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KINETIC STUDIES OF THE PHOTOCATALYTIC DEGRADATION OF THE HERBICIDE "PARAQUAT"

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ABSTRACT

The photocatalytic degradation of aqueous paraquat solutions with titanium oxide illuminated with ultraviolet light (365 nm) was investigated to determine the effect of paraquat initial concentration on the reaction rate. The experimental data were used to evaluate the apparent reaction rate constant assuming that paraquat photocatalytic reaction follows a pseudo first order reaction rate. Since the numerical value of the apparent rate constant decreases with initial paraquat concentration, the experimental data were also used to determine the kinetic constant and the adsorption constant of the Palmisano model that is a simplified form of the Langmuir-Hinshelwood equation. This model can only be used to predict the paraquat concentration at any time for very diluted solutions. The overall concentration of all the organic intermediate reaction products was calculated from the total organic carbon content of the reaction mixture and the paraquat concentration determined by HPLC. This information was used to evaluate the kinetic constant for the disappearance of the intermediate reaction products and the adsorption constant of the same intermediate products. The two ordinary differential equations of our kinetic model can be used to predict the concentration of paraquat and the overall concentration of all the organic intermediate reaction products at any time for diluted or concentrated solutions.

INTRODUCTION

Paraquat (1,1'-dimethyl-4,4'-bipyridinium di-chloride) belongs to bipyridinium nitrogenated pesticides. It is the active component of several commercial herbicides that are used around the world [1]. Residual paraquat from low concentration water solutions can be adsorbed on any type of soil particles where it can be degraded by microbiological and photochemical processes [2,3]. However, it is well known that any pesticide solution may contaminate the environment [4,5]. Therefore, any pesticide rinsate solution must be degraded by an advanced oxidation process before disposal. It has been demonstrated [6-8] that aqueous solutions of several herbicides can be completely oxidized by photocatalytic processes, in which photo induced holes in semiconductor particles oxidize hydroxide ions or water molecules adsorbed on the surface of the particles to produce •OH and •O₂⁻ radicals which subsequently attack adsorbed organic molecules [9-11]. Since the photocatalytic degradation process is an excellent method to treat paraquat solu-

tions, several authors [1,12-15] have studied the degradation of pure paraquat solutions with TiO₂ catalyst illuminated by long wave UV light in order to understand the reaction mechanism and to determine the effect of several reaction parameters on the overall conversion of paraquat. Florencio et al. [15] identified six of the organic intermediate reaction products by several spectroscopy techniques and proposed a reaction mechanism. However, they were not able to quantify those organic products. Kang [1] demonstrated that paraquat solution can be completely mineralized with a TiO₂ film of about 200 nm deposited on the wall of a UV lamp. Moctezuma et al. [14] investigated the effect of the following reaction parameters: catalyst weight, kind of dissolved gas in the reaction mixture, flow of oxidizing gas and paraquat initial concentration on the final conversion of the photocatalytic degradation experiments. Martyanov [13] reported that initial paraquat reaction rate is a strong function of the light intensity. However, none of those studies have reported a kinetic equation to describe the complete dependency of paraquat degradation rate as a function

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of paraquat concentration. In this study, several kinetic experiments were carried out to investigate the effect the initial paraquat concentration on the reaction rate. The kinetic parameters of three LH-HW kinetic models were experimentally determined.

EXPERIMENTAL DETAILS

1. Materials

High purity paraquat (1,1'-dimethyl-4,4'-bipyridinium dichloride) was purchased from Aldrich. Titanium dioxide (P25, 80% anatase, 20% rutile, specific surface area of $55 \text{ m}^2 \text{ g}^{-1}$) [16] was donated by Degussa Corporation. It was calcined at 450°C during 4 h before using it in any reaction. Mobile phase for HPLC analysis was prepared with the sodium salt of 1-hexasulfonic acid (Pic B6, Aldrich), phosphoric acid and methanol chromatographic grade (Mallinckrodt). Potassium biphtalate and sodium bicarbonate (Nakalai Teske) were used as standards for total organic carbon analysis. The water used in all the experiments was purified with Milli-Q-Plus system.

2. Photoreactor and Photodegradation Experiments

Photocatalytic degradation experiments were carried in a reactor system that has been already described [14]. It has a Pyrex glass tube reactor (200 mL) that can be irradiated with four long wave UV light lamps ($\lambda_{\text{max}} = 365 \text{ nm}$, Cole-Palmer E-09815-55). Since the concentration of organic pollutants is a very important parameter in the wastewater treatment processes [17-19], we have studied the effect of paraquat initial concentration on the reaction rate in order to develop a kinetic model for the photocatalytic degradation of paraquat. Several experiments were carried out with paraquat aqueous solutions with different initial concentration (10 to 150 ppm). For each of the experiments 100 mL of a paraquat solution were placed inside the glass reactor and mixed with 0.2 g of TiO_2 . This slurry was agitated with a magnetic stirrer. Pure oxygen was bubbled through the system at a rate of 100 mL min^{-1} . Samples for analysis were taken at different times to monitor the reaction. Each sample was analyzed by HPLC with a Waters Chromatographer, model 600 E equipped with a UV detector tuned at 257 nm and a C18 Symmetry Column. The mobile phase was a solution of 0.005 M Pic B-6 /methanol (70:30), $\text{pH} = 3.0$ and the flow rate was 1.0 mL min^{-1} . The total organic carbon (TOC) in each sample was measured with a Shimadzu carbon analyzer model TOC 5000 A.

RESULTS AND DISCUSSION

Figure 1 shows the photocatalytic disappearance of paraquat as a function of irradiation time for each

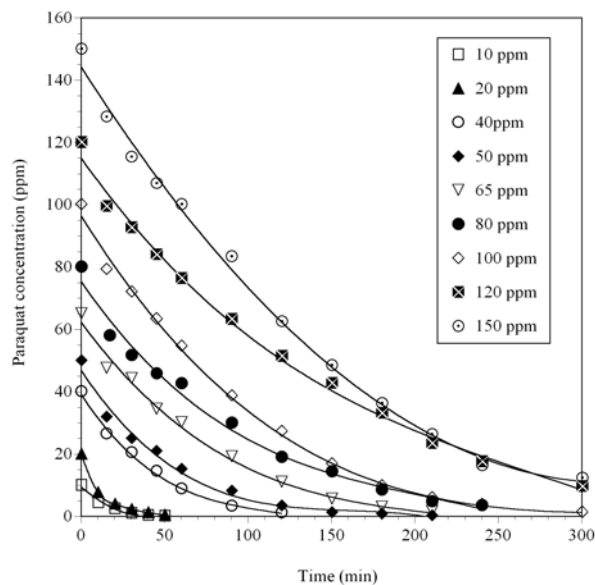


Fig. 1. Paraquat concentration as a function of time for the photocatalytic degradation of paraquat.

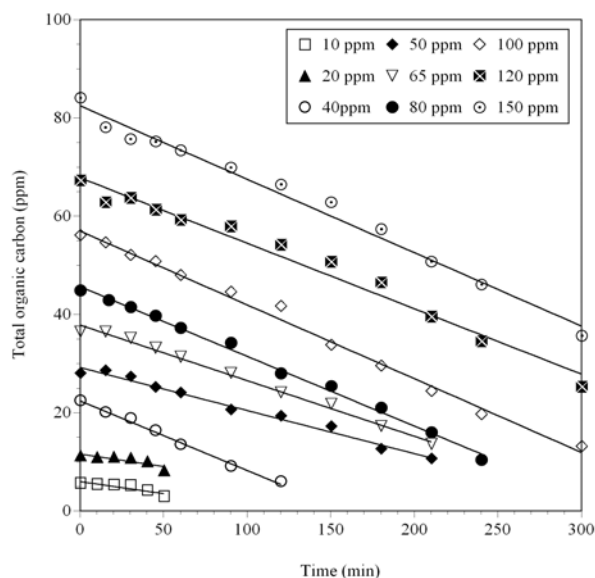


Fig. 2. Total organic carbon concentration as a function of time for the photocatalytic degradation of paraquat.

of the reaction experiments. All the reaction samples were analyzed by HPLC and paraquat concentration was determined with a calibration curve. As expected, these results clearly indicate that low concentration paraquat solutions are easily degraded by photocatalytic reactions and that high concentration paraquat solutions required longer reaction times to degrade the original molecule. It is important to mention that several organic reaction products were detected during the HPLC analysis. However, we could not fully identify them by simple HPLC analysis.

Figure 2 shows the concentration of TOC as a function of reaction time. It confirms that paraquat is transformed to other organic intermediate reaction

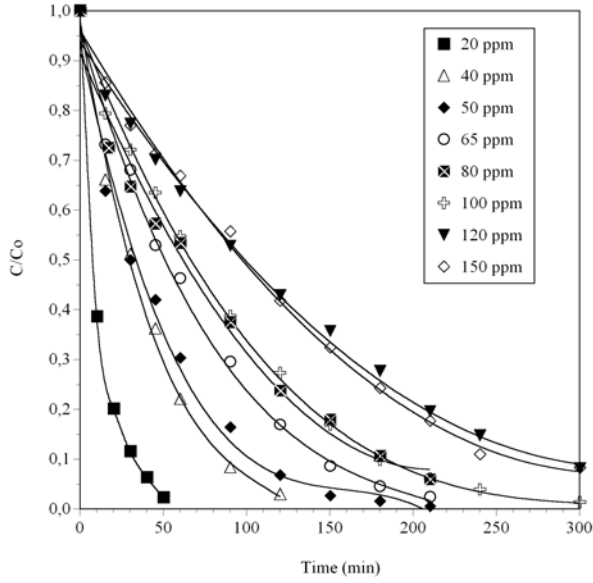
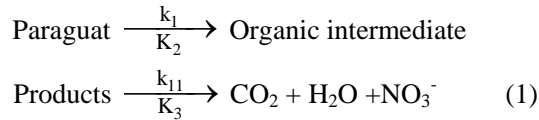


Fig. 3. Relative paraquat concentration (C/C_0) as a function of time for the photocatalytic degradation of paraquat.

products before complete mineralization to CO_2 as demonstrated by others [1,12,15].

The overall reaction can be represented by the Eq 1.



Each line in Fig. 1 indicates that the first step on the photocatalytic reaction follows a pseudo first order kinetic law, according to the equation:

$$-r_p = -\frac{dC}{dt} = k_{app} C \quad (2)$$

This expression can be integrated

$$\ln\left(\frac{C}{C_0}\right) = -k_{app} t \quad (3)$$

Therefore, raw data for paraquat concentration were normalized (C/C_0) and plotted as a function of time on Fig. 3. The natural logarithms of normalized concentrations were plotted on Fig. 4. The apparent rate constants presented on Table 1 were determined by linear regression [20]. The value of the apparent rate constant decreases with initial paraquat concentration indicating that paraquat reaction follows a LH-HW mechanism (4). Other researchers [21-23] have reported similar results for the photocatalytic degradation of phenol and several nitrophenols.

$$-r_p = -\frac{dC}{dt} = \frac{k_1 C}{1 + K_2 C + \sum_i K_i C_i} \quad (4)$$

At very short reaction times, paraquat concentra-

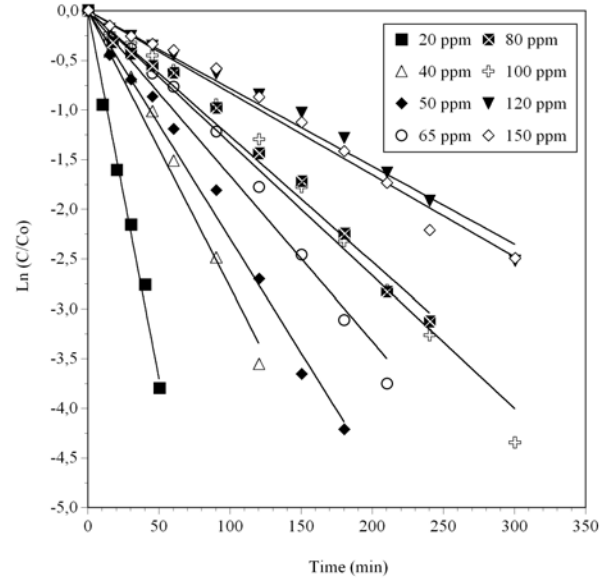


Fig. 4. Logarithmic plots of the relative paraquat concentration (C/C_0) as a function of time for the photocatalytic degradation of paraquat.

Table 1. Pseudo first order rate constants for the photocatalytic degradation of paraquat

Paraquat initial concentration (ppm)	k_{app} (10^3 min^{-1})	R^2
5	114.34	0.9888
10	88.53	0.9885
20	71.40	0.985
40	29.54	0.9889
50	24.89	0.9889
65	17.64	0.9808
80	18.31	0.9876
100	14.33	0.9878
120	7.84	0.9867
150	8.26	0.9865

tion is almost equal to its initial concentration and the concentration of all the intermediate reaction products is very low. Therefore, the adsorption term for the intermediate reaction products can be neglected. Under these restrictions, the LH-HW model can be represented by Eq. 5.

$$-r_p = -\frac{dC}{dt} = \frac{k_1 C}{1 + K_2 C} \quad (5)$$

Initial reaction rates of paraquat that are presented on the following table were calculated with Eq. 2 at $t = 0$ and $C = C_0$.

The kinetic constant (k_1) and the paraquat adsorption constant (K_2) were calculated by linear regression of a plot of Eq. 6 that represents the double reciprocal of Eq. 5 using all the data points reported on Table 2.

Table 2. Paraquat initial reaction rates for the photocatalytic degradation of paraquat (0.2 g of TiO₂/100 mL of aqueous solution)

Paraquat initial concentration (ppm)	Initial reaction rate (ppm min ⁻¹)
5	0.3835
10	0.597
20	0.9466
40	1.1613
50	1.582
65	1.64
80	1.5058
100	1.8323
120	1.8227
150	1.7517

$$\frac{C_0}{-r_p} = \frac{K_2 C_0}{k_1} + \frac{1}{k_1} \quad (6)$$

The values for the constants k_1 and K_2 are 0.0886 min⁻¹ and 0.0419 ppm⁻¹ respectively. Therefore, the final form of the initial reaction rate equation is as follow:

$$-\frac{dC}{dt} = \frac{0.0886C}{1 + 0.0419C} \quad (7)$$

In order to validate the LH-HW model, the experimental reaction rates and the reaction rates calculated with Eq. 7 were plotted on Fig. 5. It shows a reasonable agreement between the calculated and the experimental points. However, Eq. 7 can only be used to calculate the initial reaction rates. Therefore, it is recommended to use Eq. 4 to calculate the degradation reaction rates for all the organic compounds at any time of reaction. Dijkstra [24] and Macanouva et al. [8] studied the photocatalytic degradation of formic acid and diuron, respectively. They calculated the concentration and the reaction rates of all the organic compounds present in the reaction mixture applying the LH-HW model (Eq. 4) for a group of parallel and serial reactions. But, it is convenient to point out that all the organic compounds present in the reaction mixture must be fully identified and quantified by NMR and GC-MS to solve the simultaneous ordinary differential equations.

Since the organic intermediate reaction products for the photocatalytic degradation of paraquat can not be easily identified nor quantified [13,15], Macanouva method [14] can not be used to predict the concentration and the reaction rate of paraquat at any time. Other researchers [17,19,21-22,25] have recommended to use the Palmisano modification to the LH-HW model (Eq. 8) to predict the reaction rate of any aromatic organic solute.

$$-r_p = -\frac{dC}{dt} = \frac{k_1 C}{1 + K_2 C_0} \quad (8)$$

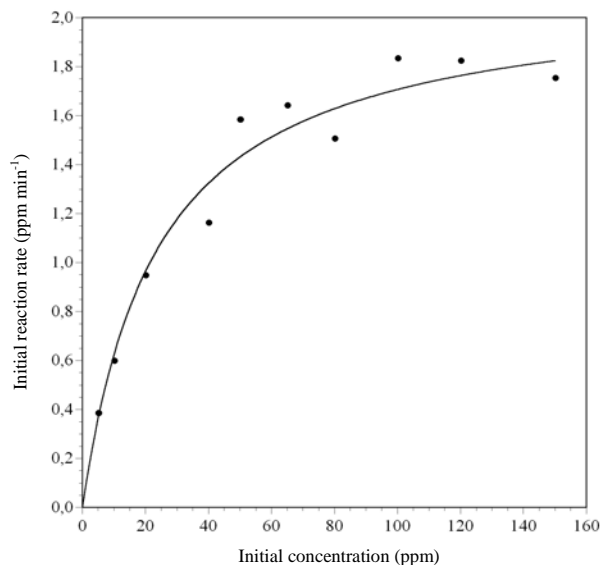


Fig. 5. Paraquat initial reaction rate vs. initial concentration.

In this case, it is assumed that the adsorption constants for all the organic intermediate reaction products are the same as paraquat adsorption constant and that none of the intermediate products is transformed to CO₂. The denominator of the right term of Eq. 4 was simplified with Eq. 9.

$$K_2 C + \sum_i K_i C_i = K_2 C_0 \quad (9)$$

The Palmisano model (Eq. 8) was integrated by a numerical method to calculate the paraquat concentration at any time. The values of k_1 and K_2 used for the integration were 0.0886 min⁻¹ and 0.0419 ppm⁻¹ respectively. Some of the results are plotted in Fig. 6. It was found that the Palmisano model can be used only to predict the paraquat concentration at any time of reaction for very diluted solutions with a concentration of 20 ppm or less. Otherwise, there is a large difference between the predicted and the experimental values of paraquat concentration. It has been suggested [26] that the denominator of the right term of Eq. 4 can be simplified with Eq. 10.

$$\sum_i K_i C_i = K_3 C_{Ti} \quad (10)$$

In this case, it is assumed that all the organic intermediate reaction products have the same adsorption constant and that some of the organic molecules are transformed to CO₂. The new LH-HW model is given by Eq. 11.

$$-r_p = -\frac{dC}{dt} = \frac{k_1 C}{1 + K_2 C + K_3 C_{Ti}} \quad (11)$$

C_{Ti} is the sum of the concentrations of the organic intermediate products in terms of paraquat con-

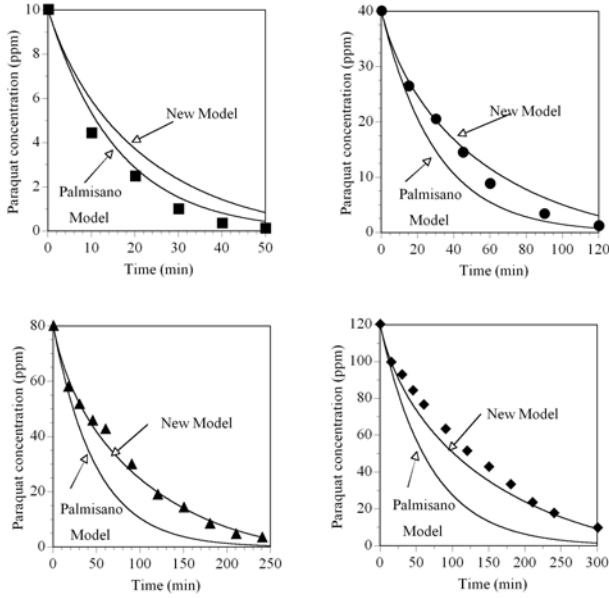


Fig. 6. Prediction of paraquat concentration by the Palmisano model and our modified kinetic model.

centration. It can be calculated by a material balance between the concentration of paraquat determined by HPLC analysis and the amount of total organic carbon determined by TOC analysis.

$$\text{TOC} = \text{Carbon in paraquat} + \text{Carbon in organic intermediate products} \quad (12)$$

Therefore, the concentration of all organic intermediate products in terms of paraquat concentration is given by the following equation:

$$C_{Ti} = \frac{[\text{TOC}]}{F_{\text{TOC}}} - C \quad (13)$$

The experimental values of paraquat concentration and TOC are given in Fig. 1 and 2 respectively.

Since the total concentration of the intermediate products increased at the beginning of the reaction experiment and decreased at the end [12], it is convenient to write the net reaction rate Eq. 14 for the intermediate products.

$$-r_{Ti} = -\frac{dC_{Ti}}{dt} = \frac{k_1 C}{1 + K_2 C + K_3 C_{Ti}} - \frac{k_{11} C_{Ti}}{1 + K_2 C + K_3 C_{Ti}} \quad (14)$$

Equations 11 and 14 were used to evaluate the kinetic constant (k_{11}) of the second step of the reaction mechanism and the adsorption constant (K_3) of the intermediate products. The values for the constants k_1 and K_2 were already calculated and they are given by Eq. 7. The numerical values of k_{11} and K_3 are 0.0651 min^{-1} and 0.1855 ppm^{-1} respectively. They can be calculated by an optimization technique using a Polymath or a Matlab program. Therefore, the reaction rate equations are written as follow:

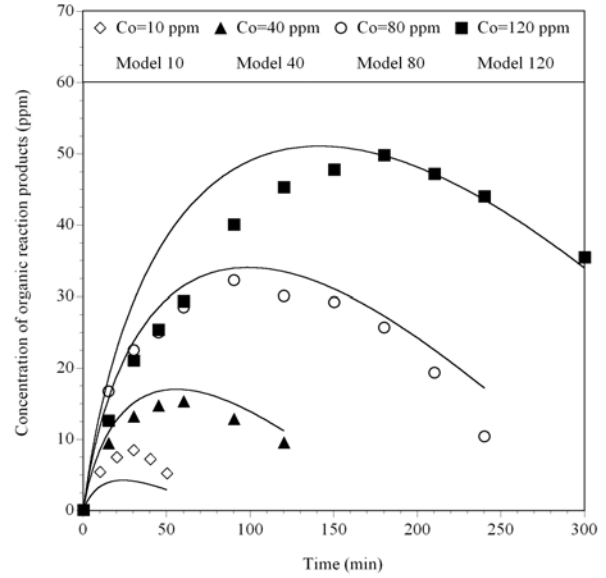


Fig. 7. Overall concentration of organic intermediate reaction products as a function of time.

$$-r_a = -\frac{dC}{dt} = \frac{0.0886C}{1 + 0.0419C + 0.18554C_{Ti}} \quad (15)$$

$$-r_L = -\frac{dC_L}{dt} = \frac{0.0886C}{1 + 0.0419C + 0.18554C_L} - \frac{0.06512C_L}{1 + 0.0419C + 0.18554C_L}$$

(16)

These two ordinary differential equations were solved by a numerical method using a Polymath program to calculate the concentration of paraquat and the concentration of all the organic reaction intermediate products at any time of reaction. The calculated paraquat concentrations were plotted in Fig. 6 together with the concentrations calculated by the Palmisano model and the experimental data points. There is a good agreement between the experimental points and the concentrations calculated by the new model. It can be used to predict the paraquat concentration at any time of reaction for all the experiments. The concentrations of the intermediate reaction products calculated by the new model were plotted in Fig. 7 together with the experimental data points. In this case, there is a noticeable difference between the predicted and the experimental points. This may be due to the fact that all the intermediate reaction products were not fully identified and that they were treated as a single organic compound.

CONCLUSIONS

The results of this study show that the photocatalytic degradation of aqueous paraquat solutions with

titanium oxide illuminated with ultraviolet light (365 nm) follows a pseudo first order kinetic equation. Since the apparent reaction rate constant decreased with the increment of paraquat initial concentration, it is convenient to describe the kinetics by a LH-HW model. At very short reaction times, the overall concentration of the intermediate reaction products can be neglected and paraquat concentration is almost equal to its initial concentration. The kinetic constant (k_1) is equal to 0.0886 min^{-1} and the paraquat adsorption constant (K_2) is equal to 0.0419 ppm^{-1} . But, the simplified LH-HW model can only be used to calculate the initial reaction rate and the paraquat concentration at the beginning of any reaction experiment. In order to develop a model to estimate the concentration of paraquat at any time, the sum of all the organic intermediate reaction products was evaluated by a material balance between the concentration of paraquat determined by HPLC analysis and the amount of TOC. Our kinetic model was developed assuming that the intermediate products have the same adsorption constant. The numerical values for the kinetic constant (k_{11}) and the adsorption constant of the organic intermediate (K_3) are 0.0651 min^{-1} and 0.1855 ppm^{-1} . Our kinetic model can be used to predict the concentration of paraquat and the overall concentration of all the organic intermediate reaction products at any time for diluted or concentrated solutions. Palmisano model can only be used to predict the concentration of paraquat for very diluted solutions because it assumes that the intermediate products have the same adsorption constant as paraquat and that intermediate products are not transformed to CO_2 .

NOMENCLATURE

C	Paraquat concentration, ppm
C_0	Paraquat initial concentration, ppm
C_i	Concentration of organic intermediate reaction products, ppm
C_{Ti}	Sum of the concentration of all organic intermediate reaction products, ppm
F_{TOC}	Fraction of organic carbon present in paraquat = 0.56 dimensionless
k_{app}	Apparent reaction rate constant min^{-1}
k_1	Paraquat degradation reaction rate constant min^{-1}
k_{11}	Reaction rate constant for the mineralization of the organic products min^{-1}
K_2	Paraquat adsorption constant, ppm^{-1}
K_3	Average adsorption constant for the organic intermediate reaction products ppm^{-1}
K_i	Adsorption constant for each of the organic intermediate reaction products, ppm^{-1}
$-r_p$	Paraquat reaction rate, ppm min^{-1}
$-r_{po}$	Paraquat reaction rate, ppm min^{-1}

$-r_{Ti}$	Net reaction rate for the organic intermediate reaction products, ppm min^{-1}
t	Time of reaction min
TOC	Total organic carbon, ppm

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