

# Application of Langmuir–Cheng model for photocatalytic degradation of multi-VOCs in air

Tongbao Cheng<sup>a,\*</sup>, Yi Jiang<sup>b</sup>, Rui Yang<sup>b</sup>, Yiping Zhang<sup>b</sup>

<sup>a</sup>*School of Civil Engineering & Architecture (SCEA), Northern Jiaotong University, Beijing, China;* <sup>b</sup>*Department of Building Science, Tsinghua University, Beijing, China*

## ABSTRACT

The paper first examines the kinetics of photocatalytic degradation of multi-volatile organic compounds (multi-VOCs) including toluene and formaldehyde. A glass-plate reactor was specifically designed for this work. A mixture of toluene and formaldehyde was used as test VOCs. The photocatalytic degradation rate was different when the mixture fraction of toluene and formaldehyde was changed. The paper then presents a model for photocatalytic degradation of multi-VOCs, which is called Langmuir–Cheng model, and then illustrates the application of the model.

## INDEX TERMS

Photocatalytic; Degradation; Multi-VOCs; Langmuir–Cheng model; Application

## INTRODUCTION

The importance of indoor air quality (IAQ) to human health and comfort cannot be overstated because most people spend most of their time indoors. In recent years, the awareness of potential IAQ problems, by both researchers and the public, has prompted active studies of indoor environments. Many experts believe that IAQ may be the most important environmental issue of our time (Guo, 2002). Air pollution with VOCs has been a serious environmental problem for these decades. It is known that VOCs are toxic in themselves and they react with NO<sub>x</sub> in air to form ozone, which is the cause of the smog conditions in urban air (Hisahiro *et al.*, 2001).

Common methods of controlling indoor air pollution include controlling pollution sources, increasing the air exchange rate and using air purifiers. At present, the use of air purifiers has become more popular in eliminating indoor air pollutants. Traditional air purifiers use filters to remove particulate matters or use sorption materials (e.g. granular activated carbon) to adsorb gases or odours. However, these techniques only transfer the contaminants to another phase rather than eliminating them. Therefore, additional disposal or handling steps are subsequently required (Zhao and Yang, 2003).

Heterogeneous photocatalytic oxidation systems using TiO<sub>2</sub> have been extensively studied for the removal of various VOCs. Irradiation of TiO<sub>2</sub> with UV or near-UV light results in the formation of highly reactive electron–hole pairs and initiates redox reactions that decompose VOCs. The photocatalytic oxidation system is effective for the destruction of VOCs under ambient conditions and it does not emit hazardous by-products such as NO<sub>x</sub> and ozone at all.

In practical research, kinetic experiments are performed to study the photocatalytic degradation of VOCs. The dependence of the degradation rate on the influencing factors (e.g. light intensity, reactants concentration, oxygen concentration, water vapour content, temperature) are investigated and gotten from the corresponding kinetic data. The kinetic models of the photocatalytic degradation process are essential for the optimization of experimental conditions. Several kinetic models have been developed and most of them cannot completely account for all possible factors affecting the degradation date. For example, the Langmuir–Hishelwood model has been widely used to formulate the rate equations for

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\* Corresponding author. E-mail: chengtongbao@263.net

photocatalytic degradation. Langmuir first developed the adsorption isotherm that leads to a uni-molecular layer of adsorbed molecules. It was Hishelwood who began the application of the Langmuir isotherms to the various reactants and products, and the model developed was thus called Langmuir–Hishelwood kinetic model. The Langmuir–Hishelwood model was useful for the degradation of a single VOC. For indoor air applications it is likely that multi-VOCs are involved in the photocatalytic degradation.

Glass-plate, packed-bed, fluidized-bed and monolith reactors have been proposed to absorb light on catalytic supports. Various aspects of the modelling of monolith and glass-plate reactors have been published (Nicolella and Rovatti, 1998). In this work, the main concerns of the mathematical modelling for photocatalytic degradation have been extended to the modelling of a reactor for the photocatalytic degradation of multi-VOCs. A glass-plate reactor is simple, so we choose this kind of photocatalytic equipment as the reactor.

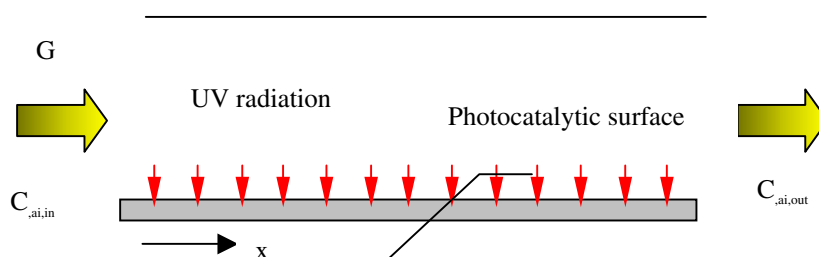
## MODEL DEVELOPMENT

### Assumptions

This study presents the modelling of the physical and chemical processes involved in the photocatalytic degradation of multi-VOCs in a glass-plate reactor.

To construct a model of physical and chemical processes involved in the photocatalytic degradation of multi-VOCs in a glass-plate reactor the following mechanisms are considered (Yamazaki, 1999): (1) mass transfer of reactants (contaminants) to the catalyst surface; (2) adsorption of reactants on the catalyst surface; (3) photochemical reaction on the surface; (4) desorption of products from the surface and (5) mass transfer of products from the surface into the bulk of the fluid (air).

It is assumed that the gas-phase temperature, composition and velocity are uniform across the glass-plate cross-section. The following additional hypothesis are adopted: (1) steady state conditions; (2) uniform pressure along the glass-plate channels; (3) negligible axial diffusion; (4) negligible conduction in the gas phase; (5) no reaction in the gas phase; (6) the adsorption of multi-VOCs is represented with the extended Langmuir equation and (7) the photocatalytic degradation is proportional to the amount of VOCs and water vapour adsorbed on the catalyst surface.



**Figure 1** Schematic of glass-plate photocatalytic reactor.

## EQUATIONS

Figure 1 shows the schematic of a glass-plate photocatalytic reactor. The assumptions adopted for the model results in the following set of equations:

Continuity equation

$$ub \frac{\partial C_{a,i}}{\partial x} + h_i (C_{a,i} - C_{s,i}) = 0 \quad (1)$$

where  $u$  is VOC inlet velocity (m/s),  $b$  is the glass plate width (m),  $C_{a,i}$  is the averaged VOC  $i$  concentration along  $x$  axis ( $\text{mg}/\text{m}^3$ ),  $h_i$  is convective mass transfer coefficient (m/s) and  $C_{s,i}$  is the VOC  $i$  concentration in the air adjacent to the air–solid interface ( $\text{mg}/\text{m}^3$ ).

Boundary equation

$$x = 0, \quad C_{a,i} = C_{a,i,\text{in}} \quad (2)$$

where  $C_{a,i,\text{in}}$  is the inlet VOC concentration ( $\text{mg}/\text{m}^3$ ).

Balance equation on photocatalytic surface

$$q_i = \frac{q_{\max,i} K_i C_{s,i}}{1 + \sum_j K_j C_{s,j} + K_w C_{s,w}} \quad (3)$$

$$q_w = \frac{q_{\max,w} K_w C_{s,w}}{1 + \sum_j K_j C_{s,j} + K_w C_{s,w}} \quad (4)$$

$$\begin{aligned} R_{\text{ph},i} &= a_i \frac{q_{\max,i} K_i C_{s,i}}{1 + \sum_j K_j C_{s,j} + K_w C_{s,w}} \frac{q_{\max,w} K_w C_{s,w}}{1 + \sum_j K_j C_{s,j} + K_w C_{s,w}} \\ &= K_i^0 \frac{K_i C_{s,i}}{1 + \sum_j K_j C_{s,j} + K_w C_{s,w}} \frac{K_w C_{s,w}}{1 + \sum_j K_j C_{s,j} + K_w C_{s,w}} \end{aligned} \quad (5)$$

$$R_{\text{ph},i} = h_i (C_{a,i} - C_{s,i}) \quad (6)$$

where  $q_i$  is amount of VOC  $i$  adsorbed on photocatalytic surface ( $\text{mg}/\text{m}^3$ ),  $q_{\max,i}$  is maximum amount of VOC  $i$  adsorbed on photocatalytic surface ( $\text{mg}/\text{m}^3$ ),  $K_i$  is VOC  $i$  adsorption parameter ( $\text{m}^3/\text{mg}$ ),  $K_w$  is water vapour adsorption parameter ( $\text{m}^3/\text{mg}$ ),  $C_{s,w}$  is water vapour concentration on photocatalytic surface ( $\text{mg}/\text{m}^3$ ),  $q_w$  is amount of water vapour adsorbed on photocatalytic surface ( $\text{mg}/\text{m}^3$ ),  $q_{\max,w}$  is maximum amount of water vapour adsorbed on photocatalytic surface ( $\text{mg}/\text{m}^3$ ),  $R_{\text{ph},i}$  is photocatalytic degradation rate per surface ( $\text{mg}/\text{m}^2\text{s}$ ),  $a_i$  and  $K_i^0$  are parameters of VOC  $i$ .

## VALIDATION OF THE MODEL

The titania-coated glass-plate were packed in a well (1 in.  $\times$  18 in.) milled from a steel block and covered by a quartz window (96% UVA transparent). Gaskets between the quartz window

and the steel block created a flow passage of 1 in. (width) by 2mm (height) above the titania-coated glass-plates. An opaque film of Degussa P-25 was deposited on flat 1 in. wide glass slides using a wash-coat process. The wash-coat was 5% by weight of titania in distilled water. A titania film was prepared by dipping the glass slide in the wash-coat several times. This process was repeated until  $0.7 \text{ mg/m}^3$  film was achieved, similar to Timothy (1996).

The test condition is as follows:

- temperature:  $25 \pm 2^\circ\text{C}$ ;
- relative humidity:  $50 \pm 5\%$ ;
- UVC radiation intensity:  $0.7 \text{ mW/cm}^2 \pm 5\%$ ;
- VOC inlet velocity: 1.3 m/s.

Formaldehyde, an aldehyde, is a major indoor air contaminant and presents a significant health effect. Toluene, representative of the aromatic contaminant class, is ubiquitous and is generally a member of the VOCs having the highest concentrations found in the indoor environment. These two contaminants are being considered as surrogates for two of the six major classes (aromatic, aldehyde, alkane, ketone, alcohol and chlorocarbon) of indoor air contaminants (VanOsdell, 1994); therefore, we choose mixture of toluene and formaldehyde as test VOCs. Table 1 shows parameters for toluene and formaldehyde. Table 2 shows the test condition of toluene and formaldehyde.

**Table 1** Parameters for toluene and formaldehyde

Content	$K_i^0$ ( $\text{mg/m}^2 \text{ s}$ )	$K_i$ ( $\text{m}^3/\text{mg}$ )	$K_w$ ( $\text{m}^3/\text{mg}$ )
Toluene	$1.74 \times 10^{-4}$	$5.13 \times 10^2$	0.489
Formaldehyde	$1.86 \times 10^{-4}$	$8.48 \times 10^2$	0.489

**Table 2** Test condition for toluene and formaldehyde

Water vapour concentration ( $\text{mg/m}^3$ )	Formaldehyde inlet concentration ( $\text{mg/m}^3$ )	Toluene inlet concentration ( $\text{mg/m}^3$ )
8939.27	0.30	1.66
10149.30	1.35	3.65
10149.00	3.99	4.23

Table 3 shows the outlet concentration comparison of formaldehyde and Table 4 shows that of toluene. From the two tables we can see the correctness of our model.

**Table 3** Comparison of outlet concentration for formaldehyde

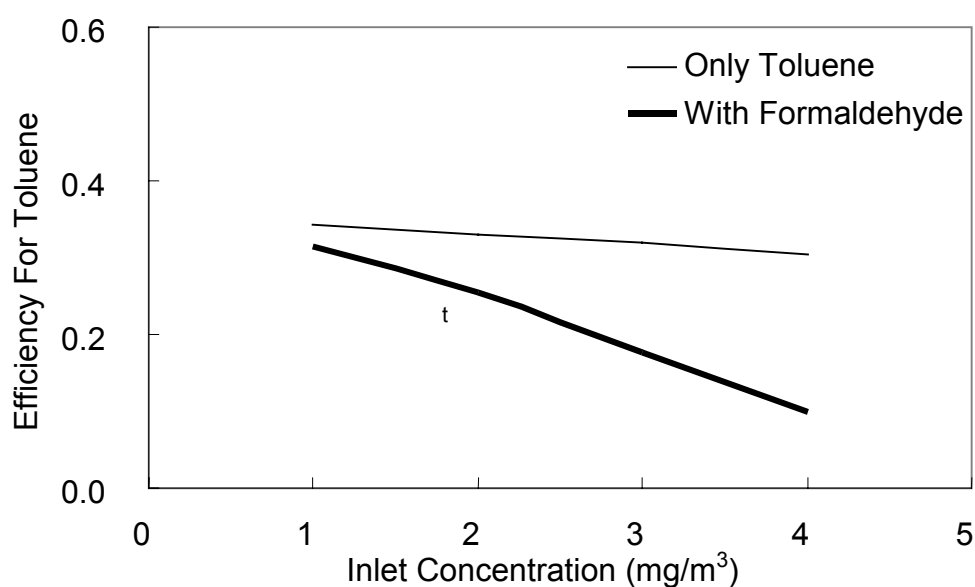
Inlet concentration ( $\text{mg/m}^3$ )	Measured outlet concentration ( $\text{mg/m}^3$ )	Predicted outlet concentration ( $\text{mg/m}^3$ )	Error (%)
0.30	0.06	0.06	0.08
1.35	0.44	0.42	-5.82
3.99	2.25	2.10	-6.76

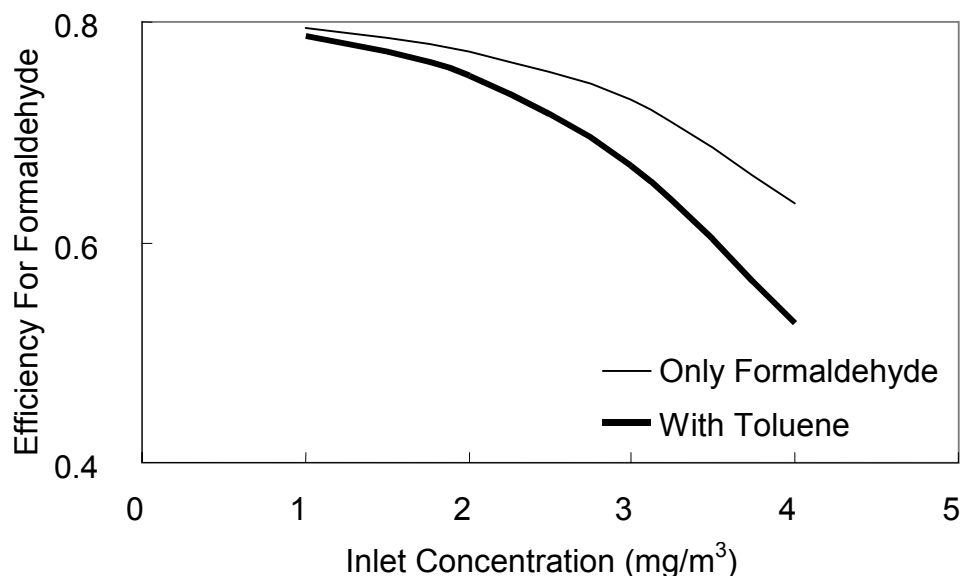
**Table 4** Comparison of outlet concentration for toluene

Inlet concentration (mg/m <sup>3</sup> )	Measured outlet concentration (mg/m <sup>3</sup> )	Predicted outlet concentration (mg/m <sup>3</sup> )	Error (%)
1.66	1.30	1.07	-17.59
3.65	2.83	2.72	-4.02
4.23	3.82	3.88	1.55

**APPLICATION OF LANGMIUR-CHENG MODEL**

To illustrate the application of the Langmuir-Cheng model, we mixed toluene and formaldehyde at different inlet concentrations, which are 1, 2, 3 and 4 mg/m<sup>3</sup> for each VOC. Figures 2 and 3 illustrate the relationship of photocatalytic equipment efficiency and outlet concentration for toluene and formaldehyde. From the two figures we can see the efficiency for mixture of toluene and formaldehyde is lower than that of only toluene or formaldehyde.

**Figure 2** Relationship of photocatalytic equipment efficiency and outlet concentration for toluene.



**Figure 3** Relationship of photocatalytic equipment efficiency and outlet concentration for formaldehyde.

## CONCLUSIONS

This paper examined the kinetics of photocatalytic degradation of multi-VOCs including toluene and formaldehyde, then the paper presented a new model, named Langmuir–Cheng model, which is useful for multi-VOCs. A glass-plate photocatalytic reactor was used to validate our model. Toluene and formaldehyde were used as the test gases. The comparison of measured result and predicted result of toluene and formaldehyde showed that the Langmuir–Cheng model is correct and can be used to predict any VOC photocatalytic degradation rate when mixed with other VOCs at different concentrations.

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