenol degradation process, the hypothesis that the first step in degradation involves the cleavage of the C–Cl bond has resulted in a simple pseudo-first order kinetic model for the 4-chlorophenol consumption rate, that has been widely used in most a number of studies [16,28,29].

In the present work, three different excilamps (XeBr, KrCl and Cl_2) have been compared to determine their effectiveness in 4-chlorophenol degradation, taking into account not only the removal efficiency, but also the energy requirements. Additionally, and considering the limit of 4-chlorophenol degradation due to the shielding effect of the photoproducts, a modified pseudo-first order kinetic model has been derived and is proposed for 4-chlorophenol degradation enabling the fitting of the experimental data as well as the estimation of the model parameters for the three excilamps under all experimental conditions tested.

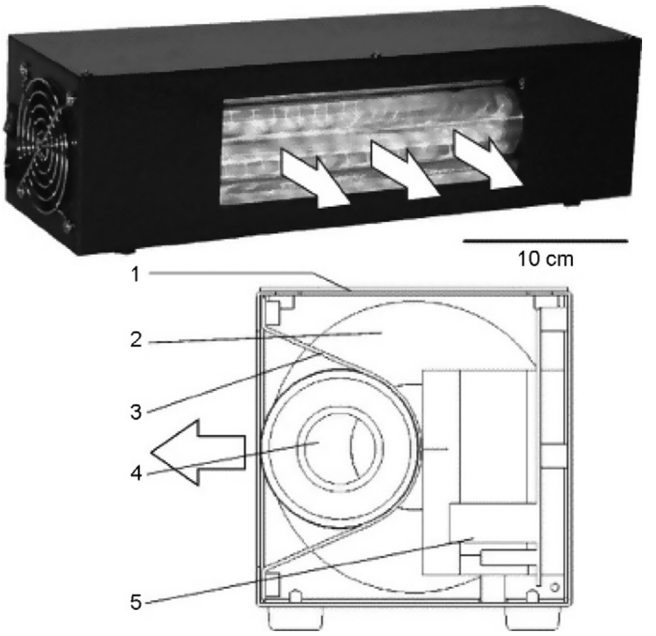

Fig. 1. General view of a barrier-discharge excilamp: (1) housing; (2) fan; (3) reflector; (4) coaxial excilamp bulb; (5) power supply. White arrows show the direction of light output (Sosnin et al. [20]).

2. Materials and methods

4-Chlorophenol (purity 99%) was purchased from Sigma–Aldrich Fine Chemicals. Three barrier-discharge excilamps (purchased from the Institute of High Current Electronics of the Siberian Branch, Russian Academy of Sciences) were used in the photodegradation of 4-chlorophenol. These were XeBr, KrCl and Cl_2 excilamps emitting maximum UV radiation at 283, 222 and 259 nm, respectively. The excilamps were of cylindrical geometry covered by a metal case having an UV exit window with an area of 75 cm^2 (Fig. 1). The exit window was oriented vertically in close proximity to a quartz tube (2.2 cm) with an operating length of 22 cm and external diameter of 2.6 cm. 4-Chlorophenol at the required concentrations, ranging from 50 to 500 mg L^{-1} (0.389–3.891 mM) were dissolved in distilled water, placed into the quartz tube covered with a reflector and irradiated at room temperature (23–25 °C) under static conditions and for exposure times ranging from 20 to 90 min.

The output power of the excilamp was measured with a H8025-222 photodetector (Hamamatsu Photonics KK) and was tested using an electrochemical actinometer of potassium ferrioxalate, $K_3Fe(C_2O_4)_3{\cdot}3H_2O$, as described in the literature [30]. The average radiation intensity delivered to the solution was 17.12, 2.47 and 0.85 mW cm^{-2} for the XeBr, KrCl, and Cl_2 excimer lamps, respectively. From the radiation intensity and exposure time of the samples, fluence for the different experiments was also estimated.

To follow the time course of the photodegradation process, samples were analyzed after the following exposure times: 1, 2, 3, 5, 10, 20, 30, 40, 60 and 90 min. Each time corresponds with an individual experiment, being the initial 4CP concentration the same for all the experiments associated to the same time course curve. In this way, there is no variation of the total reaction volume along the different experimental data. Also, duplicates were done for all the experiments and average values were obtained. Standard deviation was calculated for the whole set of data corresponding to each excilamp, being the results 3.98, 2.49 and 3.01% for the KrCl, XeBr and Cl_2, respectively.

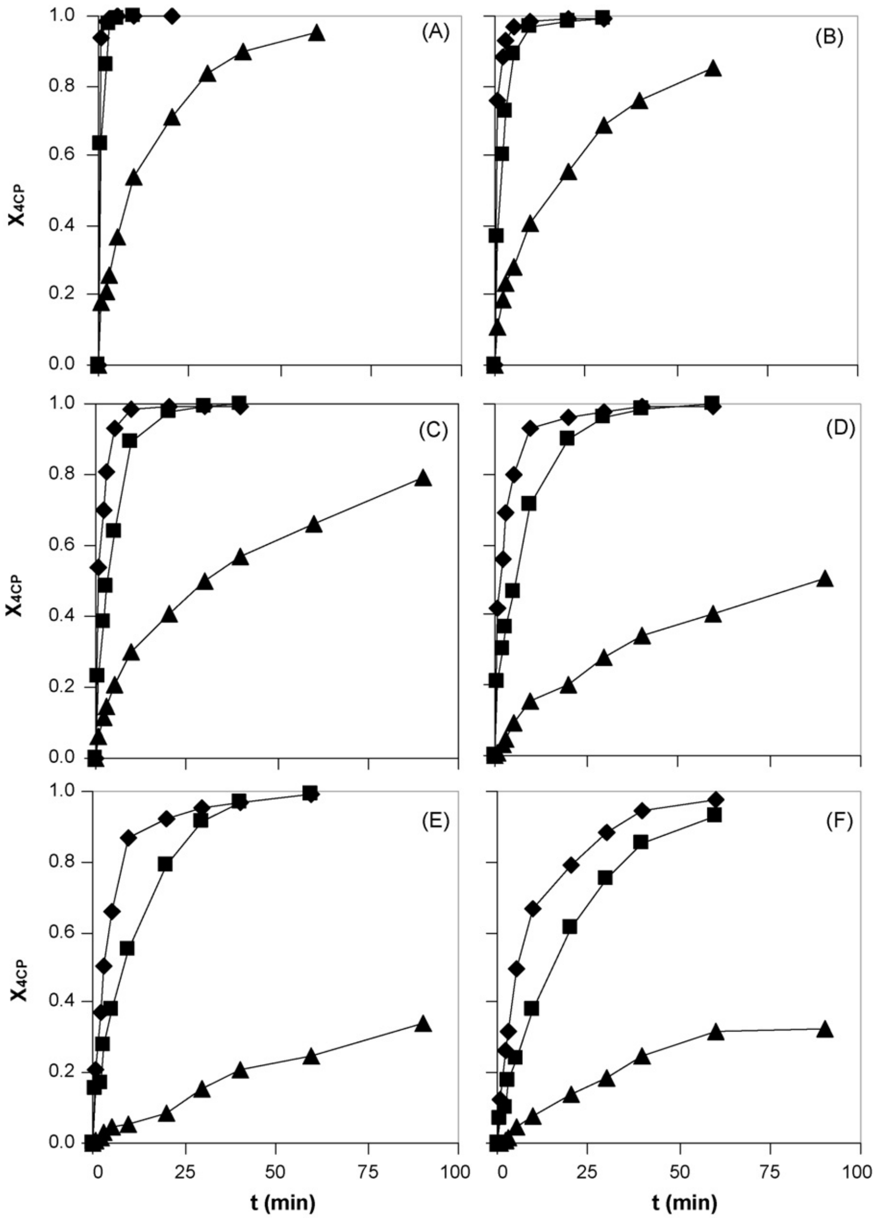

Fig. 2. 4CP conversion vs time. Comparison of the results obtained with the three excilamps for all 4CP initial concentrations tested: (A) 50 mg L^{-1}; (B) 100 mg L^{-1}; (C) 150 mg L^{-1}; (D) 250 mg L^{-1}; (E) 350 mg L^{-1}; (F) 500 mg L^{-1}; (♦) XeBr; (■) KrCl; (▲) Cl_2.

4-Chlorophenol concentrations and the two main photoproducts of the photodegradation process, hydroquinone and benzoquinone [21], were determined, at the above mentioned time intervals, by HPLC analysis using a Varian Prostar 210 chromatograph with UV detector and a C18 reverse phase column. The mobile phase was a mixture of methanol, acetic acid and water (60:2.5:37.5, v/v) with a flow rate of 1 mL min^{-1}. Simultaneous determination of 4CP and HQ was carried out at a wavelength of 283 nm, where 4CP and HQ present strong absorption bands at retention times of 6.2 and 2.2 min, respectively. BQ was determined, independently, at a wavelength of 237 nm and retention time of 2.4 min.

3. Results

3.1. Removal efficiency and power consumption of excilamps

To analyze the time course of the photodegradation process, the following expressions were used for 4-chlorophenol, hydroquinone and benzoquinone conversions:

$$X_{4CP} = \frac{[4CP]_0 - [4CP]}{[4CP]_0} \quad (1)$$

$$X_{HQ} = \frac{[HQ]}{[4CP]_0} \quad (2)$$

$$X_{BQ} = \frac{[BQ]}{[4CP]_0} \quad (3)$$

These conversion expressions, apart from being used to normalize the value of the different compound concentrations ranging from 0 to 1, represent the fraction of the initial amount of 4CP degraded after time t and the fraction of 4CP converted to HQ and BQ, respectively, but not degraded further to more simple molecules. As a consequence, the conversion values provide some relevant information related to the state of the 4CP photodegradation process.

The highest 4CP conversions are achieved using the XeBr excilamp (Fig. 2). When low initial concentrations of 4CP are used

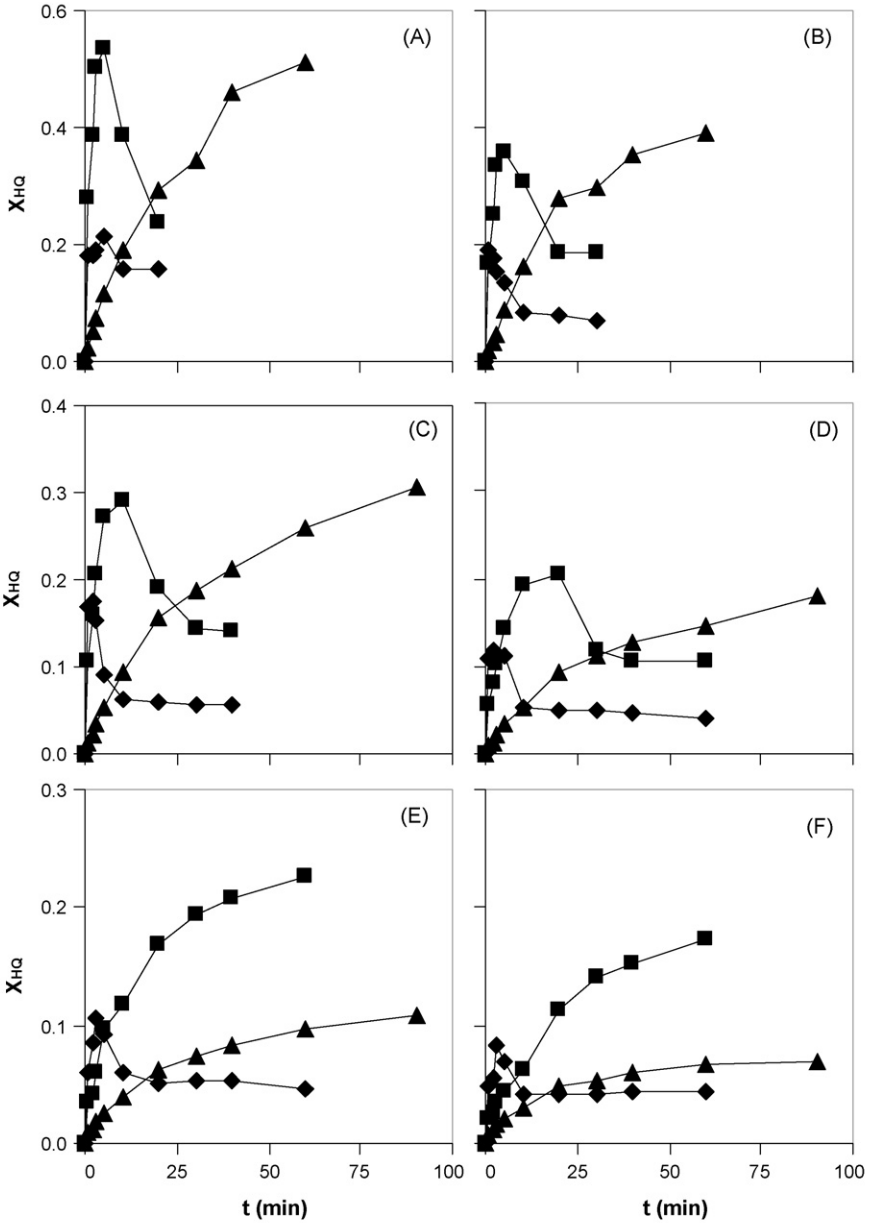

Fig. 3. HQ conversion vs time. Comparison of the results obtained with the three excilamps for all 4CP initial concentrations tested: (A) 50 mg L^{-1}; (B) 100 mg L^{-1}; (C) 150 mg L^{-1}; (D) 250 mg L^{-1}; (E) 350 mg L^{-1}; (F) 500 mg L^{-1}; (♦) XeBr; (■) KrCl; (▲) Cl_2.

(50 and 100 mg L^{-1}), the results obtained with both the XeBr and KrCl excilamps are very similar, with progressively lower degradation rates by the latter lamp for the higher concentrations tested. However, both lamps achieved practically total 4CP degradation. Much lower conversions were achieved with the Cl_2 excilamp where almost total degradation was seen with long exposure times (60 min) for the lowest initial 4CP concentration (50 mg L^{-1}).

Fig. 3 shows that with the XeBr excilamp, HQ has a transient increase and is quickly degraded, reaching a low residual value indicating that HQ does not accumulate significantly during degradation of low concentrations of 4CP. A similar trend, but with a higher transient accumulation is shown in the curves corresponding to the KrCl experiments. Exceptions were evident for the systems treating concentrations of 350 and 500 mg L^{-1} when there is a continual increase in HQ. The use of the Cl_2 excilamp leads to continuous accumulation of HQ for all the 4CP concentration tested.

Fig. 4 shows the changes in BQ production and removal. For all the excilamps, BQ shows initial increases and then values fall to low levels. The trends are the same for all lamps indicating that the photoproduct benzoquinone is not a significant by-product.

In Fig. 5, 4CP conversions are plotted semi-logarithmically against fluence or UV dose (J cm^{-2}). It can be seen that the KrCl excilamp is the one that attains high degradation levels of 4-chlorophenol with low UV dose. On the contrary, the use of the XeBr excilamp manifests in a high UV dose, due to its high average radiation intensity (17.12 mW cm^{-2} compared to 2.47 mW cm^{-2} in the case of the KrCl). The Cl_2 excilamp has the lowest radiation intensity (0.85 mW cm^{-2}), so it would need long exposure time to achieve maximum 4CP degradation level. From the experimental data, the KrCl excilamp clearly demonstrates better efficiency in 4CP conversion and the energy required for the photodegradation is in good agreement with previously reported data [31].

In the previous discussion, only the radiation intensity and the total fluence of the excilamps have been taken into account to explain the different conversions achieved. But, in the literature, a dependence of quantum yield on temperature, similar

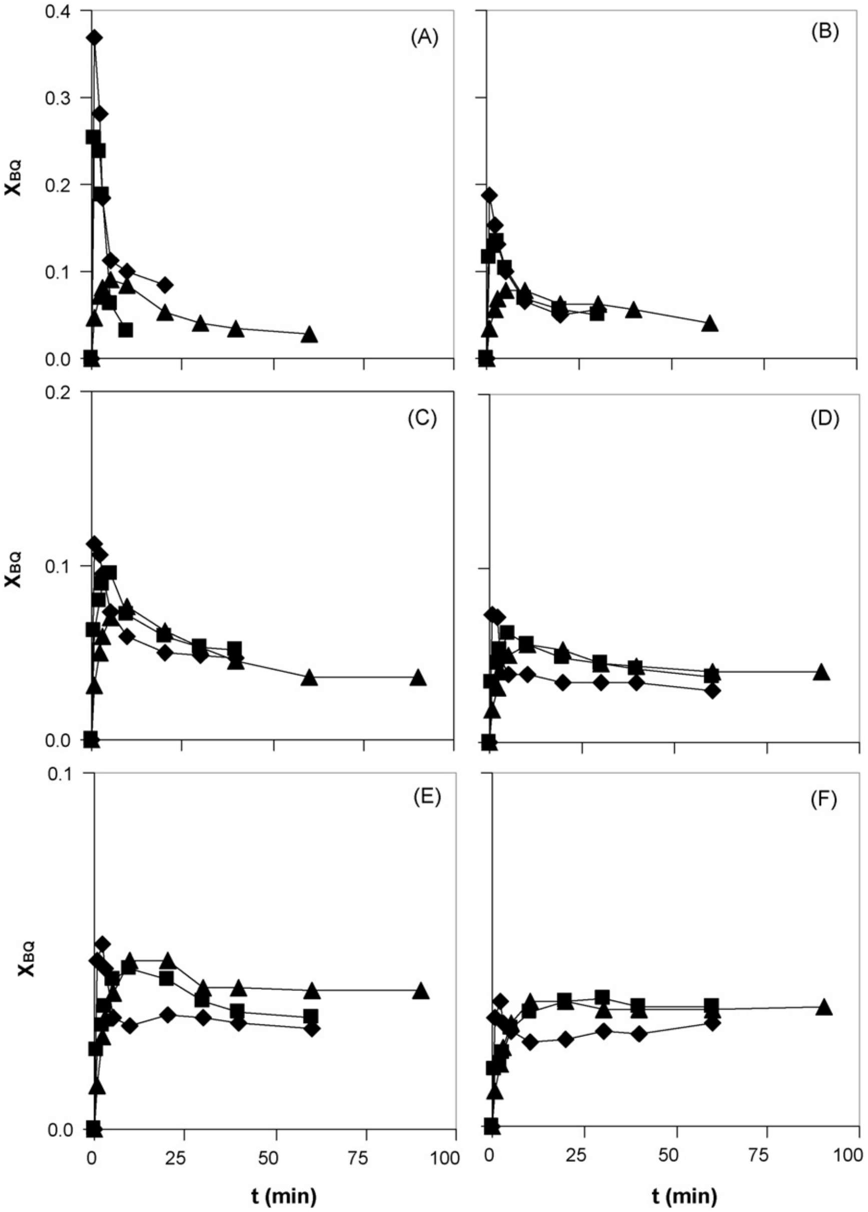

Fig. 4. BQ conversion vs time. Comparison of the results obtained with the three excilamps for all 4CP initial concentrations tested: (A) 50 mg L^{-1}; (B) 100 mg L^{-1}; (C) 150 mg L^{-1}; (D) 250 mg L^{-1}; (E) 350 mg L^{-1}; (F) 500 mg L^{-1}; (♦) XeBr; (■) KrCl; (▲) Cl_2.

to the Arrhenius law, has been described [32,33]. This influence of the temperature must be considered in the kinetic analysis of photodegradation processes carried out in a wide range of temperatures. In the present research, due to the proximity of the quartz tube to the excilamps, temperature can have an effect on the different conversions obtained. In order to check this possible influence, an additional assay, with 250 mg L^{-1} of 4-chlorophenol initial concentration, has been carried out for each one of the three excilamps. In Table 1, variation of temperature of the samples with time is shown. It can be seen that from an initial temperature of 16 °C, maximum temperatures of about 26–27 °C are attained after 90 min of exposure to the excilamps. Also, the variation of temperature with time is practically identical for the three excilamps and, as a consequence, the observed differences in the 4CP conversions cannot be attributed to differences in the temperature of the sample, but to the different radiation intensities and fluence values. Anyway, the impact of the temperature is not significant, because the total increase is of about 10 °C after 1 h of exposure, being the average temperature along the assay of about 22–23 °C.

3.2. Kinetics of 4-chlorophenol photodegradation

As indicated, the kinetics of 4-chlorophenol photodegradation has been widely studied, with a pseudo-first order being the most common kinetic model proposed in the literature [16,28,29]. Taking into account the experimental results obtained in this work, it appears that a simple first order kinetic model is not appropriate

Table 1
Variation of temperature with time along an assay.

t (min)	KrCl, *T* (°C)	XeBr, *T* (°C)	Cl_2, *T* (°C)
0	16.0	16.0	16.0
5	18.0	18.0	18.0
10	21.0	21.0	22.0
20	24.0	24.0	24.0
40	26.0	25.0	25.0
60	27.0	26.0	25.0
90	27.0	26.0	25.0
T average	22.7	22.3	22.1

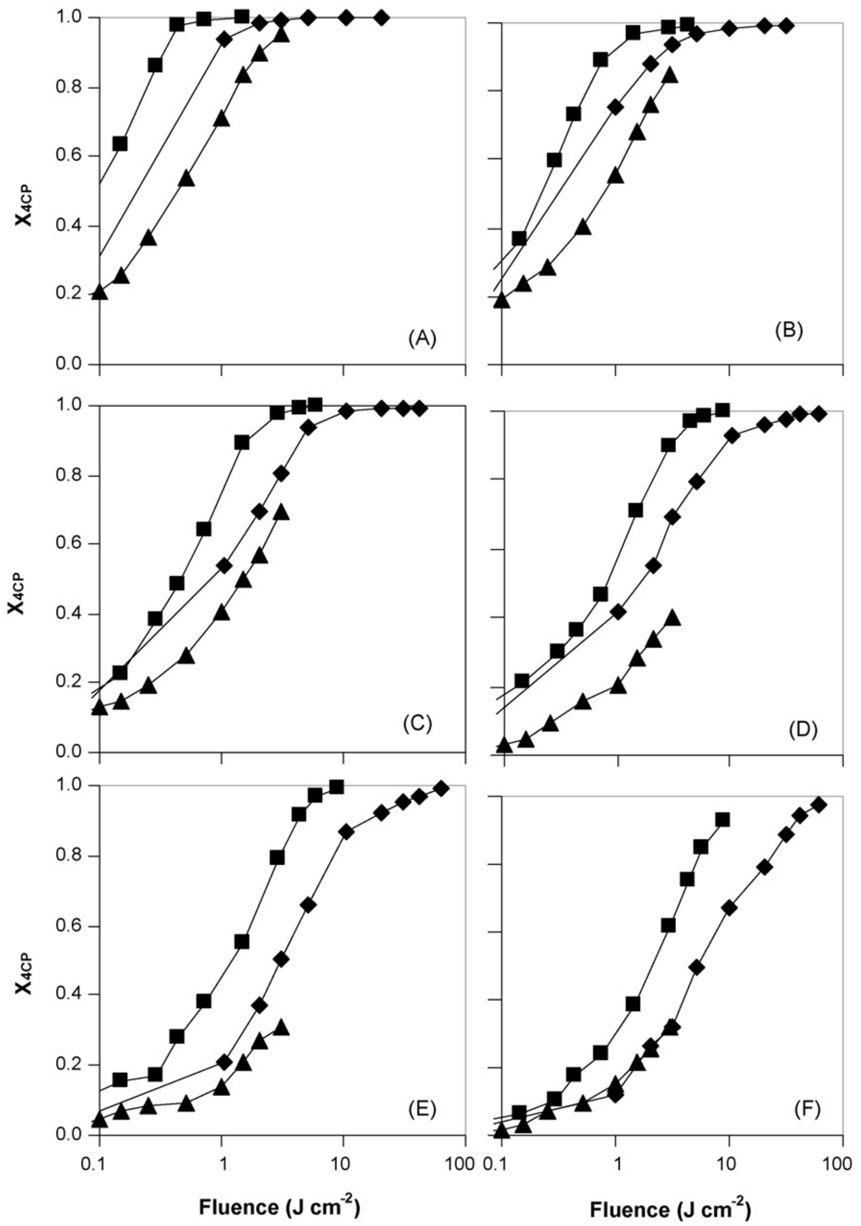

Fig. 5. 4CP conversion vs UV dose. Comparison of the results obtained with the three excilamps for all 4CP initial concentrations: (A) 50 mg L^{-1}; (B) 100 mg L^{-1}; (C) 150 mg L^{-1}; (D) 250 mg L^{-1}; (E) 350 mg L^{-1}; (F) 500 mg L^{-1}; (♦) XeBr; (■) KrCl; (▲) Cl_2.

for explaining some of the experimental conditions tested. For high initial 4-chlorophenol concentration, a shielding effect can hamper degradation due the formation of coloured by-products with high capacity for absorption of radiation, mainly benzoquinone, as well as a partial adsorption of these by-products on the wall of the quartz tube diminishing the efficiency of the radiation emitted by the excilamp. In Fig. 6, a photographs showing a sample of 250 mg L^{-1} of 4-chlorophenol, before treatment and after 60 min of treatment with the KrCl excimer lamp, is shown. The yellow colour (which appears as grey colour because the figure is presented in grey scale) after exposure to the lamp indicates the formation of the coloured by-products and shows evidence of the shielding effect. Also, some experiments have been carried out using the quartz tube from a previous assay, without cleaning, and lower conversions values than the ones obtained with a clean tube were obtained, due to the yellow by-products partially deposited on the wall in the previous experiment.

As a consequence, for some of the experimental conditions tested a residual concentration of 4-chlorophenol remains non-degraded after extended treatment. This effect is not significant for the XeBr and KrCl excilamps, due to the high radiation flux from these lamps, but it is very important for the low power Cl_2 excilamp. Thus, in Fig. 2 it is seen that after 90 min of photo-treatment using the Cl_2 excilamp, the fraction of 4-chlorophenol degraded is very low in comparison with the degradation obtained for the other excilamps.

To take into account this effect, the pseudo-first order kinetic model has been modified by defining a 4-chlorophenol limit concentration, $[4CP]_{Lim}$, as the residual concentration of 4-chlorophenol that remains non-degraded after extended photo-treatment. From this definition, and according to the adopted nomenclature, the 4CP degradation rate is not only proportional to the 4CP concentration, but also to the difference between the prevailing 4CP concentration and the limit concentration. Thus the

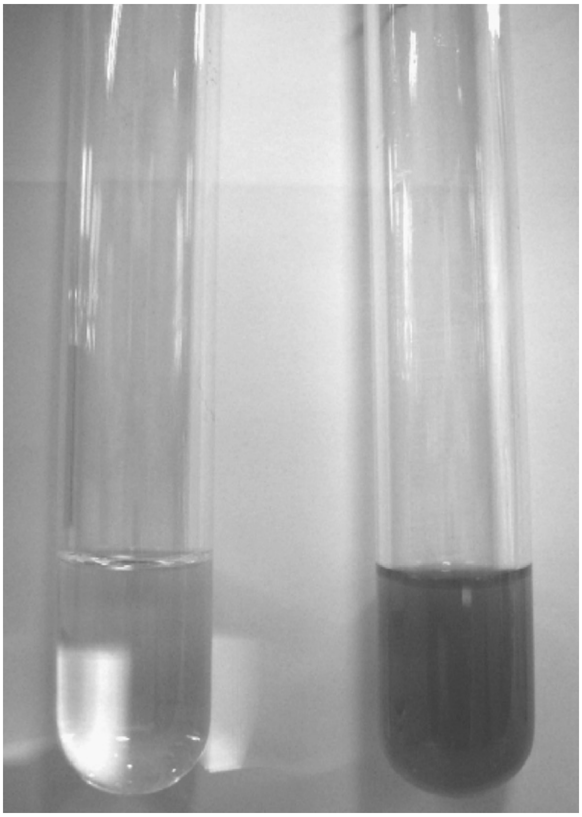

Fig. 6. A view of the quartz tube with a sample of 250 mg L^{-1} of 4CP before the assay (tube on the left) and after 60 min of exposure to the KrCl excilamp (tube on the right).

pseudo-first order model should be formulated as follows:

$$\frac{\mathrm{d}[4\mathrm{CP}]}{\mathrm{d}t} = -k([4\mathrm{CP}] - [4\mathrm{CP}]_{\mathrm{Lim}}) \tag{4}$$

with the initial condition:

$$t = 0; \quad [4\mathrm{CP}] = [4\mathrm{CP}]_0; \tag{5}$$

Eq. (4) has analytical solution and the 4CP concentration change with time is given by:

$$[4\mathrm{CP}] = [4\mathrm{CP}]_{\mathrm{Lim}} + ([4\mathrm{CP}]_0 - [4\mathrm{CP}]_{\mathrm{Lim}})\exp(-kt) \tag{6}$$

From the 4CP conversion defined in Eq. (1), the 4CP, prevailing and limit concentrations, are given by:

$$[4\mathrm{CP}] = [4\mathrm{CP}]_0(1 - X_{4\mathrm{CP}}) \tag{7}$$

$$[4\mathrm{CP}]_{\mathrm{Lim}} = [4\mathrm{CP}]_0(1 - X_{4\mathrm{CPmax}}) \tag{8}$$

where $X_{4\mathrm{CPmax}}$ is the maximum 4CP conversion achieved at the end of photo-treatment and corresponding with the 4CP limit concentration. By substituting Eqs. (7) and (8) in (6), the following expression for 4CP conversion with time is obtained:

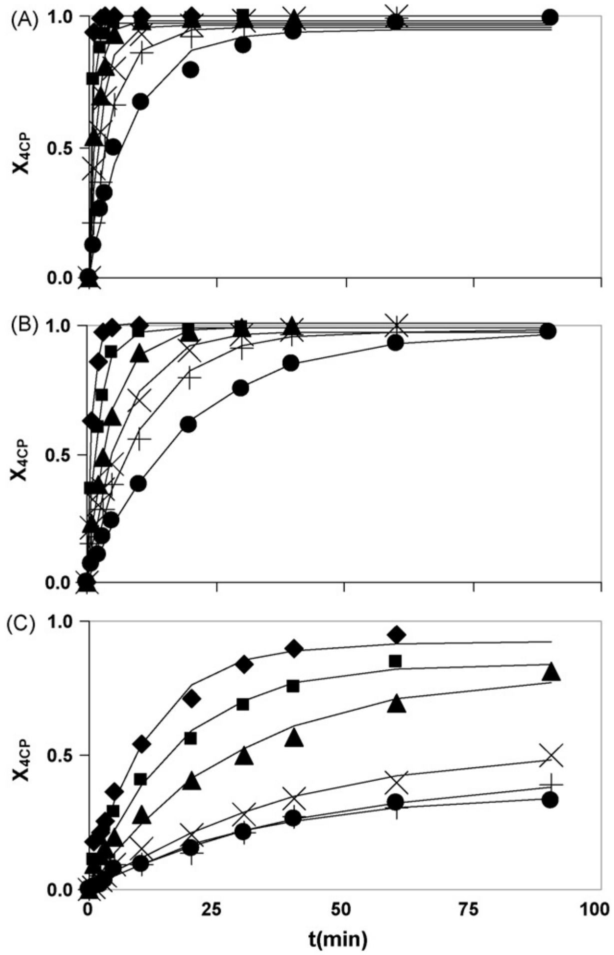

Fig. 7. Fitting the 4CP conversion to the model for the three excilamps and all initial concentrations tested: (A) XeBr; (B) KrCl; (C) Cl$_2$; (◆) 50 mg L^{-1}; (■) 100 mg L^{-1}; (▲) 150 mg L^{-1}; (×) 250 mg L^{-1}; (+) 350 mg L^{-1}; (●) 500 mg L^{-1}.

$$X_{4\mathrm{CP}} = X_{4\mathrm{CPmax}}(1 - \exp(-kt)) \tag{9}$$

To fit the experimental data, Eq. (9) has been defined as a user function in the software Sigma Plot V8.2, as follows:

$$X_{4\mathrm{CP}} = a(1 - \exp(-bt)) \tag{10}$$

The definition of these new parameters *a*, *b*, related to the ones of the original model, makes it easier to formulate the previous equation in the Sigma Plot workspace. The result of fitting the 4CP conversion values to Eq. (10), for each one of excilamps, is shown in Fig. 7(A)–(C), respectively. The points correspond with the experimental conversion data and the solid continuous lines with the values calculated using the model. For the model parameters corresponding to Eq. (10), their values are presented in Table 2, as well as the values of the correlation coefficient, *R*. An excellent degree

Table 2
Pseudo-first order kinetic parameters.

$[4\mathrm{CP}]_0$ (mg L^{-1})	XeBr excilamp			KrCl excilamp			Cl$_2$ excilamp		
	a	*b*	*R*	*a*	*b*	*R*	*a*	*b*	*R*
50	1.00	2.78	0.9999	1.01	0.99	0.9996	0.92	0.09	0.9955
100	0.98	1.38	0.9979	0.99	0.46	0.9998	0.84	0.06	0.9932
150	0.98	0.66	0.9961	0.99	0.23	0.9889	0.80	0.04	0.9866
250	0.97	0.43	0.9939	0.98	0.14	0.9942	0.54	0.03	0.9948
350	0.96	0.24	0.9989	0.98	0.09	0.9962	0.43	0.02	0.9835
500	0.95	0.12	0.9936	0.98	0.05	0.9991	0.37	0.03	0.9968

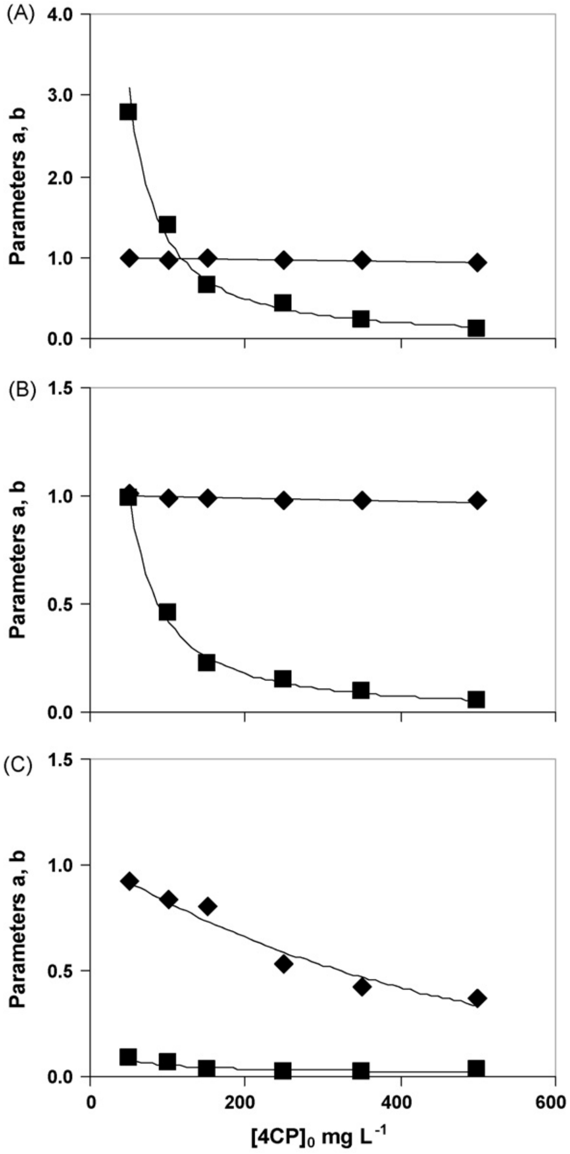

Fig. 8. Variation of the model parameters, *a* and *b*, with the initial concentration of 4-clorophenol, for the three excilamps: (A) XeBr; (B) KrCl; (C) Cl_2; (♦) *a* (dimensionless); (■) *b* (min^{-1}).

of agreement between the experimental conversion data and those predicted by the model has been obtained, as it can be seen from Fig. 7 and from the high values of correlation coefficients in Table 2.

According to Eq. (10), the parameter units shown in Table 2 are min^{-1} for *b*, with parameter *a* being dimensionless. These parameters have been plotted against the initial 4CP concentration in Fig. 8 and it can be seen that, in all cases, the *b* parameter, which corresponds with the pseudo-first order rate constant, depends on the initial 4CP concentration, decreasing when this concentration increases. This can be attributed to the shielding effect of by-products that are higher at high 4CP concentration. On the other hand, the parameter *a*, which corresponds with the 4CP maximum conversion achieved, is very close to unity and practically constant for XeBr and KrCl excilamps. This parameter is strongly dependent on the initial 4CP concentration for the Cl_2 excilamp because the shielding effect is higher for this lamp due to its lower radiation power. The above dependence of parameters *a* and *b* to $[4CP]_0$ has been characterized, empirically, by the following equations:

$$b = b_0([4CP]_0)^{-b_1} \tag{11}$$

Table 3
Dependence of model parameters, *a* and *b*, on initial 4CP concentration.

Parameter	Equation type	Excilamp	b_0	b_1	R
b	$b = b_0([4CP]_0)^{-b_1}$	XeBr	556.93	1.33	0.9935
		KrCl	142.39	1.26	0.9968
		Cl_2	0.74	0.56	0.9118
Parameter	Equation type	Excilamp	a_0	a_1	R
a	$a = a_0\exp(-a_1[4CP]_0)$	XeBr	0.9953	1.00E−04	0.9604
		KrCl	0.9995	6.00E−05	0.8247
		Cl_2	1.0298	2.20E−04	0.9787

$$a = a_0\exp(-a_1[4CP]_0) \tag{12}$$

In Table 3, the values obtained for a_0, a_1, b_0 and b_1 are shown, as well as the correlation coefficients, whose high values confirm that Eqs. (11) and (12) are valid in predicting the parameters *a* and *b*. Eqs. (11) and (12), together with Eq. (10), complete a single semi-theoretical model valid in predicting the time course of 4CP degradation by each of the three excilamps tested, for 4CP concentrations in the interval from 50 to 500 mg L^{-1}.

4. Conclusions

In the photodegradation treatment of 4-chlorophenol carried out with three different excimer lamps (XeBr, KrCl and Cl_2), both the XeBr and the KrCl have been effective in the removal of almost all the 4-chlorophenol at the concentrations tested (50–500 mg L^{-1}), while the removal efficiency attained with the Cl_2 lamp is considerably lower. Although in using the XeBr shorter reaction times are required, the KrCl has much lower energy requirements and, as a result, it is the most effective taking into account both efficient 4CP degradation and low energy consumption. Differences in degradation of 4CP and the main by-products HQ and BQ are related to the energy of emission wavelengths produced by the different excilamps and absorbed by the different molecules. With regard to the kinetics of the 4CP photodegradation process, the definition of a 4CP limit concentration and its inclusion in the pseudo-first order kinetic equation, has improved the fitting of the experimental data to the kinetic model, and, from the values of the kinetic parameters, *a* and *b*, for the three lamps, a strong influence of the shielding effect on the kinetic rate constant, *b*, has been delineated. This influence has significance on parameter *a* only for the Cl_2 excilamp.

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