A KrCl exciplex flow-through photoreactor for degrading 4-chlorophenol: Experimental and modelling

M. Gomez *, M.D. Murcia, J.L. Gomez, E. Gomez, M.F. Maximo, A. Garcia

Department of Chemical Engineering, Murcia University, 30071 Murcia, Spain

Abstract

A KrCl exciplex flow-through photoreactor has been used for the removal of 4-chlorophenol. UV/H_2O_2 and photo-Fenton processes were tested. Considering the degradation of the different compounds, the molar ratio H_2O_2:4-chlorophenol did not show a significant influence on 4-chlorophenol while an optimum ratio of 25:1 was established for the photoproducts. The presence of the Fenton reagent led to a considerable improvement in the photodegradation of both the substrate and by-products, and an optimum Fe^{2+} concentration of 5 mg L^{-1} was determined. Under these conditions, total degradation was attained for a range of substrate concentrations between 50 and 150 mg L^{-1} and for reaction volumes of 500 mL. A photodegradation mechanism was also proposed, based on the formation of two intermediate compounds that quickly degrade to the primary photoproducts previously identified. A kinetic model was developed and theoretical conversion values of the 4-chlorophenol and the photoproducts were compared with the experimental ones, reaching a high degree of agreement ($x_{calc} = 0.9964 \, x_{exp}$, $R^2 = 0.9986$) and validating the proposed model. This system simulation using relatively high reaction volumes and including the by-products in the kinetic equations represents a first approach with a view to operating in continuous or semi-continuous systems that allow the scaling up of the process.

1. Introduction

The negative impact of industrial effluents on the world water resources is a topic of increasing concern [1]. Among these effluents there is a significant group from different industrial areas, such as the high-temperature coal conversion, petroleum refining and the manufacture of plastics, resins, textile, iron, steel and paper, which contains high organic loads with the presence of different phenolic compounds, among other contaminants [2-4]. These phenolics are highly toxic, persistent and difficult to degrade with conventional treatments that are usually effective only within low concentration ranges of the contaminants. Among these traditional methods much work has been developed based on membrane technologies [5,6], biodegradation with enzymes and microorganisms [7,8], adsorption [9,10], etc.

Some alternative methods for the removal of phenolics from industrial effluents are focused on photodegradation processes. These technologies normally use mercury lamps as UV radiation sources in combination with heterogeneous catalysts, being titanium dioxide the most commonly used [11,12].

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). They offer a wide range of possibilities and combinations, including processes combining, alternatively, UV radiation with H_2O_2, ozone or Fenton reactions [13–15].

Recently new UV sources called excimer lamps or excilamps have been developed and efficiently used alone [16-18] or in combination with hydrogen peroxide [19]. These lamps are based on transitions of exciplex (rare gas halides) or excimer molecules (rare gas or halogen dimers) 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 [20,21]. 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. In this way, and with the aim of increasing the sample volume to be treated, the use of excilamps in flow-through photoreactors appears as a promising alternative, as it was reported by Oppenländer [22] in a first work, where also a comparison with a standard medium-pressure Hg lamp was made. But optimum conditions for a scaling-up still need to be determined and a proper kinetic study and system simulation can be very useful in order to do so.

Different authors have studied the kinetics of 4-chlorophenol photodegradation [11, 23]. Some of them support the hypothesis of the initial formation of two unstable intermediate compounds once the C-Cl bond is broken, as a first step of the photodegradation pathway. The next steps lead to the formation of the primary photoproducts, being hydroquinone and benzoquinone the main compounds followed by 1,2,4-trihydroxybenzene, catechol, resorcinol and even some chlorohydroxybenzenes. These primary photoproducts are degraded to smaller compounds until their final transformation, in further steps, into CO_2 and H_2O [24, 25]. The photodegradation process is highly complex and depending on the experimental conditions (UV radiation wavelength, pH, concentration of dissolved oxygen, presence of H_2O_2, etc). As a result, in most cases a pseudo first order kinetic has been proposed for the UV/H_2O_2 and photo-Fenton processes, focusing only on the initial compound but without formulation of kinetic equations for the photoproducts [26-29].

Our Research Group has developed different kinetic studies based on 4-chlorophenol photodegradation with excimer lamps in discontinuous processes. Firstly a simplified kinetic model was proposed for a KrCl excilamp taking into account the formation of two main photoproducts, hydroquinone and benzoquinone [30]. In another study, three different excilamps, of KrCl, XeBr and Cl_2, were compared and the KrCl was chosen as the most effective one in terms of both 4-chlorophenol removal and energy consumption [17]. This study included a modified pseudo-first order kinetic model considering the shielding effect and introducing a 4-chlorophenol limit concentration. In further studies, new photoproducts were identified and H_2O_2 was added to the reaction media establishing the optimum molar ratio H_2O_2:4-chlorophenol as 25:1 [19].

In the present work a KrCl flow-through photoreactor has been used for the removal of 4-chlorophenol and UV/H_2O_2 and photo-Fenton processes have been tested with the aim of optimizing the experimental conditions for higher reaction volumes. Additionally, a detailed photodegradation mechanism and a kinetic model that consider both the substrate and all the identified photoproducts are proposed as a first step to simulate the

system behaviour and open a new research area focused on continuous or semi-continuous systems that allow the scaling up of the process.

2. Materials and Methods

2.1. Reagents

The following chemicals and reagents were obtained from Sigma-Aldrich Co: 4-chlorophenol (99%), hydrogen peroxide (35%), hydroquinone (99%), resorcinol (ACS, 99%), catechol (99%), 4-chlororesorcinol (98%), 4-chlorohydroquinone (85%), 4-chlorocatechol (97%) and benzoquinone (98%). 1,2,4-trihydroxybenzene (99%), phenol (99.5 %) and $FeSO_4$ were purchased from Alfa Aesar GMBH & Co KG, Panreac and Probus, respectively. 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. The output power of the excilamp was measured using an electrochemical actinometer of potassium ferrioxalate, $K_3Fe(C_2O_4)_3.3H_2O$, as described in the literature [31], and the average radiation intensity delivered to the solution was 2.38 mW cm^{-2}. The solution to be treated was fed to the photoreactor through a quartz tube with a length of 30 cm (like the irradiation length of the lamp) and an internal diameter of 2 cm, which provides an irradiation area of 188.5 cm^2. Figure 1A shows a scheme of the photoreactor, where the main element, the lamp bulb (indicated by number 2) can be seen inside the carcase (number 1) and with the hole to introduce the quartz tube also indicated (number 7).

Figure 1

The 4-chlorophenol initial solution at the required concentration was pumped from a stirred feed tank to the photoreactor. In the UV/H_2O_2 and photo-Fenton assays the corresponding volumes of hydrogen peroxide and $FeSO_4$ were added to the feed tank together with the 4-chlorophenol. After the photodegradation takes place along the irradiation zone length of the lamp, the whole volume was recycled to the feed tank, so that the system acts as a batch reactor. All the experiments were done at room temperature (23-25 ºC), with an operational time of 60 min and with a total volume of 500 ml. Figure 1B shows a scheme of the system. Duplicates experiments were carried out and average values were obtained. Standard deviation calculated for the whole set of data was 1.95 %.

Samples were taken at different reaction times (0, 1, 2, 3, 4, 5, 10, 15, 20, 30, 40 and 60 minutes) from the feed tank, being this one constantly stirred to assure homogenization. The samples were taken to 2 ml vials and mixed with catalase to degrade the hydrogen peroxide and avoid its interference with different photoproducts during sample analyses.

The 4-chlorophenol remaining after treatment, as well as the major and minor photoproducts of the photodegradation process were determined by HPLC analysis

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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} [14]. Table 1 shows the different retention times and wavelengths of analysis of chlorophenol and the main photoproducts identified under the conditions used.

Also, and only for the assay with the optimal hydrogen peroxide:4-chlorophenol molar ratio, without the Fenton reagent, the residual concentration of hydrogen peroxide along the phototreatment was determined. For this determination, a colorimetric method [32] was used, as follows: To 20 μl of the sample containing hydrogen peroxide, 4.0 ml of HCl (50 mM), 0.4 ml of KI (1.0 mM), 0.4 ml of ammonium molybdate (1 mM prepared in 0.5 mM H_2SO_4), and 0.4 ml of starch solution (consisting of 5.0 g of soluble starch dissolved in 100 ml of water) were added. After 20 minutes the absorbance versus a water control was measured at 570 nm.

Table 1

3. Experimental results: Influence of operational conditions

3.1. Variation of molar ratio H_2O_2:4-chlorophenol

4-chlorophenol initial concentration was 100 mg L^{-1}. Initially, the peristaltic pump used in the system was calibrated and it was tested at different rpm, being 20 rpm (corresponding flow rate of 46 ml min^{-1}) the selected one since with higher flow rates no improvement in 4-chlorophenol degradation was observed (data not shown).

The following molar ratios H_2O_2:4-chlorophenol were tested: 0:1, 15:1, 25:1 and 30:1. The obtained results are shown in Figure 2 where the concentrations of 4-chlorophenol, the different photoproducts and the total concentration are depicted over the reaction time. As it can be seen, 4-chlorophenol was completely degraded in the absence of hydrogen peroxide. This result also agrees with a previous work from Benitez et al [13] who established that the overall reaction rate, for the photo-degradation process, is the sum of the reaction rate of the direct photolysis, without H_2O_2, and an additional reaction rate between the generated hydroxyl radicals and the phenolic compound, being the contribution of the direct photolysis to the overall reaction rate higher than that of the reaction with hydroxyl radicals.

In the case of the photoproducts, however, there was a clear influence of the molar ratio. In the absence of H_2O_2, all the photoproducts showed a continuous increase of concentration along the reaction time and the total concentration that initially showed a decreasing trend remained practically constant after 30 minutes (see Figure 2A). When H_2O_2 was added, the behaviour of most by-products changed, showing a maximum concentration and then starting to decrease, with the exception of the 1,2,4-trihydroxybenzene that did not reach that maximum concentration under these experimental conditions and did not show any significant degradation. Molar ratio of 25:1 was selected as the optimum one since no improvement was obtained with the highest one tested (30:1).

Figure 2

3.2. Variation of Fe^{2+} concentration

Once the optimum molar ratio H_2O_2:4-chlorophenol was selected and since complete degradation of the photoproducts could not be reached, the photo-Fenton process was tested with different concentrations of Fe^{2+}: 1, 3, 5 and 7 mg L^{-1}. As in the previous series, 4-chlorophenol initial concentration was 100 mg L^{-1} and the flow rate was 46 ml min^{-1}.

The obtained results presented in Figure 3 confirmed the positive influence of the Fenton reagent on the degradation of both the phenolic substrate and the by-products, as it can be clearly seen from the curves corresponding to the total concentration versus time. The time required for the total 4-chlorophenol degradation decreased from 60 to 10 min with a Fe^{2+} concentration of 3 mg L^{-1} or higher. As for the photoproducts, using a Fe^{2+} concentration of 5 mg L^{-1} the only one remaining at very low concentrations (0.009 mM) was the 1,2,4-trihydroxybenzene. No significant improvement was obtained with higher Fe^{2+} concentrations, so 5 mg L^{-1} was chosen.

Figure 3

3.3. Variation of initial 4-chlorophenol concentration

In the last experimental series, different initial 4-chlorophenol concentrations (50, 100 and 150 mg L^{-1}) were tested, using the previously optimized flow rate (46 ml min^{-1}), molar ratio H_2O_2:4-chlorophenol (25:1) and Fe^{2+} concentration (5 mg L^{-1}). The results are shown in Figure 4.

As it can be seen from the obtained results, total 4-chlorophenol removal was attained in all cases, from reaction times between 5 minutes, for the lowest concentration tested, and 30 minutes, for the highest one. The by-products elimination was very efficient as well, with only small traces (less than 6 ppm) of 1,2,4-trihydroxybenzene, hydroquinone and resorcinol remaining in the experiment corresponding to 150 mg L^{-1} 4-chlorophenol initial concentration.

Figure 4

3.4. Efficiency of the excilamp: Comparison with static assays.

In previous works [17, 19] authors used a KrCl excilamp to degrade 4-clorophenol under static conditions, both in absence of hydrogen peroxide [17] and in the presence of this oxidizing reagent [19]. With the results obtained in the present work and taking some experimental data from the above mentioned works, a comparison of the efficiency of the KrCl excilamp in both static and flow-through operating systems has been made as follows.

The experimental data of the assays with initial 4-chlorophenol concentration of 100 mg L^{-1}, without hydrogen peroxide (from reference 17) and with 25:1 hydrogen peroxide:4-chlorophenol molar ratio (reference 19), together with the ones for the same conditions in the present work, were used for this comparison.

Taking into account the average intensity of the radiation delivered to the solution (2.38 mW cm^{-2} in the flow-through photoreactor and 2.47 mW cm^{-2} in the static assays), and the irradiation surface areas for both systems (188.2 cm^2 for the flow-through and 25.6 cm^2 in the static assays), as well as the sample volume to be treated (500 ml for the flow-through system and 10 ml in the static assays) and the initial concentration of 4-chlorophenol in the sample (100 mg l^{-1}), the specific energy irradiated to the sample (J mg^{-1}) in both systems after an irradiation time can be easily evaluated.

Figure 5

For the assays without hydrogen peroxide, the conversions in both experimental equipments (defined as mg of 4-chlorophenol degraded per initial 4-chlorophenol mg) were compared. Figure 5A shows the results of this comparison. As it can be seen in the figure, an excellent degree of agreement between the experimental conversions in both experimental systems was obtained, which indicates that the efficiency of the KrCl excilamp is practically the same in both systems. The only important difference is that with the flow-through system samples with higher volumes can be easily treated, which is very important for the design of processes at higher scale levels.

Similarly, for the assays with hydrogen peroxide, the residual concentrations of 4-chlophenol and hydrogen peroxide were plotted versus the specific energy irradiated. As it can be seen in Figure 5B, for the same amount of specific energy irradiated to the sample, the residual concentrations of 4-chlorophenol and hydrogen peroxide are practically equals, both in the flow-through and in the static phototreatment. Additionally, it can be observed in the figure that in the static assay the total amount of specific energy irradiated to the sample was much higher than the one for the flow-through treatment and, as a consequence, the decrease in the concentrations of 4-chlorophenol and hydrogen peroxide was much higher as well. From these results it can be affirmed that, for both the flow-through photoreactor and the static assay, the efficiency of the KrCl exciplex lamp is the same and the removal degree attained only depends on the total specific energy irradiated to the sample. In the static assay, the sample volume was 10 ml, very small, the initial amount of 4-chlorophenol was 1 mg and the specific energy irradiated to the sample was very high. In the flow-through reactor, the sample volume was 500 ml and the initial amount of 4-chlorophenol was 50 mg, much higher than the one of the static assay and, although the irradiation surface of the flow-through photoreactor was higher than the one for the static assay, the specific energy irradiated to the sample was lower and, as a consequence, for the same irradiation time the removal degree obtained was much lower than the one in the static assay. Only when the specific energy irradiated to the sample is the same for both experimental equipments, the same degree of photodegradation can be expected to be attained. From these results it can be said that by using the same excilamp and for the same irradiation time, a higher degree of removal can be obtained with the static assays but smaller volumes of sample can be treated. Alternatively, with the flow-through

photoreactor, higher volumes of sample can be treated but, for the same irradiation time, lower removal degrees will be reached. To attain with the flow-through photoreactor the same removal degree than the one for static assays, additional irradiation time must be used.

4. Theoretical analysis: kinetic model

4.1. Proposed mechanism

Figure 6 shows a scheme of the proposed 4-chlorophenol photodegradation model. As it can be observed, the intermediate compounds I and J are formed from the initial substrate. Both of them are unstable and easily degrade to form the N primary photoproducts P_i, which will degrade further to produce the secondary photoproducts Q_i (not identified in this study) that will finally produce CO_2 and H_2O. From this mechanism, the mass balance equations for 4-chlorophenol, the intermediates and the different primary photoproducts can be formulated and the corresponding equations of concentration change versus time can be obtained, as described below.

Figure 6

4.2. Variation of 4-chlorophenol concentration with time

From the proposed mechanism, a new constant k_0 can be defined as follows:

$$k_0 = k_{01} + k_{02} \tag{1}$$

As a result, the 4-chlorophenol degradation rate is given by:

$$\frac{d[4CP]}{dt} = -k_0[4CP] \tag{2}$$

with the initial condition:

$$t = 0; \ [4CP] = [4CP]_0 \tag{3}$$

The previous equation can be easily integrated leading to:

$$[4CP] = [4CP]_0 \, e^{-k_0 t} \tag{4}$$

4.3. Intermediate compounds I and J

The intermediate compounds *I* and *J* are formed from the 4-chlorophenol and during the photodegradation process they lead to the N primary photoproducts P_i. Within these photoproducts, the ones from i = 1 to M are formed from the intermediate compound *I* and the rest (from i = M + 1 to N) are formed from the intermediate *J*.

For the intermediate compound *I*, and by defining a k_I constant:

$$k_I = \sum_{i=1}^{M} k_i \tag{5}$$

it can be verified that:

$$\frac{d[I]}{dt} = k_{01}[4CP] - k_I[I] \tag{6}$$

with the initial condition:

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

Equation (7) is a linear differential equation of first order and constant coefficients, with initial conditions equal to 0, which can be solved by using the Laplace Transform. The obtained result is indicated below:

$$[I] = \frac{k_{01}[4CP]_0}{k_I - k_0} \left(e^{-k_0 t} - e^{-k_I t} \right) \tag{8}$$

In a similar way, another constant can be defined for the intermediate compound *J*:

$$k_J = \sum_{i=M+1}^{N} k_i \tag{9}$$

And the equation for the variation of this compound over time would be:

$$\frac{d[J]}{dt} = k_{02}[4CP] - k_J[J] \tag{10}$$

with the initial condition:

$$t = 0; [J] = 0 \tag{11}$$

Equation (10) can be solved in the same way that equation (6) giving:

$$[J] = \frac{k_{02}[4CP]_0}{k_J - k_0} \left(e^{-k_0 t} - e^{-k_J t} \right) \tag{12}$$

4.4. Primary photoproducts, P_i

For each one of the M primary photoproducts, P_i, formed from the intermediate compound I, it can be verified:

$$\frac{d[P_i]}{dt} = k_i[I] - k_{i2}[P_i]$$ (13)

with the initial condition:

$$t = 0;\ [P_i] = 0$$ (14)

This equation is also a linear differential one with constant coefficients, so it can be solved by the Laplace Transform with the following result:

$$[P_i] = \frac{k_i k_{01}[4CP]_0}{k_I - k_0}\left(\frac{1}{(k_{i2} - k_0)}\left(e^{-k_0 t} - e^{-k_{i2} t}\right) - \frac{1}{(k_{i2} - k_I)}\left(e^{-k_I t} - e^{-k_{i2} t}\right)\right)$$ (15)

The previous equation is valid for: $M \geq i \geq 1$

The same procedure can be applied to the primary photoproducts formed from the intermediate compound J, leading to:

$$[P_i] = \frac{k_i k_{02}[4CP]_0}{k_J - k_0}\left(\frac{1}{(k_{i2} - k_0)}\left(e^{-k_0 t} - e^{-k_{i2} t}\right) - \frac{1}{(k_{i2} - k_J)}\left(e^{-k_J t} - e^{-k_{i2} t}\right)\right)$$ (16)

In this case: $N \geq i \geq M + 1$

4.5. Conversions of 4-chlorophenol and primary photoproducts

From the following definitions of conversions of 4-chlorophenol and the primary photoproducts:

$$X_{4CP} = \frac{[4CP]_0 - [4CP]}{[4CP]_0}$$ (17)

$$X_{P_i} = \frac{[P_i]}{[4CP]_0}$$ (18)

It can be obtained:

$$[4CP] = [4CP]_0(1 - X_{4CP})$$ (19)

$$[P_i] = [4CP]_0 X_{P_i}$$ (20)

And by substituting these values in equations (4), (15) and (16):

$$X_{4CP} = \left(1 - e^{-k_0 t}\right) \tag{21}$$

$$X_{P_i} = \frac{k_i k_{01}}{k_I - k_0}\left(\frac{1}{(k_{i2} - k_0)}\left(e^{-k_0 t} - e^{-k_{i2} t}\right) - \frac{1}{(k_{i2} - k_I)}\left(e^{-k_I t} - e^{-k_{i2} t}\right)\right) \tag{22}$$

$$X_{P_i} = \frac{k_i k_{02}}{k_J - k_0}\left(\frac{1}{(k_{i2} - k_0)}\left(e^{-k_0 t} - e^{-k_{i2} t}\right) - \frac{1}{(k_{i2} - k_J)}\left(e^{-k_J t} - e^{-k_{i2} t}\right)\right) \tag{23}$$

4.6. Model fitting: General procedure

The fitting of the proposed model to the experimental results has been done using the software Sigma Plot V8.2. Equation (21) has been used directly for the fitting of 4-chlorophenol experimental conversions. However, some modifications have been introduced in equations (22) and (23) to make them suitable to be used in the previously mentioned software. Since both equations have been modified in the same way, only the new equation (22) is shown, as follows:

$$X_{P_i} = \frac{k_i k_{01}}{(k_I - k_0)(k_{i2} - k_I)}\left(e^{-k_{i2} t} - \frac{k_{i2} - k_0}{k_I - k_0}e^{-k_I t} + \frac{k_{i2} - k_I}{k_I - k_0}e^{-k_0 t}\right) \tag{24}$$

By defining the following parameters:

$$a = \frac{k_i k_{01}}{(k_{i2} - k_0)(k_{i2} - k_I)} \tag{25}$$

$$b = k_{i2} \tag{26}$$

$$c = \frac{k_{i2} - k_0}{k_0 - k_I} \tag{27}$$

$$d = k_I \tag{28}$$
$$f = k_o \tag{29}$$

It is finally obtained:

$$X_{P_i} = a\left(e^{-bt} + ce^{-dt} - (1+c)e^{-ft}\right) \tag{30}$$

being the parameter $f = k_o$ known after the 4-chlorophenol fitting.

In particular, if $b \rightarrow 0$ (no significant formation of Q_i) the previous equation leads to:

$$X_{P_i} = a\left(1 + ce^{-dt} - (1+c)e^{-ft}\right) \tag{31}$$

The general procedure used in the fitting of the data has been the following one:

- In the series of variation of the molar ratio H_2O_2:4-chlorophenol, with constant initial chlorophenol concentration, the average experimental data of 4-chlorophenol variation over time was fitted to equation (21), since it was previously observed that the molar ratio has no influence on the 4-chlorophenol removal rate. In this way, a unique value of the constant k_0 was obtained, being this value the f parameter of equations (30) and (31), which was kept constant for the fitting of the different primary photoproducts in this series so that only the remaining parameters, a, b, c and d, needed to be determined.

- Additionally, the value of the parameter d obtained from the best fitting of the previous series (the one with higher correlation coefficient) was selected as the value of the constant k_I for the intermediate compound. This value was kept constant in equations (30) and (31) and the fitting of all the by-products was repeated, giving new values for the parameters a, b and c.

- Under these conditions, when a good degree of fitting of the different photoproducts to the proposed model was obtained (high values of the correlation coefficients) it was assumed that the chosen value for the parameter d was appropriate, also indicating that all the primary photoproducts had been formed from the same intermediate. In case any photoproduct did not show a good fitting, the value of the parameter d leading to an optimum fitting was determined. This new value would correspond, according to the proposed mechanism, with the degradation constant of the other intermediate compound.

- Those fittings leading to a negative value of the parameter b were not accepted since this parameter, corresponding with the value of the kinetic constant k_{i2}, cannot be negative. In these cases the value of b was considered rather negligible and was given the value 0, using equation (31) for the fitting.

4.7. Model fitting: Results and Discussion

Figures 7-10 show the results of the fitting of the experimental conversions of 4-chlorophenol (Fig. 7) and the primary photoproducts (Fig. 8-10) to equations (21), (30) and (31). In these figures, the points correspond with the experimental conversion values and the continuous lines with the values calculated using the model. As it can be seen an excellent degree of agreement was attained in all cases.

Figures 7 - 10

As a final test to validate the model, the experimental conversion values were plotted versus the calculated ones, for all the experimental data. The result is presented in Figure 11 and the high proximity to the diagonal ($x_{calc} = 0.9964\ x_{exp}$, $R^2 = 0.9986$) confirms the validity of the model.

Figure 11

The kinetic parameters d and f, corresponding to the values of the intermediate compound and 4-chlorophenol degradation rate constants, respectively, are shown in Tables 2 to 4.

Tables 2 - 4

It can be observed that the values of the parameters d and f increase when higher Fe^{2+} concentrations or lower 4-chlorophenol are used (see Tables 3 and 4, respectively). This fact confirms the positive influence of the photo-Fenton process previously commented in the results of the experimental series. Additionally, it proves that the initial 4-chlorophenol concentration has a significant influence on the kinetic parameters, which has been explained by applying the Lambert-Beer law in a previous work where the same behaviour was observed [30].

On the other hand, in the series of molar ratio H_2O_2:4-chlorophenol variation (see Table 2), there was no change in the kinetic parameter f, which confirms that the increase of this molar ratio has no significant influence on 4-chlorophenol degradation, although it improves the photoproducts formation until the optimum H_2O_2 concentration is reached (increasing values of d). Finally, the formation of two intermediate compounds was observed in this series, as it can be seen from the different value of the parameter d in the case of the benzoquinone, which indicates a different formation pathway. This behaviour did not occur in the presence of the Fenton reagent, suggesting that maybe the catalytic action of the Fe^{2+} is more selective and only leads to the formation of one of the intermediate products presented in the proposed mechanism.

5. Conclusions

Complete degradation of both 4-chlorophenol and its photoproducts was attained using a KrCl flow-through photoreactor in combination with the Fenton reagent, for a substrate concentration range of 50 to 150 mg L^{-1} and under the following experimental conditions: 500 mL reaction volume, flow rate of 46 ml min^{-1}, molar ratio H_2O_2:4-chlorophenol of 25:1 and Fe^{2+} concentration of 5 mg L^{-1}. The presence of H_2O_2 improved the photoproducts degradation until the optimum concentration was reached and the addition of Fe^{2+} led to much shorter reaction times and allowed total removal of all the species present in the reaction media.

A comparison between the degradation level previously obtained with the same excilamp in static assays and the one obtained in this work for the flow-through system was made and, from the results, it can be affirmed that the efficiency of the KrCl exciplex lamp is the same in both systems and the removal degree attained only depends on the total specific energy irradiated to the sample.

Also, the proposed photodegradation mechanism, based on the formation of two intermediate compounds that quickly degrade to the primary photoproducts previously identified, as well as its corresponding kinetic model, were validated with the experimental conversion data. The main kinetic parameters were determined with their values also supporting the experimental results. The simulation of the system behaviour was successfully undertaken with promising results that can allow further research using continuous or semi-continuous systems leading to the future scaling up of the process.

Acknowledgements

Nomenclature

4CP	4-chlorophenol
[4CP]	4-chlorophenol concentration at a time, t (mM)
$[4CP]_0$	4-chlorophenol initial concentration (mM)
$[H_2O_2]$	Hydrogen peroxide concentration at a time, t (mM)
a	Parameter defined in equation 25 (dimensionless)
b	Parameter defined in equation 26 (min^{-1})
c	Parameter defined in equation 27 (dimensionless)
d	Parameter defined in equation 28 (min^{-1})
f	Parameter defined in equation 29 (min^{-1})
I	Intermediate compound formed from 4-chlorophenol
$[I]$	Intermediate compound I concentration at a time t (mM)
J	Intermediate compound formed from 4-chlorophenol
$[J]$	Intermediate compound J concentration at a time t (mM)
k_0	Pseudo-first order kinetic constant for 4-chlorophenol photodegradation (min^{-1})
k_{01}	Intermediate compound I formation constant (min^{-1})
k_{02}	Intermediate compound J formation constant (min^{-1})
k_I	Intermediate compound I degradation constant (min^{-1})
k_J	Intermediate compound J degradation constant (min^{-1})
k_i	Primary photoproduct formation constant (min^{-1})
k_{i2}	Primary photoproduct degradation constant (min^{-1})
P	Photoproduct
P_i	Primary photoproducts
$[P_i]$	Primary photoproducts concentration at a time t (mM)
Q_i	Secondary photoproducts
t	Time (min)
X_{4CP}	4-chlorophenol conversion defined in equation 17 (dimensionless)
X_{4CP_c}	4-chlorophenol conversion calculated with the proposed kinetic model
X_P	Photoproduct conversion defined in equation 18 (dimensionless)
X_{P_c}	Photoproduct conversion calculated with the proposed kinetic model

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A KrCl exciplex flow-through photoreactor for degrading 4-chlorophenol: Experimental and modelling

M. Gomez *, M.D. Murcia, J.L. Gomez, E. Gomez, M.F. Maximo, A. Garcia

Department of Chemical Engineering, Murcia University, 30071 Murcia, Spain

Abstract

A KrCl exciplex flow-through photoreactor has been used for the removal of 4-chlorophenol. UV/H_2O_2 and photo-Fenton processes were tested. Considering the degradation of the different compounds, the molar ratio H_2O_2:4-chlorophenol did not show a significant influence on 4-chlorophenol while an optimum ratio of 25:1 was established for the photoproducts. The presence of the Fenton reagent led to a considerable improvement in the photodegradation of both the substrate and by-products, and an optimum Fe^{2+} concentration of 5 mg L^{-1} was determined. Under these conditions, total degradation was attained for a range of substrate concentrations between 50 and 150 mg L^{-1} and for reaction volumes of 500 mL. A photodegradation mechanism was also proposed, based on the formation of two intermediate compounds that quickly degrade to the primary photoproducts previously identified. A kinetic model was developed and theoretical conversions values of the 4-chlorophenol and the photoproducts were compared with the experimental ones, reaching a high degree of agreement ($x_{calc} = 0.9964\ x_{exp}$, $R^2 = 0.9986$) and validating the proposed model. This system simulation using relatively high reaction volumes and including the by-products in the kinetic equations represents a first approach with a view to operating in continuous or semi-continuous systems that allow the scaling up of the process.

1. Introduction

The negative impact of industrial effluents on the world water resources is a topic of increasing concern [1]. Among these effluents there is a significant group from different industrial areas, such as the high-temperature coal conversion, petroleum refining and the manufacture of plastics, resins, textile, iron, steel and paper, which contains high organic loads with the presence of different phenolic compounds, among other contaminants [2-4]. These phenolics are highly toxic, persistent and difficult to degrade with conventional treatments that are usually effective only within low concentration ranges of the contaminants. Among these traditional methods much work has been developed based on membrane technologies [5,6], biodegradation with enzymes and microorganisms [7,8], adsorption [9,10], etc.

Some alternative methods for the removal of phenolics from industrial effluents are focused on photodegradation processes. These technologies normally use mercury lamps as UV radiation sources in combination with heterogeneous catalysts, being titanium dioxide the most commonly used [11,12].

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, the radicals are produced by combining ozone, hydrogen peroxide and UV radiation. The combination of hydrogen peroxide with ferrous ions in the so-called Fenton reagent is also used [13–15].

Recently new UV sources called excimer lamps or excilamps have been developed and efficiently used alone [16-18] or in combination with hydrogen peroxide [19]. 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 [20,21]. 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.

Different authors have studied the kinetics of 4-chlorophenol photodegradation [11,22]. Some of them support the hypothesis of the initial formation of two unstable intermediate compounds once the C-Cl bond is broken, as a first step of the photodegradation pathway. The next steps lead to the formation of the primary photoproducts, being hydroquinone and benzoquinone the main compounds followed by 1,2,4-trihydroxybenzene, catechol, resorcinol and even some chlorohydroxybenzenes. These primary photoproducts are degraded to smaller compounds until their final transformation, in further steps, into CO_2 and H_2O [23, 24]. The photodegradation process is highly complex and depending on the experimental conditions (UV radiation wavelength, pH, concentration of dissolved oxygen, presence of H_2O_2, etc). As a result, in most cases a pseudo first order kinetic has been proposed for the UV/H_2O_2 and photo-Fenton processes, focusing only on the initial compound but without formulation of kinetic equations for the photoproducts [25-28].

Our Research Group has developed different kinetic studies based on 4-chlorophenol photodegradation with excimer lamps in discontinuous processes. Firstly a simplified kinetic model was proposed for a KrCl excilamp taking into account the formation of two main photoproducts, hydroquinone and benzoquinone [29]. In another study, three different excilamps, of KrCl, XeBr and Cl_2, were compared and the KrCl was chosen as the most effective one in terms of both 4-chlorophenol removal and energy consumption [17]. This study included a modified pseudo-first order kinetic model considering the shielding effect and introducing a 4-chlorophenol limit concentration. In further studies, new photoproducts were identified and H_2O_2 was added to the reaction media establishing the optimum molar ratio H_2O_2:4-chlorophenol as 25:1 [19].

In the present work a KrCl flow-through photoreactor has been used for the removal of 4-chlorophenol and UV/H_2O_2 and photo-Fenton processes have been tested with the aim of optimizing the experimental conditions for higher reaction volumes. Additionally, a detailed photodegradation mechanism and a kinetic model that consider both the substrate and all the identified photoproducts are proposed as a first step to simulate the system behaviour and open a new research area focused on continuous or semi-continuous systems that allow the scaling up of the process.

2. Materials and Methods

2.1. Reagents

The following chemicals and reagents were obtained from Sigma-Aldrich Co: 4-chlorophenol (99%), hydrogen peroxide (35%), hydroquinone (99%), resorcinol (ACS, 99%), catechol (99%), 4-chlororesorcinol (98%), 4-chlorohydroquinone (85%), 4-chlorocatechol (97%) and benzoquinone (98%). 1,2,4-trihydroxybenzene (99%), phenol (99.5 %) and $FeSO_4$ were purchased from Alfa Aesar GMBH & Co KG, Panreac and Probus, respectively. 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. Figure 1 shows a scheme of the photoreactor.

Figure 1

The 4-chlorophenol initial solution at the required concentration was pumped from a stirred feed tank to the photoreactor. In the UV/H_2O_2 and photo-Fenton assays the corresponding volumes of hydrogen peroxide and $FeSO_4$ were added to the feed tank together with the 4-chlorophenol. After the photodegradation takes place along the irradiation zone length of the lamp, the whole volume was recycled to the feed tank, so that the system acts as a batch reactor. All the experiments were done at room temperature (23-25 ºC), with an operational time of 60 min and with a total volume of 500 ml. Figure 2 shows a scheme of the system. Duplicates experiments were carried out and average values were obtained. Standard deviation calculated for the whole set of data was 1.95 %.

Figure 2

Samples were taken at different reaction times (0, 1, 2, 3, 4, 5, 10, 15, 20, 30, 40 and 60 minutes) from the feed tank, being this one constantly stirred to assure homogenization. The samples were taken to 2 ml vials and mixed with catalase to degrade the hydrogen peroxide and avoid its interference with different photoproducts during samples analysis.

The 4-chlorophenol remaining after treatment, as well as the major and minor photoproducts of the photodegradation process 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} [14]. Table 1 shows the different retention times and wavelengths of analysis of chlorophenol and the main photoproducts identified under the conditions used.

Table 1

3. Experimental results: Influence of operational conditions

3.1. Variation of molar ratio H_2O_2:4-chlorophenol

4-chlorophenol initial concentration was 100 mg L^{-1}. Initially, the peristaltic pump used in the system was calibrated and it was tested at different rpm, being 20 rpm (corresponding flow rate of 46 ml min^{-1}) the selected one since with higher flow rates no improvement in 4-chlorophenol degradation was observed (data not shown).

The following molar ratios H_2O_2:4-chlorophenol were tested: 0:1, 15:1, 25:1 and 30:1. The obtained results are shown in Figure 3 where the concentrations of 4-chlorophenol, the different photoproducts and the total concentration are depicted over the reaction time. As it can be seen, 4-chlorophenol was completely degraded in the absence of hydrogen peroxide. This result also agrees with a previous work from Benitez et al [13] who established that the overall reaction rate, for the photo-degradation process, is the sum of the reaction rate of the direct photolysis, without H_2O_2, and an additional reaction rate between the generated hydroxyl radicals and the phenolic compound, being the contribution of the direct photolysis to the overall reaction rate higher than that of the reaction with hydroxyl radicals.

In the case of the photoproducts, however, there was a clear influence of the molar ratio. In the absence of H_2O_2, all the photoproducts showed a continuous increase of concentration along the reaction time and the total concentration that initially showed a decreasing trend remained practically constant after 30 minutes (see Figure 3A). When H_2O_2 was added, the behaviour of most by-products changed, showing a maximum concentration and then starting to decrease, with the exception of the 1,2,4-trihydroxybenzene that did not reach that maximum concentration under these experimental conditions and did not show any significant degradation. Molar ratio of 25:1 was selected as the optimum one since no improvement was obtained with the highest one tested (30:1).

Figure 3

3.2. Variation of Fe^{2+} concentration

Once the optimum molar ratio H_2O_2:4-chlorophenol was selected and since complete degradation of the photoproducts could not be reached, the photo-Fenton process was tested with different concentrations of Fe^{2+}: 1, 3, 5 and 7 mg L^{-1}. As in the previous series, 4-chlorophenol initial concentration was 100 mg L^{-1} and the flow rate was 46 ml min^{-1}.

The obtained results presented in Figure 4 confirmed the positive influence of the Fenton reagent on the degradation of both the phenolic substrate and the by-products, as it can be clearly seen from the curves corresponding to the total concentration versus time. The time required for the total 4-chlorophenol degradation decreased from 60 to 10 min with a Fe^{2+} concentration of 3 mg L^{-1} or higher. As for the photoproducts, using

a Fe^{2+} concentration of 5 mg L^{-1} the only one remaining at very low concentrations (0.009 mM) was the 1,2,4-trihydroxybenzene. No significant improvement was obtained with higher Fe^{2+} concentrations, so 5 mg L^{-1} was chosen.

Figure 4

3.3. Variation of initial 4-chlorophenol concentration

In the last experimental series, different initial 4-chlorophenol concentrations (50, 100 and 150 mg L^{-1}) were tested, using the previously optimized flow rate (46 ml min^{-1}), molar ratio H_2O_2:chlorophenol (25:1) and Fe^{2+} concentration (5 mg L^{-1}). The results are shown in Figure 5.

As it can be seen from the obtained results, total 4-chlorophenol removal was attained in all cases, from reaction times between 5 minutes, for the lowest concentration tested, and 30 minutes, for the highest one. The by-products elimination was very efficient as well, with only small traces (less than 6 ppm) of 1,2,4-trihydroxybenzene, hydroquinone and resorcinol remaining in the experiment corresponding to 150 mg L^{-1} 4-chlorophenol initial concentration.

Figure 5

4. Theoretical analysis: kinetic model

4.1. Proposed mechanism

Figure 6 shows a scheme of the proposed 4-chlorophenol photodegradation model. As it can be observed, the intermediate compounds *I* and *J* are formed from the initial substrate. Both of them are unstable and easily degrade to form the N primary photoproducts P_i, which will degrade further to produce the secondary photoproducts Q_i (not identified in this study) that will finally produce CO_2 and H_2O. From this mechanism, the mass balance equations for 4-chlorophenol, the intermediates and the different primary photoproducts can be formulated and the corresponding equations of concentration change versus time can be obtained, as described below.

Figure 6

4.2. Variation of 4-chlorophenol concentration with time

From the proposed mechanism, a new constant k_0 can be defined as follows:

$$k_0 = k_{01} + k_{02} \tag{1}$$

As a result, the 4-chlorophenol degradation rate is given by:

$$\frac{d[4CP]}{dt} = -k_0[4CP] \tag{2}$$

with the initial condition:

$$t = 0;\ [4CP] = [4CP]_0 \tag{3}$$

The previous equation can be easily integrated leading to:

$$[4CP] = [4CP]_0\, e^{-k_0 t} \tag{4}$$

4.3. Intermediate compounds I and J

The intermediate compounds *I* and *J* are formed from the 4-chlorophenol and during the photodegradation process they lead to the N primary photoproducts P_i. Within these photoproducts, the ones from i = 1 to M are formed from the intermediate compound *I* and the rest (from i = M + 1 to N) are formed from the intermediate *J*.

For the intermediate compound *I*, and by defining a k_I constant:

$$k_I = \sum_{i=1}^{M} k_i \tag{5}$$

it can be verified that:

$$\frac{d[I]}{dt} = k_{01}[4CP] - k_I[I] \tag{6}$$

with the initial condition:

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

Equation (7) is a linear differential equation of first order and constant coefficients, with initial conditions equal to 0, which can be solved by using the Laplace Transform. The obtained result is indicated below:

$$[I] = \frac{k_{01}[4CP]_0}{k_I - k_0}\left(e^{-k_0 t} - e^{-k_I t}\right) \tag{8}$$

In a similar way, another constant can be defined for the intermediate compound *J*:

$$k_J = \sum_{i=M+1}^{N} k_i \qquad (9)$$

And the equation for the variation of this compound over time would be:

$$\frac{d[J]}{dt} = k_{02}[4CP] - k_J[J] \qquad (10)$$

with the initial condition:

$t = 0; [J] = 0$ (11)

Equation (10) can be solved in the same way that equation (6) giving:

$$[J] = \frac{k_{02}[4CP]_0}{k_J - k_0} \left(e^{-k_0 t} - e^{-k_J t} \right) \qquad (12)$$

4.4. Primary photoproducts, P_i

For each one of the M primary photoproducts, P_i, formed from the intermediate compound I, it can be verified:

$$\frac{d[P_i]}{dt} = k_i[I] - k_{i2}[P_i] \qquad (13)$$

with the initial condition:

$t = 0; [P_i] = 0$ (14)

This equation is also a linear differential one with constant coefficients, so it can be solved by the Laplace Transform with the following result:

$$[P_i] = \frac{k_i k_{01}[4CP]_0}{k_I - k_0} \left(\frac{1}{(k_{i2} - k_0)} \left(e^{-k_0 t} - e^{-k_{i2} t} \right) - \frac{1}{(k_{i2} - k_I)} \left(e^{-k_I t} - e^{-k_{i2} t} \right) \right) \qquad (15)$$

The previous equation is valid for: $M \geq i \geq 1$

The same procedure can be applied to the primary photoproducts formed from the intermediate compound J, leading to:

$$[P_i] = \frac{k_i k_{02}[4CP]_0}{k_J - k_0} \left(\frac{1}{(k_{i2} - k_0)} \left(e^{-k_0 t} - e^{-k_{i2} t} \right) - \frac{1}{(k_{i2} - k_J)} \left(e^{-k_J t} - e^{-k_{i2} t} \right) \right) \qquad (16)$$

In this case: $N \geq i \geq M + 1$

4.5. Conversions of 4-chlorophenol and primary photoproducts

From the following definitions of conversions of 4-chlorophenol and the primary photoproducts:

$$X_{4CP} = \frac{[4CP]_0 - [4CP]}{[4CP]_0} \tag{17}$$

$$X_{P_i} = \frac{[P_i]}{[4CP]_0} \tag{18}$$

It can be obtained:

$$[4CP] = [4CP]_0 (1 - X_{4CP}) \tag{19}$$

$$[P_i] = [4CP]_0 X_{P_i} \tag{20}$$

And by substituting these values in equations (4), (15) and (16):

$$X_{4CP} = \left(1 - e^{-k_0 t}\right) \tag{21}$$

$$X_{P_i} = \frac{k_i k_{01}}{k_I - k_0} \left(\frac{1}{(k_{i2} - k_0)} \left(e^{-k_0 t} - e^{-k_{i2} t}\right) - \frac{1}{(k_{i2} - k_I)} \left(e^{-k_I t} - e^{-k_{i2} t}\right) \right) \tag{22}$$

$$X_{P_i} = \frac{k_i k_{02}}{k_J - k_0} \left(\frac{1}{(k_{i2} - k_0)} \left(e^{-k_0 t} - e^{-k_{i2} t}\right) - \frac{1}{(k_{i2} - k_J)} \left(e^{-k_J t} - e^{-k_{i2} t}\right) \right) \tag{23}$$

4.6. Model fitting: General procedure

The fitting of the proposed model to the experimental results has been done using the software Sigma Plot V8.2. Equation (21) has been used directly for the fitting of 4-chlorophenol experimental conversions. However, some modifications have been introduced in equations (22) and (23) to make them suitable to be used in the previously mentioned software. Since both equations have been modified in the same way, only the new equation (22) is shown, as follows:

$$X_{P_i} = \frac{k_i k_{01}}{(k_I - k_0)(k_{i2} - k_I)} \left(e^{-k_{i2} t} - \frac{k_{i2} - k_0}{k_I - k_0} e^{-k_I t} + \frac{k_{i2} - k_I}{k_I - k_0} e^{-k_0 t} \right) \tag{24}$$

By defining the following parameters:

$$a = \frac{k_i k_{01}}{(k_{i2} - k_0)(k_{i2} - k_I)} \tag{25}$$

$$b = k_{i2} \tag{26}$$

$$c = \frac{k_{i2} - k_0}{k_0 - k_I} \tag{27}$$

$$d = k_I \tag{28}$$

$$f = k_o \tag{29}$$

It is finally obtained:

$$X_{P_i} = a\left(e^{-bt} + ce^{-dt} - (1+c)e^{-ft}\right) \tag{30}$$

being the parameter $f = k_o$ known after the 4-chlorophenol fitting.

In particular, if $b \rightarrow 0$ (no significant formation of Q_i) the previous equation leads to:

$$X_{P_i} = a\left(1 + ce^{-dt} - (1+c)e^{-ft}\right) \tag{31}$$

The general procedure used in the fitting of the data has been the following one:

- In the series of variation of the molar ratio H_2O_2:4-chlorophenol, with constant initial chlorophenol concentration, the average experimental data of 4-chlorophenol variation over time was fitted to equation (21), since it was previously observed that the molar ratio has no influence on the 4-chlorophenol removal rate. In this way, a unique value of the constant k_0 was obtained, being this value the f parameter of equations (30) and (31), which was kept constant for the fitting of the different primary photoproducts in this series so that only the remaining parameters, a, b, c and d, needed to be determined.

- Additionally, the value of the parameter d obtained from the best fitting of the previous series (the one with higher correlation coefficient) was selected as the value of the constant k_I for the intermediate compound. This value was kept constant in equations (30) and (31) and the fitting of all the by-products was repeated, giving new values for the parameters a, b and c.

- Under these conditions, when a good degree of fitting of the different photoproducts to the proposed model was obtained (high values of the correlation coefficients) it was assumed that the chosen value for the parameter d was appropriate, also indicating that all the primary photoproducts had been formed from the same intermediate. In case any photoproduct did not show a good fitting, the value of the parameter d leading to an optimum fitting was determined. This new value would correspond, according to the proposed mechanism, with the degradation constant of the other intermediate compound.

- Those fittings leading to a negative value of the parameter b were not accepted since this parameter, corresponding with the value of the kinetic constant k_{i2}, cannot be negative. In these cases the value of b was considered rather negligible and was given the value 0, using equation (31) for the fitting.

4.7. Model fitting: Results and Discussion

Figures 7-10 show the results of the fitting of the experimental conversions of 4-chlorophenol (Fig. 7) and the primary photoproducts (Fig. 8-10) to equations (21), (30) and (31). In these figures, the points correspond with the experimental conversion values and the continuous lines with the values calculated using the model. As it can be seen an excellent degree of agreement was attained in all cases.

Figures 7 - 10

As a final test to validate the model, the experimental conversion values were plotted versus the calculated ones, for all the experimental data. The result is presented in Figure 11 and the high proximity to the diagonal ($x_{calc} = 0.9964\ x_{exp}$, $R^2 = 0.9986$) confirms the validity of the model.

Figure 11

The kinetic parameters d and f, corresponding to the values of the intermediate compound and 4-chlorophenol degradation rate constants, respectively, are shown in Tables 2 to 4.

Tables 2 - 4

It can be observed that the values of the parameters d and f increase when higher Fe^{2+} concentrations or lower 4-chlorophenol are used (see Tables 3 and 4, respectively). This fact confirms the positive influence of the photo-Fenton process previously commented in the results of the experimental series. Additionally, it proves that the initial 4-chlorophenol concentration has a significant influence on the kinetic parameters, which has been explained by applying the Lambert-Beer law in a previous work where the same behaviour was observed [29].

On the other hand, in the series of molar ratio H_2O_2:4-chlorophenol variation (see Table 2), there was no change in the kinetic parameter f, which confirms that the increase of this molar ratio has no significant influence on 4-chlorophenol degradation, although it improves the photoproducts formation until the optimum H_2O_2 concentration is reached (increasing values of d). Finally, the formation of two intermediate compounds was observed in this series, as it can be seen from the different value of the parameter d in the case of the benzoquinone, which indicates a different formation pathway. This behaviour did not occur in the presence of the Fenton reagent, suggesting that maybe the catalytic action of the Fe^{2+} is more selective and only leads to the formation of one of the intermediate products presented in the proposed mechanism.

5. Conclusions

Complete degradation of both 4-chlorophenol and its photoproducts was attained using a KrCl flow-through photoreactor in combination with the Fenton reagent, for a substrate concentration range of 50 to 150 mg L^{-1} and under the following experimental conditions: 500 mL reaction volume, flow rate of 46 ml min^{-1}, molar ratio H_2O_2:4-

chlorophenol of 25:1 and Fe^{2+} concentration of 5 mg L^{-1}. The presence of H_2O_2 improved the photoproducts degradation until the optimum concentration was reached and the addition of Fe^{2+} led to much shorter reaction times and allowed total removal of all the species present in the reaction media.

The proposed photodegradation mechanism, based on the formation of two intermediate compounds that quickly degrade to the primary photoproducts previously identified, as well as its corresponding kinetic model, were validated with the experimental conversion data. The main kinetic parameters were determined with their values also supporting the experimental results. The simulation of the system behaviour was successfully undertaken with promising results that can allow further research using continuous or semi-continuous systems leading to the future scaling up of the process.

Acknowledgements

Nomenclature

4CP	4-chlorophenol
[4CP]	4-chlorophenol concentration at a time, t (mM)
$[4CP]_0$	4-chlorophenol initial concentration (mM)
a	Parameter defined in equation 25 (dimensionless)
b	Parameter defined in equation 26 (min^{-1})
c	Parameter defined in equation 27 (dimensionless)
d	Parameter defined in equation 28 (min^{-1})
f	Parameter defined in equation 29 (min^{-1})
I	Intermediate compound formed from 4-chlorophenol
$[I]$	Intermediate compound I concentration at a time t (mM)
J	Intermediate compound formed from 4-chlorophenol
$[J]$	Intermediate compound J concentration at a time t (mM)
k_0	Pseudo-first order kinetic constant for 4-chlorophenol photodegradation (min^{-1})
k_{01}	Intermediate compound I formation constant (min^{-1})
k_{02}	Intermediate compound J formation constant (min^{-1})
k_I	Intermediate compound I degradation constant (min^{-1})
k_J	Intermediate compound J degradation constant (min^{-1})
k_i	Primary photoproduct formation constant (min^{-1})
k_{i2}	Primary photoproduct degradation constant (min^{-1})
P	Photoproduct
P_i	Primary photoproducts
$[P_i]$	Primary photoproducts concentration at a time t (mM)
Q_i	Secondary photoproducts
t	Time (min)
X_{4CP}	4-chlorophenol conversion defined in equation 17 (dimensionless)

X_{4CP_c} 4-chlorophenol conversion calculated with the proposed kinetic model
X_P Photoproduct conversion defined in equation 18 (dimensionless)
X_{P_c} Photoproduct conversion calculated with the proposed kinetic model

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Table 1

Table 1. Retention time and wavelength of analysis for the 4-chlorophenol and the different photoproducts.

Compound	Retention time (min)	Wavelength (nm)
1, 2, 4-trihydroxybenzene	1.875	222
Hydroquinone	1.979	280
Resorcinol	2.200	274
Benzoquinone	2.333	246
Catechol	2.567	227
4-chlororesorcinol	3.200	283
Phenol	3.633	271
4-chlorocatechol	4.859	285
4-chlorophenol	8.067	225

Table 2

Table 2. Model parameters for the series of variation of molar ratio H_2O_2:4-chlorophenol.

Compound	0:1		15:1		25:1		30:1	
	d (min^{-1})	f (min^{-1})	d (min^{-1})	f (min^{-1})	d (min^{-1})	f (min^{-1})	d (min^{-1})	f (min^{-1})
4CP, Pi	0.0672	0.0606	0.0667	0.0606	0.1224	0.0606	0.1699	0.0606
benzoquinone	0.0672	0.0606	0.4616	0.0606	0.4660	0.0606	0.3143	0.0606

Table 3

Table 3. Model parameters for the series of variation of Fe^{2+} concentration.

Compound	1 mg L^{-1}		3 mg L^{-1}		5 mg L^{-1}		7 mg L^{-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})
4CP, Pi	0.1538	0.1360	0.1860	0.6278	0.2472	1.6054	0.3779	2.6014

Table 4

Table 4. Model parameters for the series of variation of 4-chlorophenol initial concentration.

Compound	50 mg L^{-1}		100 mg L^{-1}		150 mg L^{-1}	
	d (min^{-1})	f (min^{-1})	d (min^{-1})	f (min^{-1})	d (min^{-1})	f (min^{-1})
4CP, Pi	1.7242	2.4445	0.2472	1.6054	0.2394	1.0613

Figure(s)

Figure 1

(A)
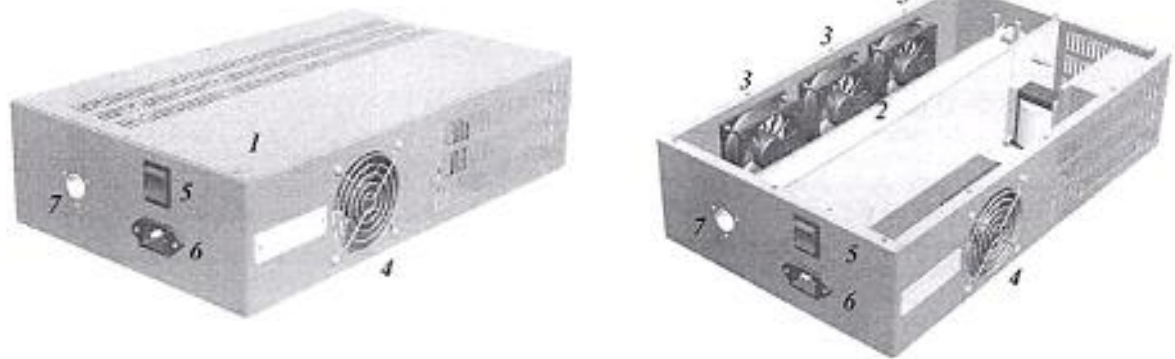
(B)
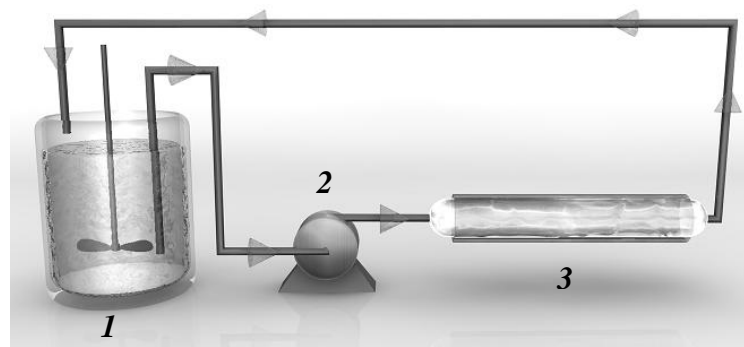
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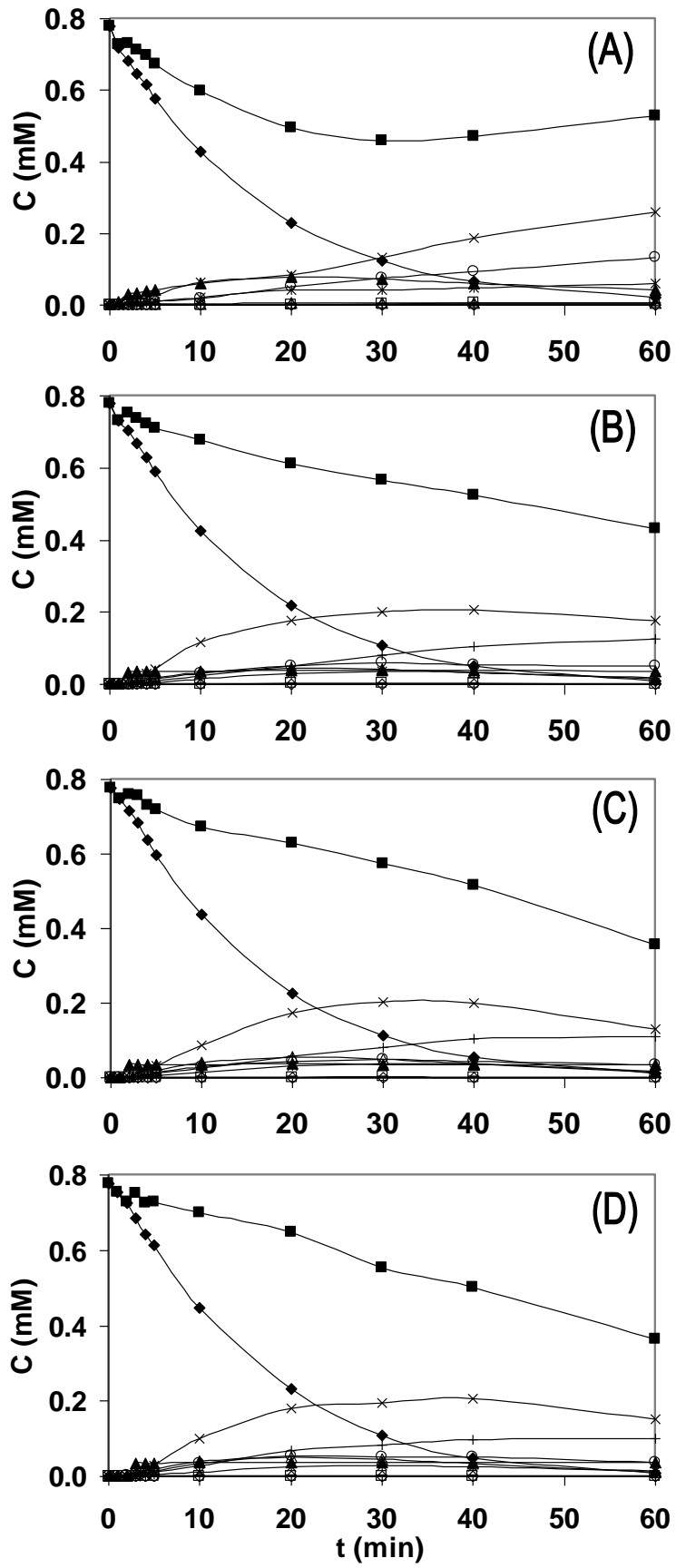
Figure 3
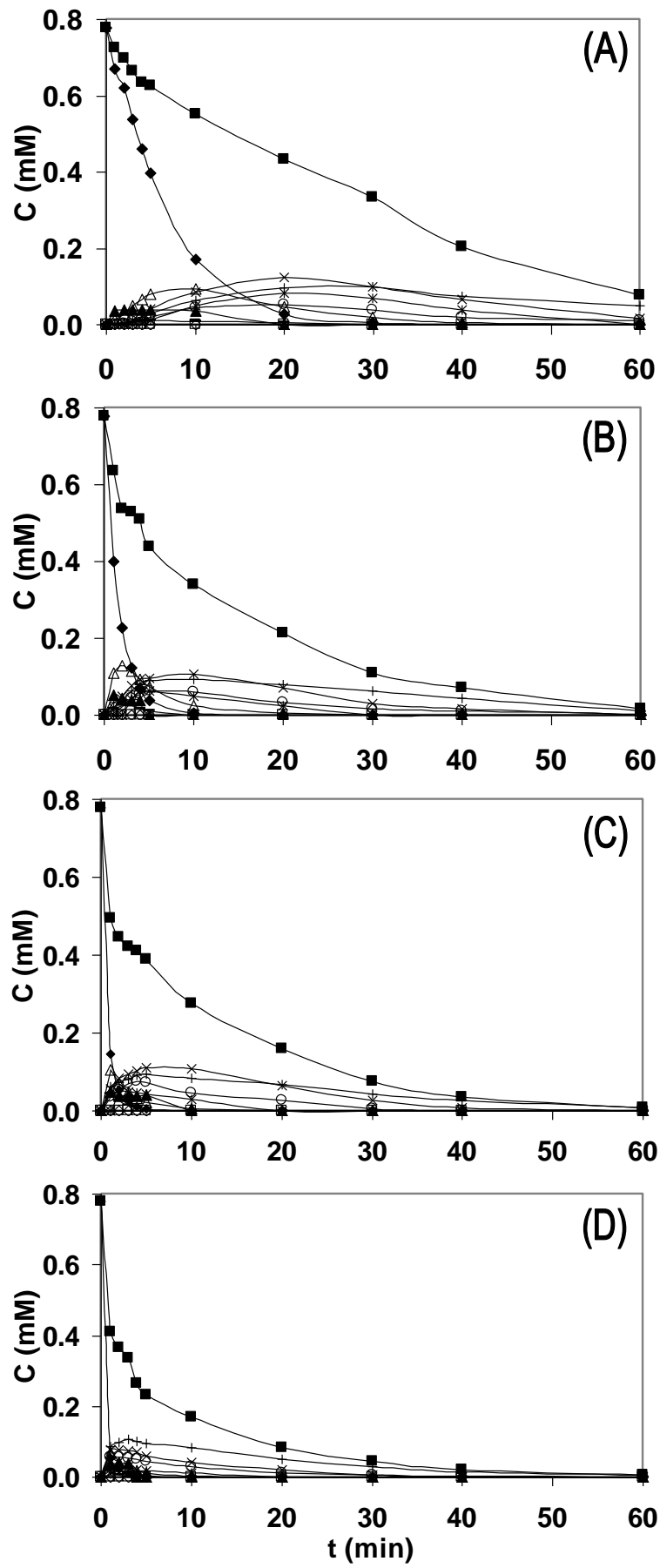
Figure 4

Figure 5

Figure 6

Figure 6

$$4CP \xrightarrow{k_{01}} I$$

$$4CP \xrightarrow{k_{02}} J$$

$$I \xrightarrow{k_1} P_1 \xrightarrow{k_{12}} Q_1$$

$$I \xrightarrow{k_2} P_2 \xrightarrow{k_{22}} Q_2$$

$$I \xrightarrow{k_M} P_M \xrightarrow{k_{M2}} Q_M$$

$$J \xrightarrow{k_{M+1}} P_{M+1} \xrightarrow{k_{M+12}} Q_{M+1}$$

$$J \xrightarrow{k_{M+2}} P_{M+2} \xrightarrow{k_{M+22}} Q_{M+2}$$

$$J \xrightarrow{k_N} P_N \xrightarrow{k_{N2}} Q_N$$
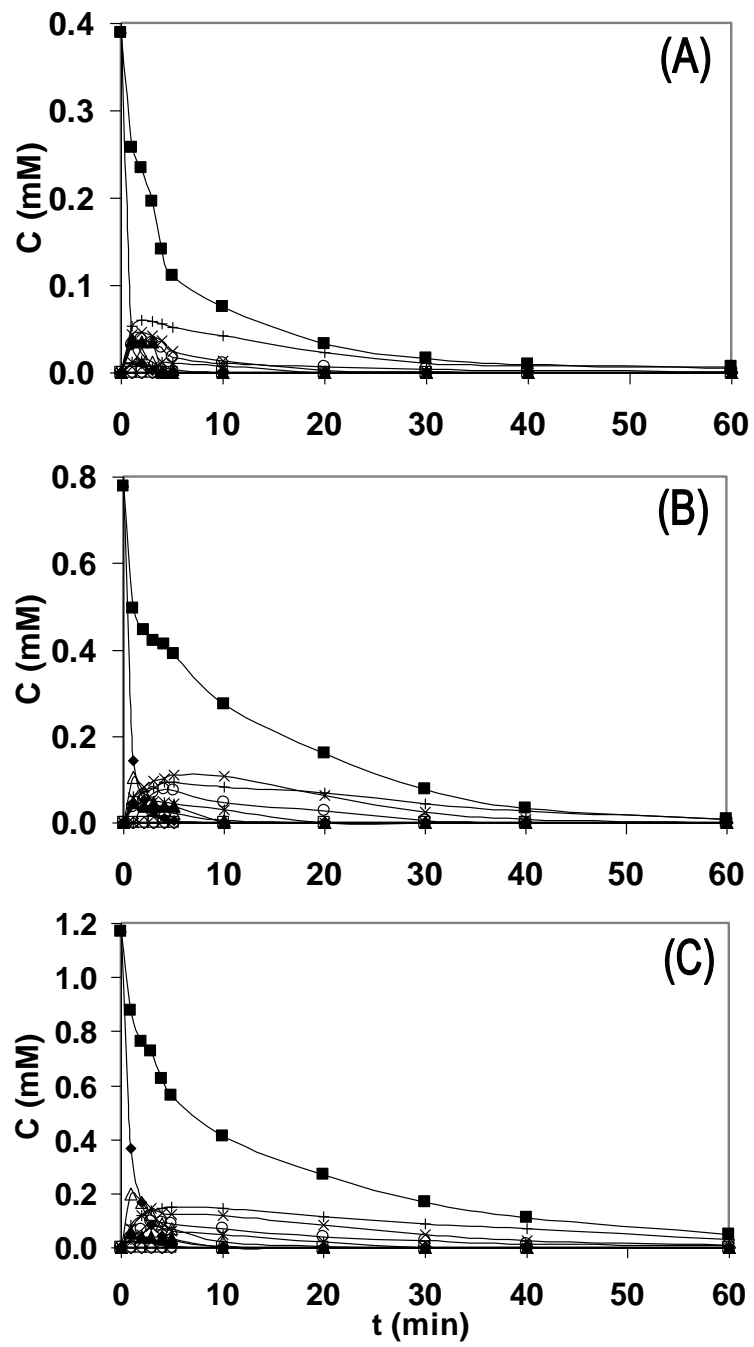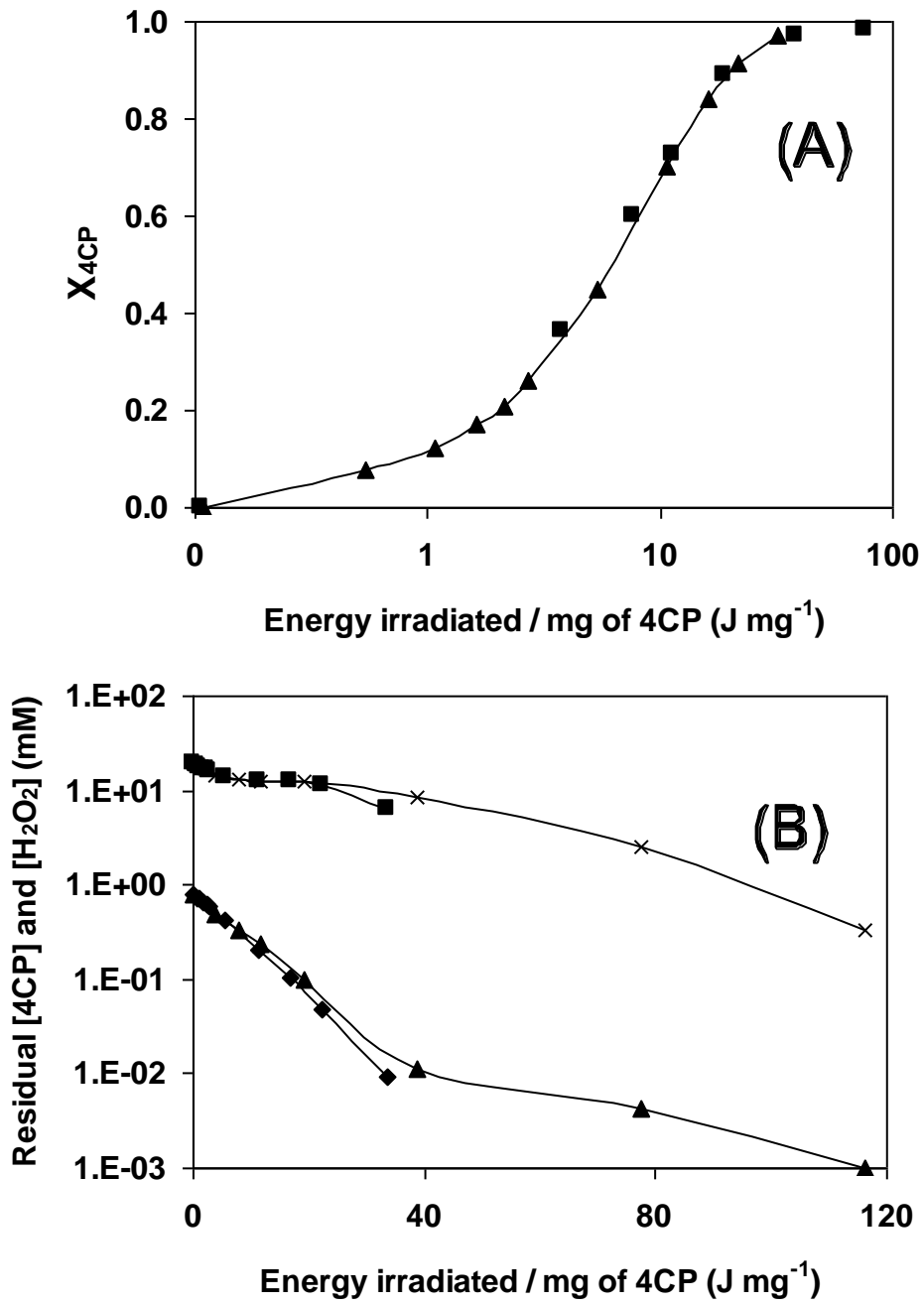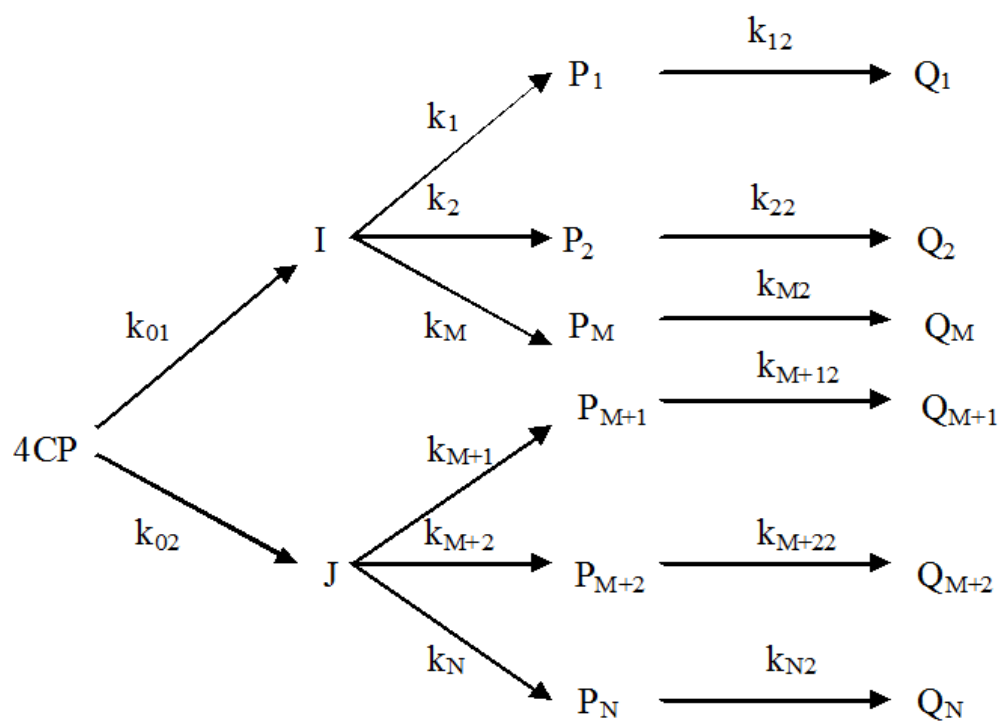
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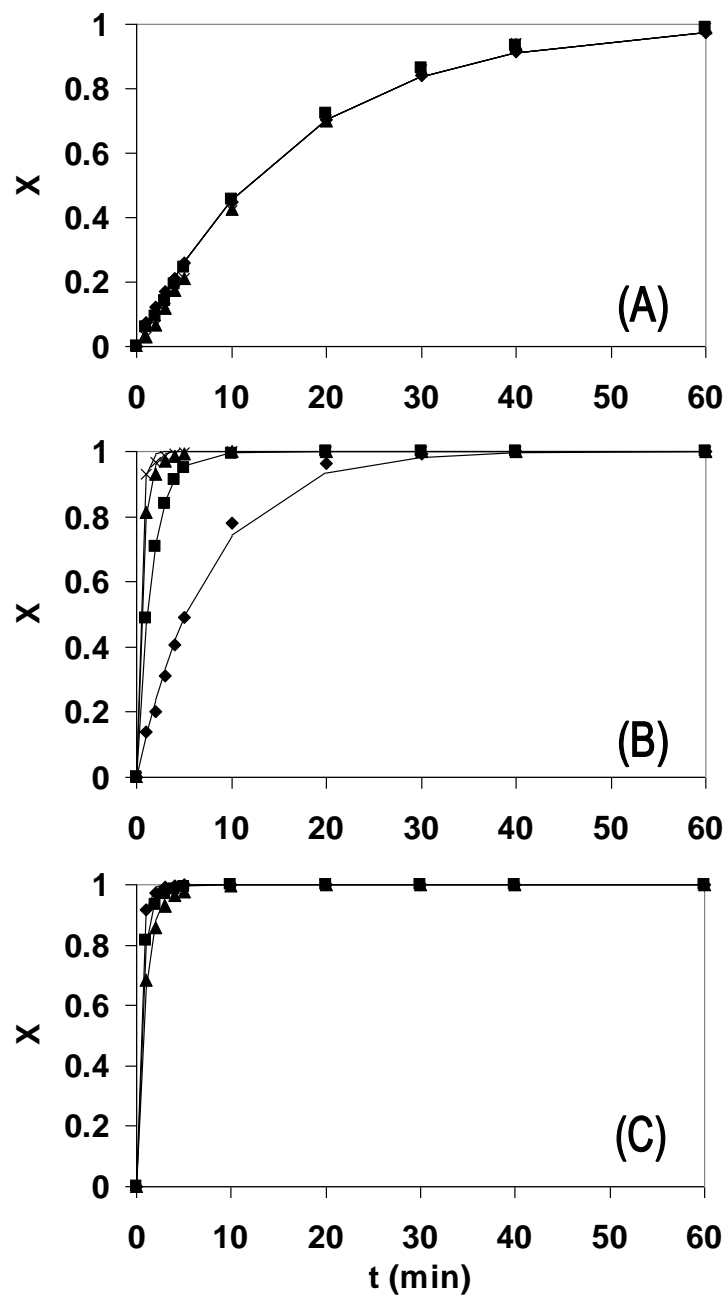
Figure 7

Figure 8
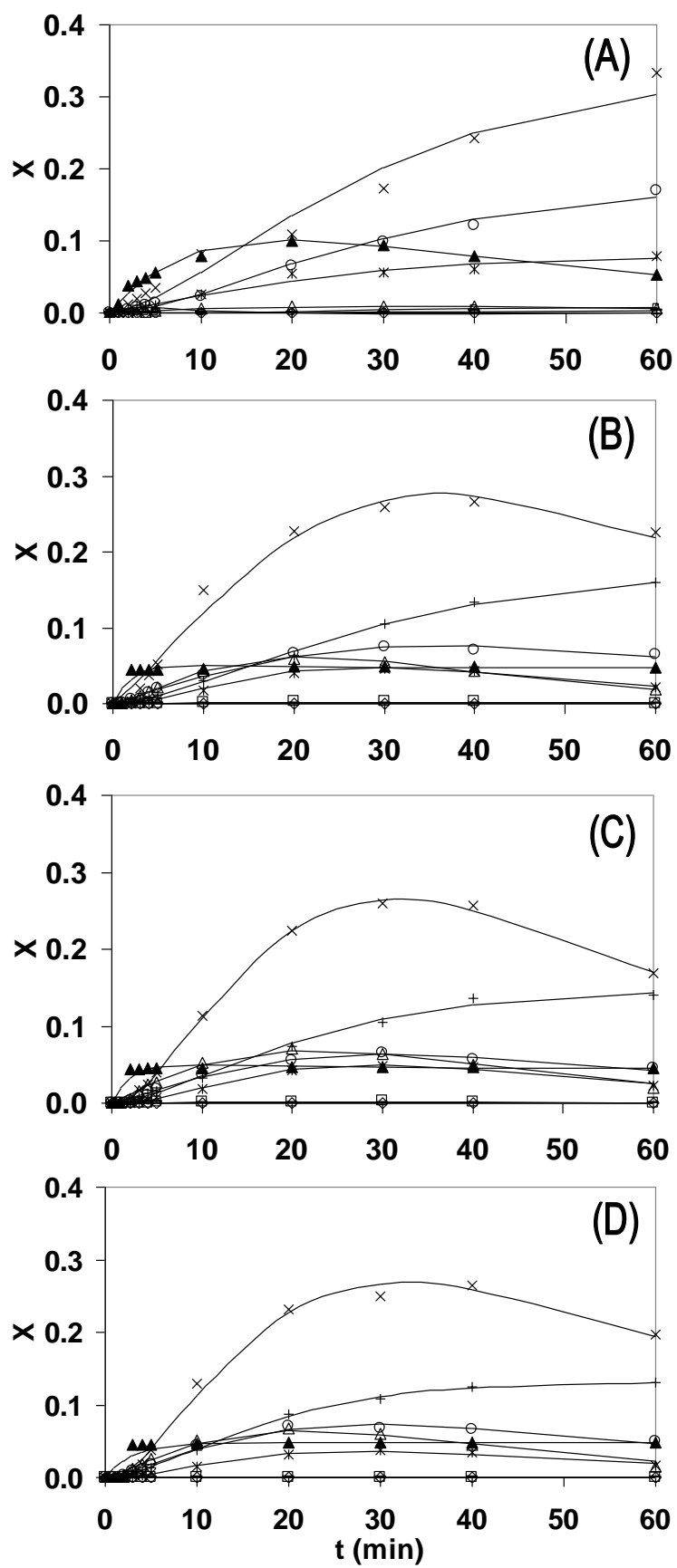
Figure 8

Figure 9
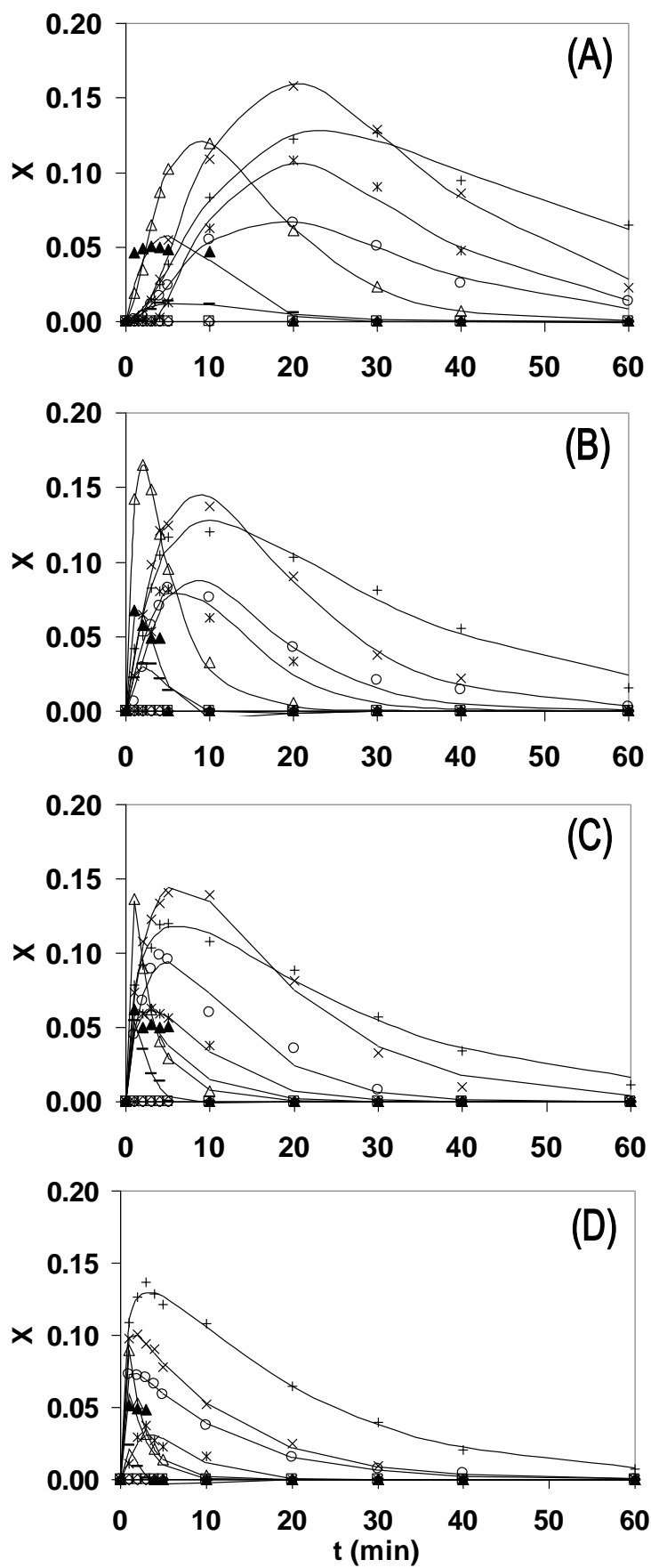
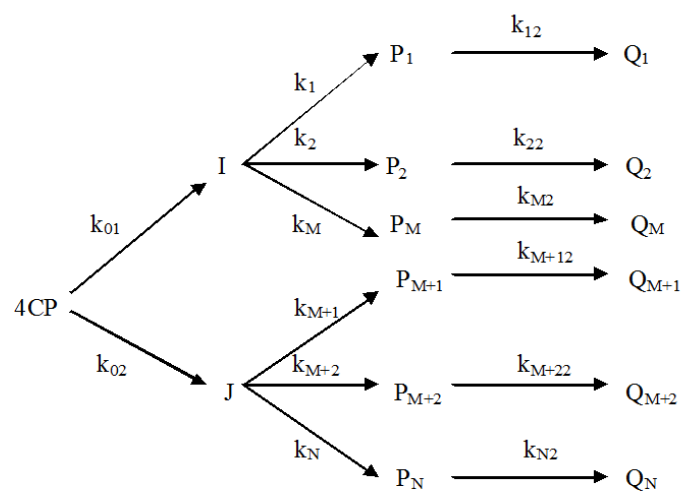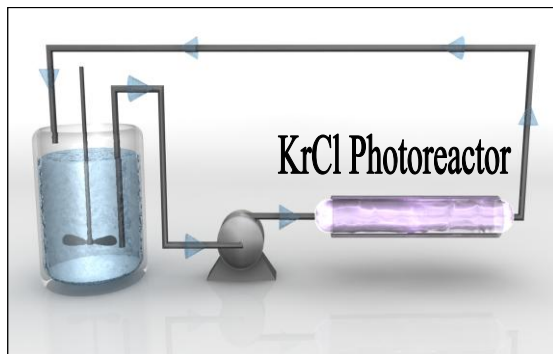Figure 9

Figure 10
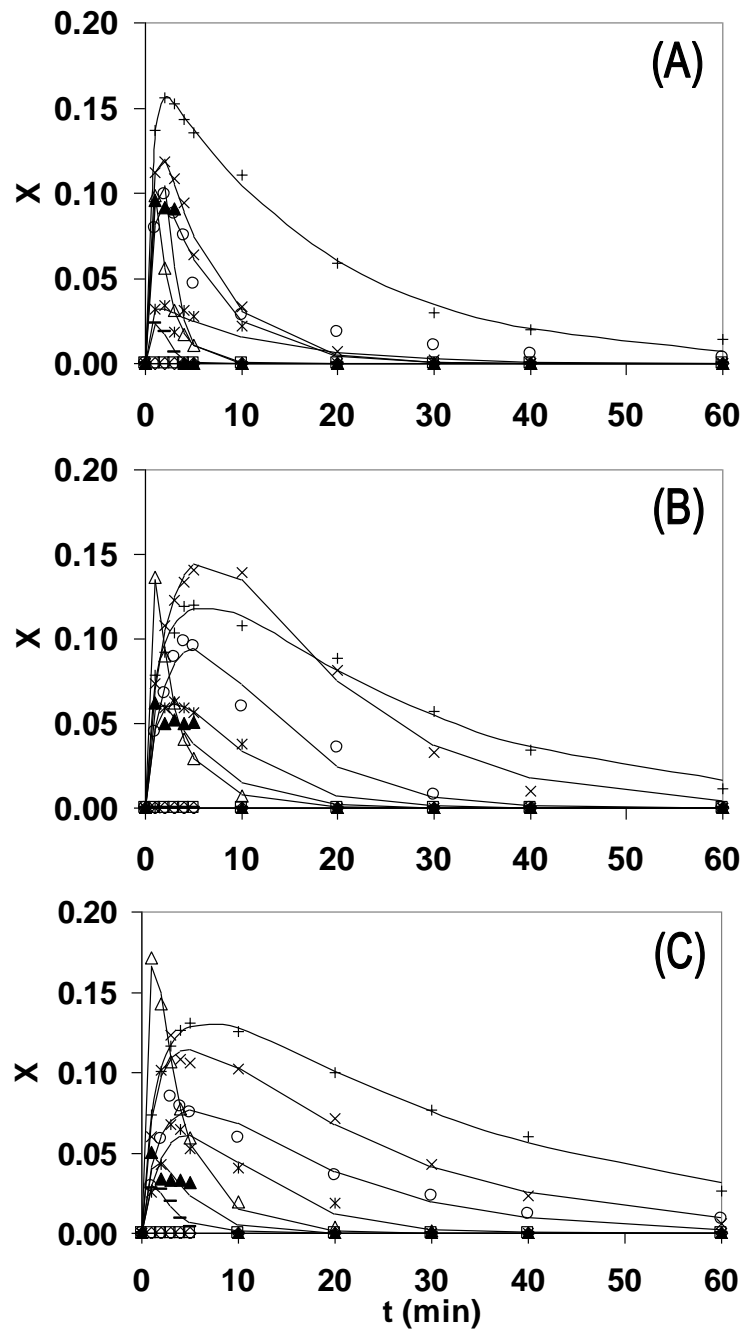
Figure 10

Figure 11

Figure 11
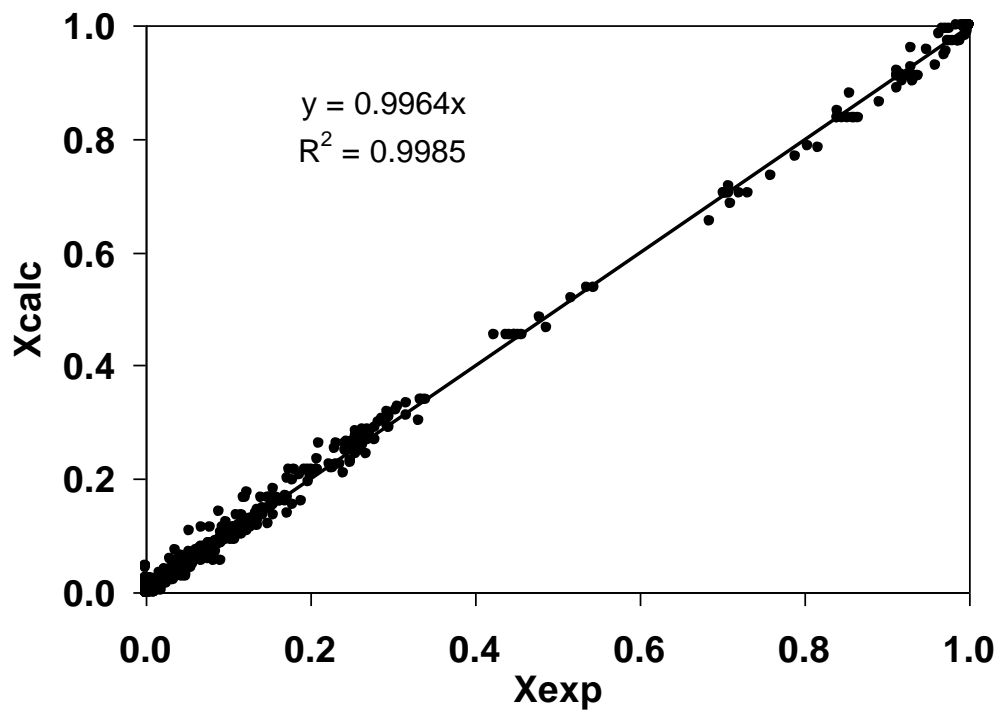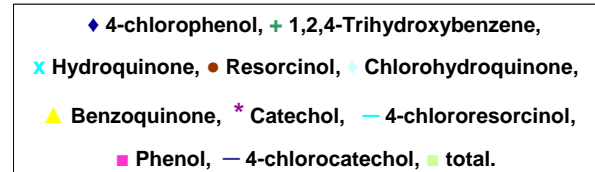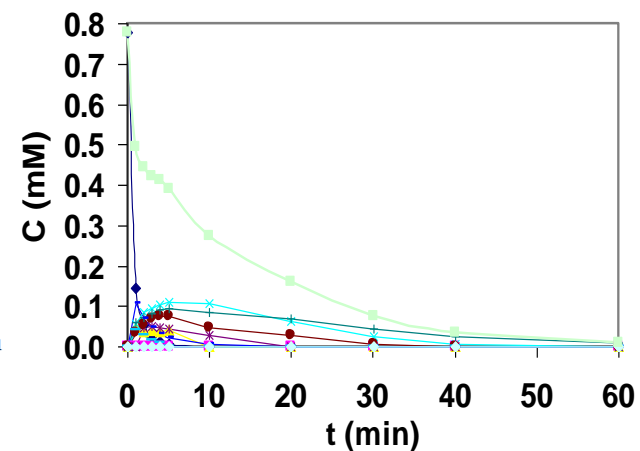
Highlights

- KrCl exciplex flow-through photoreactor successfully used to remove 4-chlorophenol
- Analysis of influence of operational conditions
- Photo-Fenton process allowed total degradation of substrate and by-products
- Mechanism and kinetic model for substrate and by-products proposed and validated

Figure Captions