Korean J. Chem. Eng., **24**(4), 577-582 (2007)

Modeling of photocatalytic oxidation of VOCs in a packed bed reactor under continuous and discontinuous illuminations

Baoqing Deng*,*, Shanshan Kong* and Chang Nyung Kim**,***,†**

*College of Urban Construction & Environmental Engineering,
University of Shanghai for Science & Technology, Shanghai, 200093, P.R. China
**Industrial Liaison Research Institute, ***College of Advanced Technology,
Kyung Hee University, Yongin 449-701, Korea
(*Received 7 September 2005 • accepted 30 November 2006*)

Abstract−In this paper, a mathematical model is presented to describe the photocatalytic degradation of VOCs in a packed bed reactor. Here, the adsorption of VOCs on the wall of the reactor is taken into account and the diffusion of VOCs in the axial direction is neglected. First-order kinetics is used to describe the photocatalytic oxidation of VOCs. The analytical solution of the present model is obtained by traveling wave method. The solution shows that the reactor performance is totally dependent on the inlet concentration of VOCs when the time is large enough. The present model is validated through the experimental result of the photocatalytic oxidation of trichloroethylene in a packed bed and the predicted results accord well with the experimental data. The influence of flow rate and inlet concentration on the performance of the reactor is discussed in detail. High flow rate offers high reaction rate and low conversion efficiency. The different inlet conditions and different reaction patterns are also investigated. The model would be useful to estimate the rate constant and help to the design of the reactor.

Key words: Traveling Wave Method, Photocatalytic Oxidation, VOCs

INTRODUCTION

During recent years, the emission of volatile organic compounds (VOCs) has attracted much attention from the public and researchers. There exist many examples that have caused much harm to people in an indoor environment. Although a ventilation strategy may reduce the concentration of VOCs in a resident building, it merely transfers VOCs from one place to another place and does not destroy VOCs. Technology including biofiltration and photocatalysis has been developed to destroy VOCs. For indoor application, a process should be able to proceed at an ambient temperature and pressure to avoid introducing other possible harm to residents and to save energy. Moreover, the final oxidation products should be innocuous. Thus, photocatalytic oxidation of VOCs is just thought to be an effective means to destroy VOCs in an indoor environment. Also, photocatalytic oxidation is excited with easily available excitation sources (i.e., sunlight or low-cost fluorescent light sources) and photocatalysts are generally nontoxic, inexpensive, and chemically and physically stable [1].

For photocatalytic oxidation, the reaction occurs on the surface of catalyst. Catalysts are usually coated on the wall of a reactor (thin film reactor) or on the surface of the support filled in a reactor (packed bed reactor). Many researchers have concentrated on the packed bed reactor to investigate the photocatalytic oxidation of VOCs, considering the merit of its large contact area. The emphasis is to determine the reaction kinetics equation. Wang et al. [2,3] studied the kinetics of photocatalytic degradation of trichloroethylene in a packed bed reactor. Titanium dioxide was coated onto the surface of glass beads. They obtained a Langmuir type reaction kinetics equation through fitting to the experimental data and discussed the effect of flow rate on reaction rate. Yamazaki et al. [4] studied the photocatalytic degradation of tetrachloroethylene in a tubular photoreactor packed with TiO_2 pellets and concluded that the reaction kinetics followed Langmuir-Hinshelwood equation. Another choice is to use first order kinetics, which is a simplification of Langmuir type kinetics at low concentrations. Arabatzis et al. [5] used first-order kinetics to discuss the variation of convention factor. These studies show that either a Langmuir type or first-order type reaction kinetics equation can be used to describe the rate expression in a packed bed reactor. There also exist many studies on the reaction kinetics equation in different kinds of reactors [6-9], where a Langmuir type or first-order type reaction kinetics equation is also assumed.

In addition to the research on the reaction kinetics, the configuration and operation of a reactor are also important issues. Mehrvar et al. [10] investigated a tellerette packed-bed photocatalytic reactor in batch mode. The model was based on first-order kinetics. They assumed a uniform concentration in the reactor and neglected the concentration distribution in the axial direction. Changrani and Raupp [11] presented a two-dimensional heterogeneous model for a reticulated-foam photocatalytic reactor. Semi-empirical Langmuir-Hinshelwood-Hougen-Watson kinetics was used to describe the heterogeneous reaction rate. The effect of the mean residence time and the dimensionless axial distance on the outlet concentration was investigated. Nicolella and Rovatti [12] developed a mathematical model to describe the photocatalytic oxidation of air contaminants in a monolith reactor. Photon flux, energy transfer and chemical rate were discussed. Mohseni and Taghipour [13] performed an experiment on photocatalytic oxidation of vinyl chloride and carried

---

†To whom correspondence should be addressed.
E-mail: cnkim@knu.ac.kr

out an analysis using CFD technique. Pareek et al. [14] simulated the multi-phase flow and the photocatalytic oxidation in an 18 *l* pilot-scale reactor using CFD technique. However, the above models focused on the steady state performance of the reactor. Little work has been performed on the transient performance of the packed bed reactor.

In this paper, a transient one-dimensional model capable of describing different reaction patterns is presented to model the photocatalytic degradation of VOCs in a packed bed reactor. Continuous and periodical reaction patterns have been investigated in detail in the present study. Also, the effect of the inlet concentration of VOCs on the reactor performance has been discussed.

MODEL DEVELOPMENT

Packed bed reactors are usually filled with a considerable amount of solid particles with a small diameter. Titanium dioxide is coated on the surface of solid particles. The polluted air stream flows into the reactor and is oxidized through the photocatalytic reaction. Macroscopically, solid particles cannot fill the reactor completely. Thus, the reactor filled with solid particles can be viewed as a kind of porous material with a porosity ε. In general, the photocatalytic oxidation involves the mass transfer of VOCs from the air stream to the surface of the catalyst, the adsorption of VOCs on the catalyst and the reaction of VOCs on the surface of the catalyst. For simplicity, the following hypothesis are assumed:

- The flow in the reactor is one dimensional;
- Negligible axial diffusion;
- Photocatalytic reaction is first-order.
- No reaction in the gas phase;
- The diffusion of VOCs within the solid particle is neglected.

Based on the porosity and the assumption of one dimensional flow, the air flow in the packed bed reactor can be described by the superficial velocity, i.e., the product of the physical velocity and the porosity. Usually the flow is assumed to be steady. Thus, only the concentration equation needs to be solved. Here, a transient concentration equation is presented to model the concentration variation of VOCs with time and the position along the axial direction

$$\frac{\partial}{\partial t}[\varepsilon C+(1-\varepsilon)C_{ad}]+u_s\frac{\partial C}{\partial x}=-\beta k_r w(t)C_{ad} \tag{1}$$

where C is the concentration of VOCs in the air, u_s the superficial velocity, ε the porosity of the reactor, k_r the first order rate constant, C_{ad} the solid-phase concentration of VOCs, w(t) a function of time, β the specific area. As for the value of the specific area β, it can be evaluated from the porosity

$$\beta=\frac{6(1-\varepsilon)}{d_p} \tag{2}$$

Here, the introduction of w(t) is used to describe the possible reaction patterns, which will be discussed later. Eq. (1) is not closed because of the existence of two concentrations. In general, instantaneous phase equilibrium is assumed between these two concentrations in Eq. (1), which reads

$$C_{ad}=f(C) \tag{3}$$

where f means the adsorption isotherm. Here, a linear adsorption isotherm, i.e., Henry's Law, is adopted, which means

$$C_{ad}=k_{ma}C \tag{4}$$

where k_{ma} is adsorption constant.

Then, Eq. (1) can be rewritten as

$$k_{ad}\frac{\partial C}{\partial t}+u_s\frac{\partial C}{\partial x}=-k_e w(t)C \tag{5}$$

with

$$k_{ad}=\varepsilon+(1-\varepsilon)k_{ma} \tag{6}$$

$$k_e=\beta k_r k_{ma} \tag{7}$$

Eq. (5) is subject to the following initial condition and boundary condition:

$$C(x,0)=C_1(x) \tag{8}$$

$$C|_{x=0}=C_2(t) \tag{9}$$

Eq. (5) describes the photocatalytic degradation of VOCs with time and the position in a packed bed reactor. Solving this equation helps to comprehend the transient performance of the photoreactor. Here, traveling wave method is used to get the analytical solution of this equation [15]. Let

$$t=\frac{k_{ad}}{k_e}z+t_0 \tag{10}$$

and [15]

$$x=\frac{u_s}{k_e}z+x_0 \tag{11}$$

The initial condition and the boundary condition are transformed as follows:

$$C\Big|_{z=-\frac{k_e}{k_{ad}}t_0}=C_1\left(\frac{u_s}{k_e}z+x_0\right) \tag{12}$$

$$C\Big|_{z=-\frac{k_e}{u_s}x_0}=C_2\left(\frac{k_{ad}}{k_e}z+t_0\right) \tag{13}$$

Then, Eq. (5) can be rewritten as

$$\frac{dC}{dz}+w\left(\frac{k_{ad}}{k_e}z+t_0\right)C=0 \tag{14}$$

Thus, we can get

$$C=C_0\exp\left[-\int_0^z w\left(\frac{k_{ad}}{k_e}z'+t_0\right)dz'\right] \tag{15}$$

Taking Eqs. (12) and (13) into account yields the solution as follows:

$$C=\begin{cases} C_1\left(x-\frac{u_s}{k_{ad}}t\right)\exp\left[\int_0^{-\frac{k_e}{k_{ad}}t} w\left(\frac{k_{ad}}{k_e}z'+t\right)dz'\right] & t-\frac{k_{ad}}{u_s}x\le 0 \\ C_2\left(t-\frac{k_{ad}}{u_s}x\right)\exp\left[\int_0^{-\frac{k_e}{u_s}x} w\left(\frac{k_{ad}}{k_e}z'+t\right)dz'\right] & t-\frac{k_{ad}}{u_s}x>0 \end{cases} \tag{16}$$

Eq. (16) is just the analytical solution of Eq. (5) with Eqs. (8) and (9) as the initial condition and the boundary condition, respectively.

Since the initial condition and the boundary condition are arbitrary functions, the present model can simulate the case with the non-uniform initial concentration distribution in the reactor instead of only zero value and the case with inlet concentration to be a function of time. On the other hand, Eq. (16) shows that the concentration distribution of VOCs in a packed bed reactor depends on the value of $t-k_{ad}x/u_s$. Let the height of the reactor be H. Then, only when $t\le k_{ad}H/u_s$ is satisfied, there exists a region in the reactor where the concentration of VOCs is dependent on the initial condition. When $t>k_{ad}H/u_s$ is satisfied, the concentration distribution of VOCs in the reactor is totally dependent on the inlet condition. Furthermore, if the boundary condition $C_2(t)$ is independent of time, the reactor would arrive at steady state when $t>k_{ad}H/u_s$ is satisfied.

As pointed out earlier, the function w(t) describes the reaction pattern in a packed bed reactor. Here, two cases of w(t) will be considered. One case corresponds to the continuous illumination of light, which reads

$$w(t)=1 \tag{17}$$

Thus, we can get the following solution by substituting Eq. (17) into Eq. (16)

$$C=\begin{cases} C_1\left(x-\frac{u_s}{k_{ad}}t\right)e^{-\frac{k_e}{k_{ad}}t} & u_st-k_{ad}x\le 0 \\ C_2\left(t-\frac{k_{ad}}{u_s}x\right)e^{-\frac{k_e}{u_s}t} & u_st-k_{ad}x>0 \end{cases} \tag{18}$$

The other case corresponds to the periodical illumination of light:

$$w(t)=\begin{cases} 1 & 0\le t<T \\ 0 & T\le t<2T \end{cases}$$
$$w(t+2T)=w(t) \tag{19}$$

where 2T is the period of illumination of light. The function w(t) can be represented by an infinite series as follows:

$$w(t)=\sum_{n=0}^{\infty}(-1)^n U(t-nT) \tag{20}$$

where U(t) is the unit step function:

$$U(t)=\begin{cases} 0 & t<0 \\ 1 & t\ge 0 \end{cases} \tag{21}$$

Thus, Eq. (16) can be rewritten as follows:

$$C=\begin{cases} C_1\left(x-\frac{u_s}{k_{ad}}t\right)e^{\sum_{n=0}^{\infty}(-1)^{n+1}\frac{k_e}{k_{ad}}(t-nT)U(t-nT)} & u_st-k_{ad}x\le 0 \\ C_2\left(t-\frac{k_{ad}}{u_s}x\right)e^{\sum_{n=0}^{\infty}(-1)^{n+1}\left\{\left(\frac{k_e}{u_s}x-\frac{k_e}{k_{ad}}(t-nT)\right)U\left(t-nT-\frac{k_{ad}}{u_s}x\right)+\frac{k_e}{k_{ad}}(t-nT)U(t-nT)\right\}} & u_st-k_{ad}x>0 \end{cases} \tag{22}$$

RESULTS AND DISCUSSION

In order to validate the present model, the predicted results were compared with the experimental data of Wang et al. [2]. They carried out photocatalytic oxidation in a stainless steel cylindrical reactor filled with 2 mm diameter glass beads. The reactor is 5 cm in diameter and 6 cm in height. The total 81.4 mg titanium dioxide was coated onto the surface of glass beads. Since they used Langmuir type reaction kinetics equation instead of the first order kinetics, the pseudo first-order rate constant was calculated based on the kinetic reaction equation offered by them. Then, the constants of k_{ad} and k_e could be obtained through Eqs. (6)-(7). Here, the startup of the reactor is simulated while the concentration of trichloroethylene in the reactor keeps uniform with a value of 6.4 μM before the startup. Fig. 1 depicts the outlet concentration of the reactor with a flow rate of 300 ml-min^{-1} and an inlet concentration of 6.4 μM. A relatively good agreement is obtained between the predicted results and the experimental data. Computation shows that it takes around 20 minutes for the reactor to arrive at a steady state, which is totally in agreement with the experimental value. It should be pointed out that this critical time is totally dependent on the adsorption capacity of the catalyst. The good agreement of this critical time proves that the present model simulates the transient behavior of the reactor well.

In Fig. 2 depicted are the concentrations at the inlet, outlet and

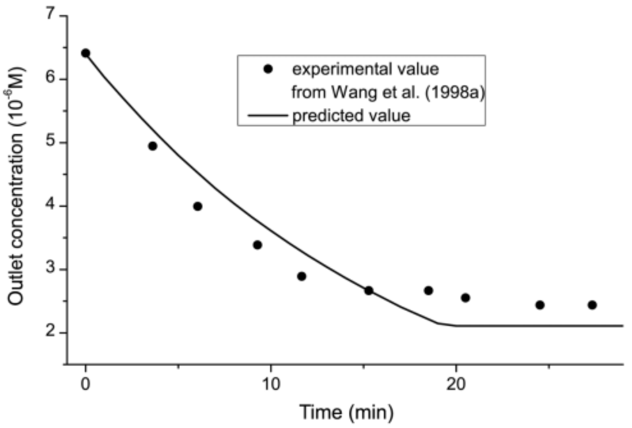

Fig. 1. The outlet concentration of VOCs at the startup of the reactor.

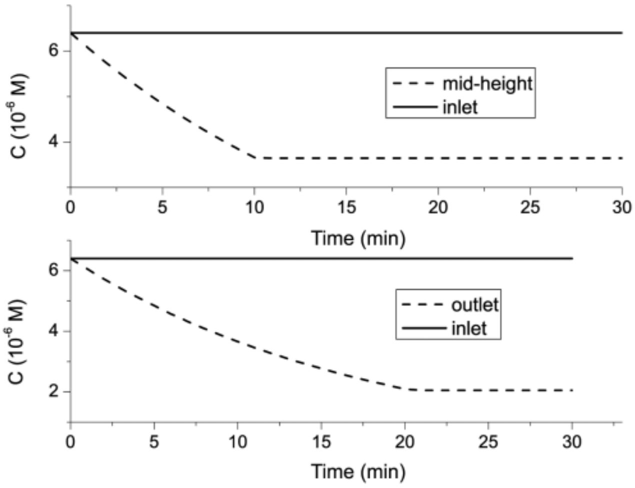

Fig. 2. The concentration at different axial positions with time.

mid-height with time at the startup. The inlet concentration is a given constant, i.e., 6.4 μM. Before the tenth minute, the outlet concentration and the mid-height concentration follow the same line. After the tenth minute, the mid-height concentration becomes a constant and does not change with time. The outlet concentration continues to decline until the twentieth minute and keeps a constant after that time. This is because the corresponding critical times are different with respect to the different positions. The concentration distributions along the axial direction at different times are illustrated in Fig. 3. At the initial time, the concentration keeps constant along the axial direction because of no reaction at this time. At $t=k_{ad}H/u_s$, the concentration assumes an exponential distribution along the axial direction. After this time, the concentration in the reactor will be independent of the time and keep a steady state. At $t=0.5k_{ad}H/u_s$, the concentration distribution in the range of x/H=0-0.5 is identical to that at the steady state while that in the range of x/H=0.5-1.0 is subject to the first part of Eq. (18). This is related with the fact that these two ranges are just corresponding to the two parts of Eq. (18).

Fig. 4 shows the influence of the flow rate on the reaction rate. There exists a relatively good agreement between the predicted values and the experimental values in the range of flow rate investigated. However, the predicted reaction rate slowly increases with the increase of the flow rate until around 3000 ml-min^{-1} while the experimental value varied little over 300 ml-min^{-1}. Further research should be carried out with the theory and the experiment in the future to clarify this problem. Despite this discrepancy, both the experiment and the model testify that the photocatalytic oxidation in the reactor is reaction-controlled.

Although high flow rates promote mass transfer between the air stream and the surface of the catalyst as well as the corresponding reaction rate, it leads to the decrease of the conversion efficiency of the photocatalytic oxidation, as shown in Fig. 5. It is due to the fact that high flow rate leads to low retention time. Therefore, only a part of VOCs is oxidized. Eq. (18) shows that the conversion efficiency depends on the height of the reactor, the superficial velocity u_s and the value of k_e. With the increase of the flow rate, the superficial velocity u_s increases much faster than the value of k_e. So the conversion efficiency decreases with the increase of the flow rate.

The influence of inlet concentration on the reaction rate is depicted in Fig. 6. A relatively good agreement is obtained between

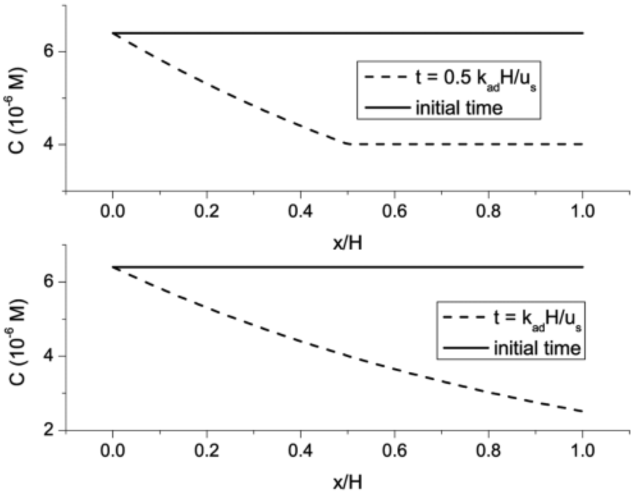

Fig. 3. The concentration distribution along axial direction at different time.

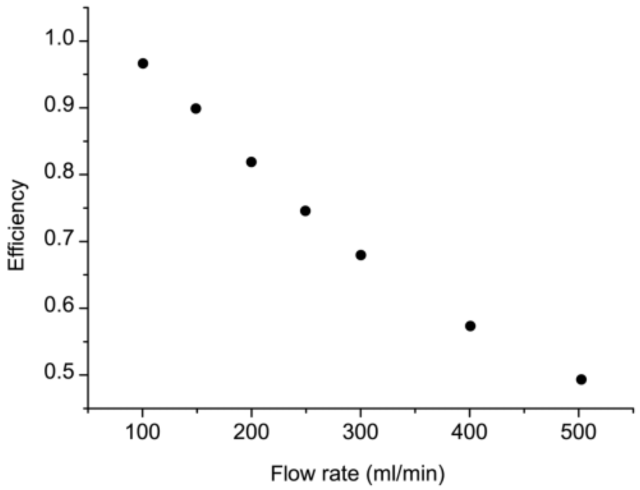

Fig. 5. The conversion efficiency under different flow rates.

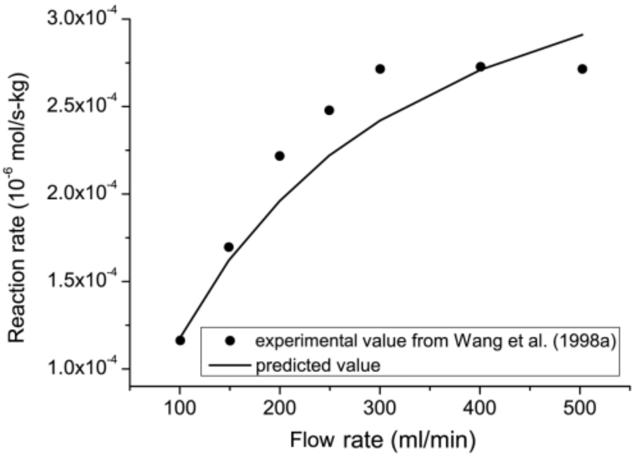

Fig. 4. The reaction rates under different flow rates.

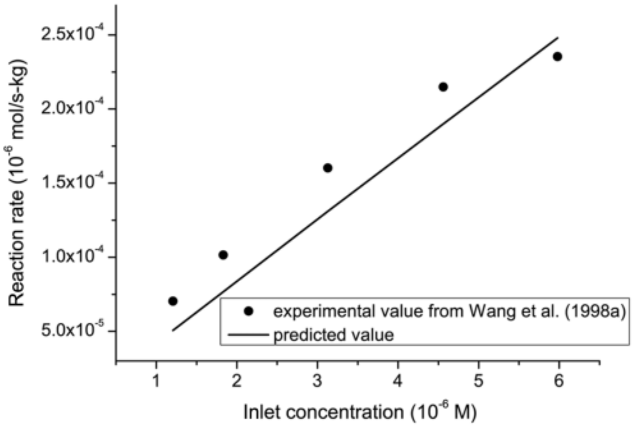

Fig. 6. The reaction rate under different inlet concentrations.

the experimental data and the predicted values. The predicted value assumes a straight line with respect to the inlet concentration, which is in accordance with the assumption of the first-order kinetics. The agreement of the experimental data with the predicted values shows that the first-order kinetics is reasonable in the range of the inlet concentration investigated.

Since the reactor may operate under different reaction patterns, an intermittent irradiation of light is simulated by using Eq. (22), where the period of light switching on-off is 60 minutes. The predicted outlet concentration with time is shown in Fig. 7. In general, the predicted results accord with the experimental data. Relatively speaking, the coincidence of the predicted results and the experimental data in the desorption stage is slightly better than that in the adsorption stage. Here, the adsorption constant and the rate constant are not taken from Wang et al. [2,3]. In fact, Eq. (18) offers an alternative to evaluate these two constants as follows:

$$k_{ad}=\frac{u_s\Delta t}{H} \tag{23}$$

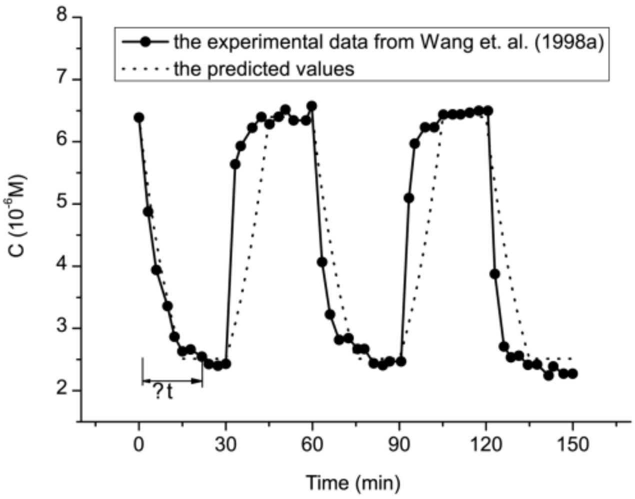

Fig. 7. The outlet concentration with time when light switching on-off.

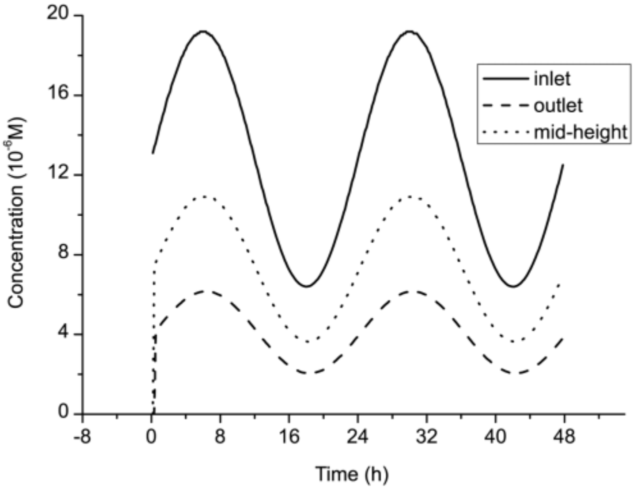

Fig. 8. The concentration at different axial positions with time for sine function.

$$k_e=-\frac{u_s}{H}\ln\frac{C_{out}}{C_{in}} \tag{24}$$

where Δt is the time interval from the light switch-on to the time when the concentration becomes steady, as shown in Fig. 7. It may be around 20 minutes.

Sometimes, the inlet concentration can be a function of time, such as that of sine and cosine functions. The selected functions are

$$C_2(t)=6.4[2.0+\cos(2\pi t/86400)]$$

and

$$C_2(t)=6.4[2.0+\sin(2\pi t/86400)]$$

That is, the period of the inlet concentration is 24 h. The inlet, outlet and mid-height concentrations for the inlet concentrations of sine and cosine functions are shown in Fig. 8 and Fig. 9, respectively. In these figures, it can be seen that the amplitude of the concentrations is attenuated as the position (x/H) becomes far from the inlet. The outlet concentrations with time corresponding to the inlet con-

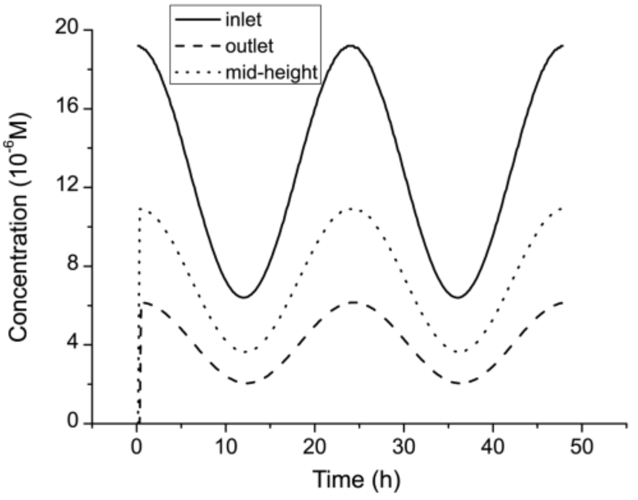

Fig. 9. The concentration at different axial positions with time for cosine function.

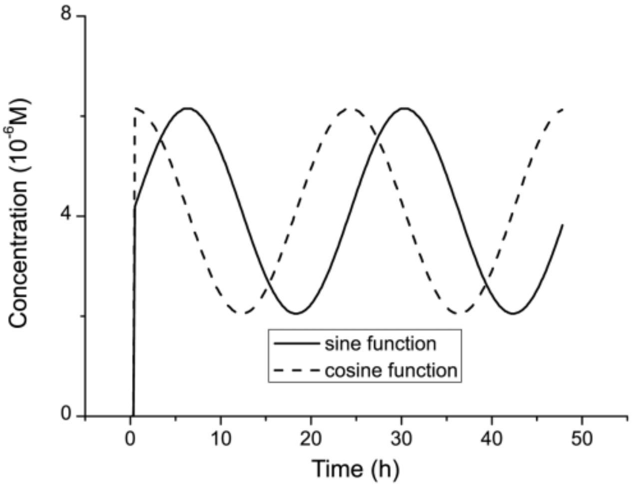

Fig. 10. The outlet concentrations with time for sine and cosine functions.

centrations of sine and cosine functions are depicted in Fig. 10. In general, the mid-height concentrations also assume sine or cosine function depending on the type of the inlet concentration. It comes from the fact that the current analysis is based on the analysis with the use of traveling wave method.

CONCLUSION

In this paper, a transient mathematical model is developed to describe the photocatalytic oxidation in a packed bed reactor. The packed bed reactor is viewed as a kind of porous material. Here, the flow is assumed to be one dimensional. Thus, the superficial velocity is used to describe the flow in the reactor. The concentrations are assumed to keep instantaneous equilibrium based on linear adsorption isotherm. The diffusion of VOCs in the axial direction is neglected compared to the effect of the flow. The analytical solution of the concentration equation is obtained through the traveling wave method when the photocatalytic oxidation is assumed to be first order and can be applied to cases with arbitrary inlet condition and initial condition.

The present model is validated through the experimental data of the startup of a reactor. The influence of the flow rate and the inlet concentration on the reaction rate is investigated in detail. In the range of flow rate investigated, a relatively good agreement between the experimental data and the predicted values is obtained. In the range of inlet concentrations studied, the predicted values reproduce the experimental data fairly well. A periodical illumination of light is modeled, which shows that the outlet concentration also varies periodically and the adsorption capacity of the reactor bed plays an important role when switching on-off occurs.

ACKNOWLEDGMENTS

This work was supported by Korea Research Foundation Grants (KRF-2001-005-E0004) and the scientific research foundation for the returned overseas Chinese scholars, state education ministry.

NOMENCLATURE

C : the concentration of VOCs in the air
C_{ad} : the solid-phase concentration of VOCs
d_p : particle diameter
H : Reactor length
k_{ad} : adsorption constant
k_e : rate constant
k_{ma} : Henry's constant.
k_r : the first order rate constant
t : time
T : period
u_s : the superficial velocity
U : the unit step function
x : coordinate
z : auxiliary variable
β : the specific area
ε : the porosity of the reactor

Subscript

in : inlet
out : outlet

REFERENCES

1. J. Zhao and X. Yang, *Building and Environment*, **38**, 645 (2003).
2. K.-H. Wang, H.-H. Tsai and Y.-H. Hsieh, *Applied Catalysis B: Environmental*, **17**, 313 (1998a).
3. K.-H. Wang, H.-H. Tsai and Y.-H. Hsieh, *Chemosphere*, **36**, 2763 (1998b).
4. S. Yamazaki, H. Tsukamoto, K. Araki, T. Tanimura, I. Tejedor-Tejedor and M. A. Anderson, *Applied Catalysis B: Environmental*, **33**, 109 (2001).
5. I. M. Arabatzis, N. Spyrellis, Z. Loizos and P. Falaras, *Journal of Materials Processing Technology*, **161**, 224 (2005).
6. J. M. Coronado, M. E. Zorn, I. Tejedor-Tejedor and M. A. Anderson, *Applied Catalysis B: Environmental*, **43**, 329 (2003).
7. S. B. Kim and S. C. Hong, *Applied Catalysis B: Environmental*, **35**, 305 (2002).
8. H.-J. Lee, D.-W. Kang, J. Chi and D. H. Lee, *Korean J. Chem. Eng.*, **20**, 503 (2003).
9. H. Liu, Z. Lian, X. Ye and W. Shangguan, *Chemosphere*, **60**, 630 (2005).
10. M. Mehrvar, W. A. Anderson and M. Moo-Young, *Advances in Environmental Research*, **6**, 411 (2002).
11. R. G. Changrani and G. B. Raupp, *AIChE J.*, **46**, 829 (2000).
12. C. Nicolella and M. Rovatti, *Chemical Engineering Journal*, **69**, 119 (1998).
13. M. Mohseni and F. Taghipour, *Chemical Engineering Science*, **59**, 1601 (2004).
14. V. K. Pareek, S. J. Cox, M. P. Brungs, B. Young and A. A. Adesina, *Chemical Engineering Science*, **58**, 859 (2003).
15. S. L. Sobolev, *Partial differential equations of mathematical physics*, Dover Publications (1989).