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Kinetic study of the photocatalytic oxidation of ethylene over TiO₂ thin films

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Abstract. The photocatalytic oxidation process has been recognized as an environmental friendly, sustainable and low-cost technology for air treatment. A photocatalytic batch reactor has been employed to assess the kinetics of the oxidation of ethylene (C₂H₄) over immobilized titanium dioxide (TiO₂) and the effect of initial pollutant concentration on the kinetics. The rate model based on the simplified mono-molecular Langmuir-Hinshelwood (LH) kinetic model was found to represent the degradation satisfactorily, however with numerical constraints. These were overcome by employing two different approaches. On one hand the Langmuir-Hinshelwood model was solved by means of the Lambert W-function and on the other hand it was reduced to a pseudo-first order rate law, both resulting in a good fit to the experimental data, thus proving that the photodegradation of C₂H₄ over TiO₂ can be modelled by a first order rate law under low concentration conditions. Moreover, both models give a linear dependence between the reaction rate and the initial C₂H₄ concentration, making an estimation of reaction rate as a function of concentration possible, for a larger interval of C₂H₄ concentrations.

1. Introduction

In our present days resources are already scarce and it is expected for them to become even scarcer in the following years. This means that energy, water and even land cannot be misused, but must be used efficiently and sustainably. Yearly in Denmark alone food waste corresponds to a loss of approx. 1.5 billion euros, out of which fruits and vegetables spoilage, occurring during transportation, storage and retail, accounts for almost a quarter [1]. One of the most significant contributors to a high fruits, vegetables and flowers spoilage is the generation and build-up of ethylene (C₂H₄) in enclosed storage spaces. Ethylene is a hydrocarbon gas released by the aforementioned produce, which drives their ripening and growth, being responsible for changes in colour, texture and softening. A prolonged exposure or a high level of C₂H₄ causes these produce to ripe and degrade prematurely. By removing the C₂H₄ or minimizing its levels from the enclosed atmosphere of storage or transportation facilities the shelf life of perishable produce can be prolonged and thus, waste reduced. However, removing ethylene from the surrounding of C₂H₄-sensitive produce is one of the main challenges that the postharvest industry is facing. Even though this C₂H₄ generation problem stems from domains such as plant metabolism, biochemistry and postharvest biology, the solution can be found in chemical engineering, photocatalysis, material science, and adsorption mechanisms [2].

Photocatalytic oxidation (PCO) processes have gained popularity in the recent decades, due to the growing attention given to indoor air quality control. Such processes are effective at removing low traces of volatile organic compounds (VOCs), nitrogen oxides (NO_x), and carbon monoxide (CO) at room temperature and pressure and may be more cost-effective than other technologies, such as



chemical scrubbers or activated carbon adsorbers, due to the fact that the catalyst is inexpensive and capable of mineralizing most VOCs [3], among which C_2H_4 . However, this technique is still under the development stage and little research has been made using C_2H_4 as a model compound at concentrations in the ppm range, typical for storage facilities of fresh produce and greenhouses. Extrapolating the collected degradation data at concentrations much higher than those of interest may not be valid [4]. In this sense several studies have shown that the inlet pollutant concentration dictates the reaction rate, where increasing inlet concentration enhances the reaction rate and may even cause a shift in reaction order [5].

The comprehensive modelling of photocatalytic reactors is complex. This involves coupling the radiation field with the fluid dynamics and the appropriate reaction kinetics [6, 7, 8]. Most of the studies have successfully modelled the effect of radiation intensity and optical properties on the PCO process, nevertheless rigorous models which can predict pollutant degradation as a function of real operating conditions and UV intensity have received little attention, especially gas phase photocatalytic reactors.

Thus, this study aims at investigating the reaction kinetics of C_2H_4 over immobilized TiO_2 thin films at concentrations in the ppm range and deriving a model for predicting the effects of pollutant initial concentration on the reaction kinetics in a batch setup.

2. Experimental setup and method

Figure 1 depicts the schematic of the experimental setup used for the gas phase PCO of C_2H_4 and figure 2 shows the reactor chamber where the oxidation takes place.

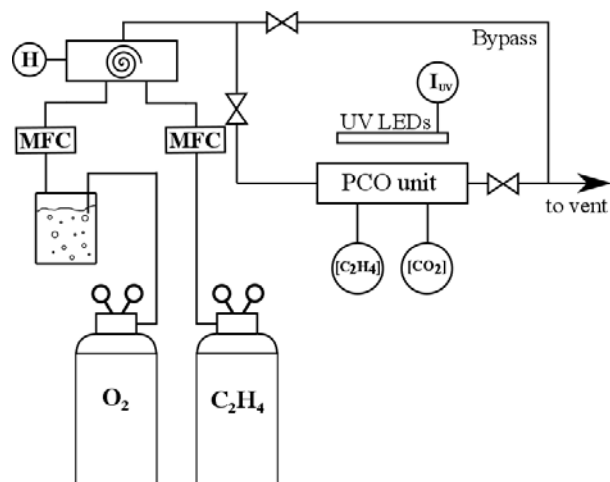


Figure 1. Schematic of the experimental batch setup.

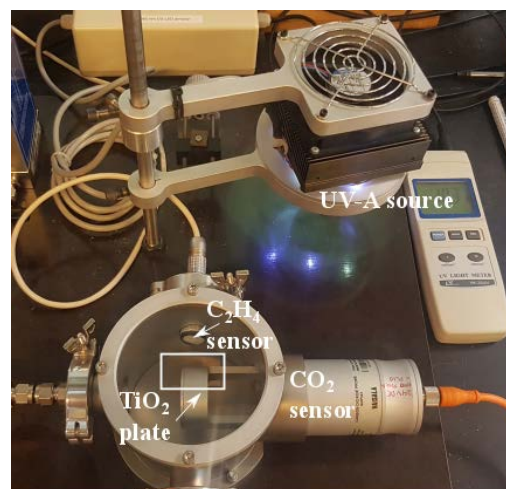


Figure 2. Reaction chamber – top view.

The cylindrical reactor has stainless steel walls, except for the top, which is made out of a 3 mm thick borosilicate glass to allow the irradiation of the catalyst. The reactor was irradiated with seven UV-A LEDs (LED ENGIN LZ-00UV00) each mounted on a 4.4mm x 4.4mm ceramic package with an integrated glass lens of Ø3.2 mm. The diodes have a radiant flux of 1.2 W UV-A and emit between wavelengths of 340 and 400 nm with a maximum irradiance peak at 365 nm. All seven LEDs are fixed on an Ebmapast 3412 NHH heat sink. Their intensity can be easily varied by adjusting the voltage received. The UV radiation incident on the catalyst surface is measured via a UV light meter (LT Lutron YK-35UV). Since the catalyst surface cannot be shadowed the UV sensor and the chamber cannot be opened before experiments due to contamination risks, the UV probe was placed outside of the chamber, as seen in figure 2. The light intensity was measured by moving the UV-A source above

the probe at the same distance to the catalyst. In addition to this, a second quartz glass is used to replicate the same medium the radiation needs to travel.

In addition to the inlet and outlet the reactor has two more openings where sensors are fitted to monitor the C_2H_4 and CO_2 concentrations. The C_2H_4 -monitoring sensor is a nonselective PID AH-2 photo ionisation device which detects all VOCs with an ionisation potential lower than 10.6 eV, in a concentration range between 5 ppb and 50 ppm. In this setup using a nonselective sensor is not an issue, since it is assumed that the only detectable VOC present in the gas mixture is C_2H_4 . The products of the oxidation are also monitored via a Vaisala GMP343 carbon dioxide probe.

The gas line consists of two streams – one containing the oxidizing agent, O_2 , and one containing the pollutant, C_2H_4 (700ppm, N_2 balance), in the same carrier gas, N_2 . The 79% N_2 + 21% O_2 gas mixture is bubbled through water to control the humidity for the reaction, after which the two gas lines are joined and mixed in a mixing unit, equipped with a Vaisala HUMICAP HMP110 humidity and temperature transmitter. The relative humidity (RH) is kept at 80% for all experiments, this being a typical value for storage units. The volumetric flow rates were adjusted by two mass flow controllers (MKS GE50A series) with a maximum rate of 500 cm³/min. The desired concentration of C_2H_4 in the gas stream was adjusted by setting the volumetric flow rate at the needed value.

TiO_2 was deposited on aluminium substrate at a normal thickness of 1 μm by a pulsed DC magnetron sputtering using an industrial CemeCon CC800/9 SinOx coating unit.

Prior to the photocatalytic reactions, the TiO_2 thin plate was irradiated in pure air to oxidize any organic impurities on the catalyst. The concentration of pollutant was set by adjusting the flow rates accordingly. Then RH and C_2H_4 concentration in the reactor were allowed to reach a steady state. Once the steady state was reached the reaction chamber was closed off and the UV-A lamps turned on. The reaction was monitored until the concentration of C_2H_4 reached a constant value, dictated by the VOC sensor.

For performing the needed experiments the concentration of C_2H_4 is varied from 10 to 27 ppm, resulting in a flow rate range of 310 to 510 cm³/min. The irradiance intensity and the relative humidity are kept constant at 60 W/m² and 80%, respectively.

3. Results and discussion

Langmuir-Hinshelwood (LH) kinetics is widely used to model the heterogeneous catalytic degradation during the photo-oxidation of organic pollutants in solution. Writing the LH kinetic rate law for a batch reactor yields the following expression:

$$r = -\frac{dC}{dt} = \frac{k_r K_{abs} C}{1 + K_{abs} C} \quad (1)$$

where r – reaction rate, [ppm s⁻¹], C – pollutant concentration, [ppm], k_r – reaction rate constant, [ppm s⁻¹] and K_{abs} – absorption constant of molecule on catalyst surface, [ppm]. In order for equation (1) to be further used in determining the reaction constants by fitting the model to experimental data sets, it needs to be integrated and linearized, obtaining equation (2).

$$\frac{1}{k_r K_{abs}} \ln \left(\frac{C_0}{C} \right) + \frac{1}{k_r} (C_0 - C) = -t \quad (2)$$

where C_0 – initial concentration of C_2H_4 , [ppm].

This equation form reveals that C cannot be directly evaluated, due to the fact that it cannot be cleared from the first term, thus an explicit solution cannot be found. The challenge lies in the fact that the term C is both inside and outside of the logarithm. Hence, the Lambert W-function is employed to be able to isolate the concentration C from equation (2), although this increases the computational time significantly.

This numerical drawback can also be circumvented by either solving equation (1) directly using the relation between the reaction rate r and the concentration C or by transforming equation (1) into a pseudo-first order rate law. Considering the fact that the contaminated flows in most photocatalytic

processes have a low molar concentration of pollutant, it can be assumed that $K_{\text{abs}}C \ll 1$. Hence, equation (1) can be rewritten into a fundamental first order equation, resulting in

$$-\frac{dC}{dt} = k_r K_{\text{abs}} C \quad (3)$$

The term $k_r K_{\text{abs}}$ is commonly defined as k_{app} , apparent first order kinetic constant; $[s^{-1}]$.

Figures 3, 4 and 5 show the experimental kinetic data and the predicted kinetics by first, direct LH and explicit LH rate laws, fitted by non-linear least square method. The predicted kinetic constant are listed in table 1.

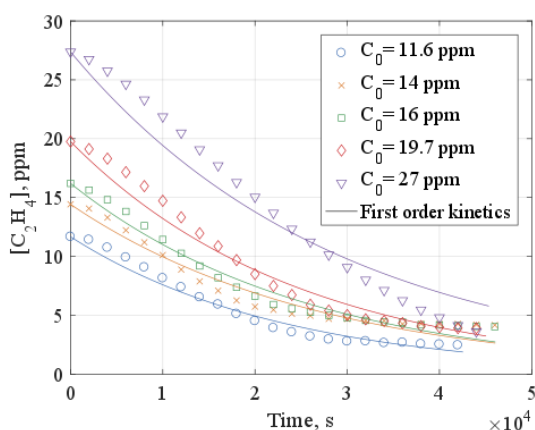


Figure 3. Experimental data vs. predicted C_2H_4 degradation by first order kinetics.

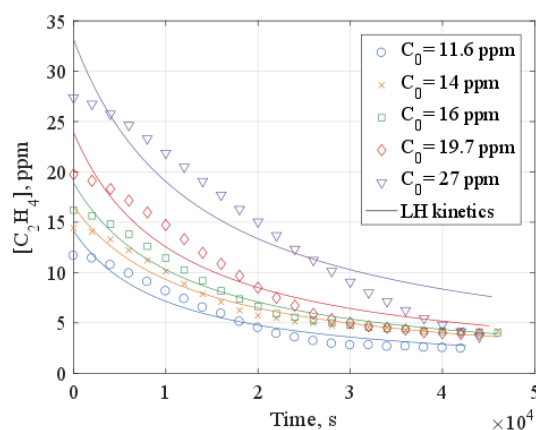


Figure 4. Experimental data vs. predicted C_2H_4 degradation by LH kinetics.

Table 1. Kinetic constants determined by non-linear least square method for the photocatalytic degradation of C_2H_4 over TiO_2 , applying first order and LH kinetic model (W-function).

C_0 (ppm)	k_{app} (s^{-1})	k_r (ppm s^{-1})	K_{abs} (ppm $^{-1}$)
11.6	4.304e-05	0.0014	0.0408
14	3.7003e-05	0.0839	4.4267e-04
16	3.8709e-05	0.0552	7.3064e-04
19.7	4.021e-05	0.0013	0.0477
27	3.434e-05	7.06e-04	0.3241

Figure 3 shows that the photodegradation of C_2H_4 over TiO_2 can be modelled by reducing the LH kinetic model to a pseudo-first order reaction rate, however there is deviation from experimental data that needs to be taken into account. Another drawback of using a first order kinetic model is the treatment of the two kinetic constants as one single term, thus a value for each constant cannot be determined, unless C_2H_4 adsorption isotherms are investigated to obtain a value for K_{abs} . Nevertheless, the model gives a linear dependence between reaction rate, r , and the initial concentration of reactant, C_0 , as shown in figure 6, making an extrapolation to other concentrations possible, keeping in mind that an increase in C_0 might cause a shift in reaction order.

When solving equation (1) directly the initial concentration of C_2H_4 is not explicitly taken into account, as depicted in figure 4. Thus, the directly solved LH model fails to predict C_0 , nevertheless it manages to estimate the end concentration, with generally less deviation than the aforementioned model. Although time consuming, as previously mentioned, using the Lambert W-function to isolate the C

term from the integrated form of the LH model, allows for the initial concentration to be considered, as readily seen in figure 5. Moreover, the fit of the model to the experimental data is superior to the previous two.

Figures 6a and 6b show the dependence of the reaction rate, r , to the initial concentration of C_2H_4 , C_0 . The reaction rate was calculated by using the kinetic constants experimentally determined and listed in table 1. Both data sets were fitted to a first order polynomial, the first order rate law having a better fit with an R^2 value of 0.94. The relatively poor fit of the LH rate law is caused by an outlier – the data point corresponding to $C_0 = 27$ ppm predicts a decrease in rate, which is against the expected behaviour. Removing it increases the R^2 to 0.9, the relation between the two parameters becoming

$$y = 2.67e-05x + 1.488e-04 \quad (4)$$

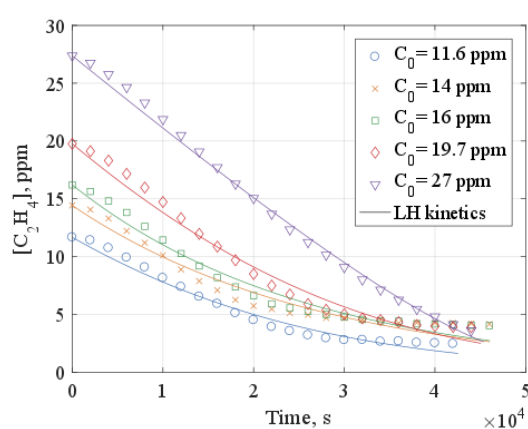


Figure 5. Experimental data vs. predicted C_2H_4 degradation by LH kinetics using Lambert W-function.

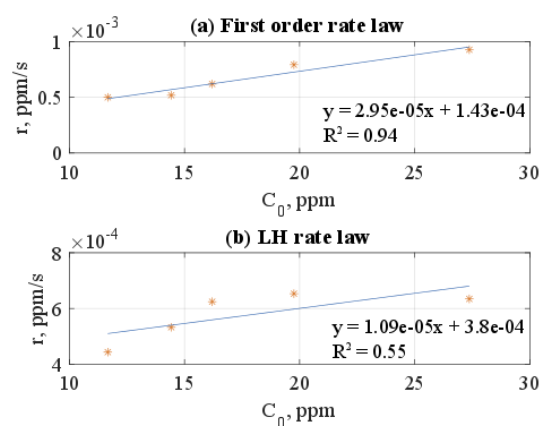


Figure 6. C_0 vs. r . (a) First order rate law. (b) LH rate law (Lambert W-function).

Often times not touched upon in literature are the numerical constrains that arise when employing the LH model and the correct way of circumventing these. It was readily shown in this study that the explicit evaluation of the C_2H_4 concentration is not possible with the LH model, unless a mathematical function, the Lambert W-function, is employed or the LH model is reduced to one of the fundamental rate models. Studies on PCO present in literature in which the LH model was reduced to a first order rate model lack the reasoning behind it and only invoke the assumption that for $K_{abs}C \ll 1$ the model reduction is reasonable. This is indeed true, as this study also has shown. The approach of assuming a first order rate law was proven to be effective and straightforward in estimating the degradation, however with minor deviations from the ideal first order equation, as also reported by [9], and experimental results (figure 3). The same approach was successfully used by [10] and [11], where the surface phenomena of TiO_2 photocatalysis and the photoelectrocatalytic degradation of C_2H_4 over TiO_2 -activated carbon were studied, respectively. Thus, the reduction of the LH rate law to a first order type is in agreement with other studies made on photocatalytic reactions.

Although the use of the Lambert W-function slows down the computations, the estimation of the decrease in concentration is characterized by a lower squared norm of the residuals when fitted to experimental data, compared to the first order rate law (figure 5). This comes to show that by using the LH rate model correctly the degradation can be simulated with higher accuracy. A similar mathematical approach was employed by [12], although applied to a photocatalytic process using different model compound and catalyst. However, the same numerical constrains have been encountered and the Lambert W-function was employed to overcome these.

The linearity of the relationship between reaction rate and initial C_2H_4 concentration meet the original expectation, according to which the higher the C_2H_4 concentration the higher the availability of molecules at the active surface, resulting in an increase in reaction rate. In [13] a similar PCO system was analyzed in terms of kinetics – C_2H_4 over TiO_2 , the authors deriving a linear relationship between initial concentration and reaction rate for concentrations ranging from 50 to 400ppm. As previously mentioned it is expected for the reaction order to shift towards a zero order as the concentration increases, and possibly also a change in dependence between concentration and reaction rate.

4. Conclusion

The kinetic analysis performed showed that the photocatalytic degradation of C_2H_4 over TiO_2 thin films can be well approximated by the most commonly used Langmuir-Hinshelwood kinetic model. Employing this model leads to an increase in computational time when performing a nonlinear fit to experimental data, due to the need of using the Lambert W-function to explicitly solve the model equation for the concentration C . It was showed that the LH kinetic model can be reduced to a pseudo-first order model, under the assumption that the pollutant concentration is low, such that $K_{abs}C \ll 1$. This allows to circumvent the use of the computationally heavy Lambert W-function. The disadvantage of reducing the LH model is the inability of estimating both k_r and K_{abs} , these being treated as one single term, k_{app} .

The determined reaction kinetics give a linear relationship between the initial concentration of C_2H_4 and the reaction rate, based on which the latter can be extrapolated for other initial concentrations outside of the experimental range.

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