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Theoretical study on photocatalytic oxidation of VOCs using nano-TiO_2 photocatalyst

Huili Yu[a], Kaili Zhang[b,*], Carole Rossi[b]

[a] *College of Engineering, Ocean University of China, China*
[b] *LAAS-CNRS, 7 Ave du Colonel Roche, 31077 Toulouse Cedex 4, France*

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Abstract

Mass transfer, diffusion, adsorption and photochemistry are figured out to be the controlling mechanisms for photocatalytic degradation of volatile organic compounds (VOCs) using nano-TiO_2 catalyst. A mathematical model for the non-steady photocatalytic degradation process is developed by incorporating these mechanisms in a plane plate air purification physical model. The governing equation and boundary conditions are solved using finite difference method. The computation results are validated using the data obtained from the experiments. And then the model is employed to study the effects of some key factors on the degradation rate of formaldehyde. These factors include UV light intensity, UV light attenuation coefficient, adsorption, catalyst thickness, diffusion, and flow rate. The model can be employed to assist the design of VOCs photocatalytic degradation system using nano-TiO_2 catalyst.

Keywords: Nano-TiO_2; Photocatalysis; Degradation; VOCs; Theoretical study

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1. Introduction

Indoor air pollution is becoming a serious problem recently. Pollutants in indoor air such as volatile organic compounds (VOCs), NOx, and SO_2 can cause adverse health impacts on occupants [1]. VOCs are the main components of the indoor air pollutants, which are from indoor furnishing, tobacco smoke, vehicular emissions, and the use of liquefied petroleum gas. Conventionally, VOCs pollutants are removed by air purifiers that employ filters to remove particulate matters or use sorption materials (e.g., granular activated carbon) to adsorb the pollutants. Nevertheless, these techniques only transfer the contaminants to another phase rather than eliminate them and additional disposal or handling steps are necessary. Improper maintenance of these purifiers may even become a source of pollutants [2]. The photocatalytic process is emerging as a promising alternative technology for the degradation of VOCs. In the photocatalytic process, a semiconductor is employed as a catalyst to degrade VOCs with the activation of ultra-violet (UV) light. The process has many merits over conventional processes, such as the ability to degrade most of VOCs, suitability for both liquid and gaseous fluids, and the potential to utilize sunlight as an UV source. Among various photocatalytic studies, the field dealing with thin film nano titanium dioxide (TiO_2) catalyst has recently received special attention [3–20]. The thin film nano-TiO_2/UV process is an advanced oxidation process. TiO_2 is superior to other photocatalysts because of its interesting characteristics: (a) it is low cost, safe and very stable showing high photocatalytic efficiency; (b) it promotes ambient temperature oxidation of the major classes of indoor air pollutants; (c) complete degradation of a broad range of pollutants can be achieved under certain operating conditions; (d) no chemical additives are needed.

However, most of the previous studies focused on the experimental investigation of the photocatalytic degradation of VOCs using nano-TiO_2 catalyst [3–20]. There are very few reliable models available to simulate the experimental results so far. It is known that the thin film nano-TiO_2 photocatalytic degradation efficiency of VOCs can be potentially limited by several parameters. The degradation efficiency may be very low inside a thick

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[*] Corresponding author at: Microsystems and Systems Integration (MIS), LAAS-CNRS, 7 Ave du Colonel Roche, 31077 Toulouse Cedex 4, France.
Tel.: +33 5 6133 6985; fax: +33 5 6133 6208.
E-mail addresses: kzhang@laas.fr, kaili_zhang@hotmail.com (K. Zhang).

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Nomenclature

A	surface area of thin film TiO_2 catalyst (m^2)
C	VOCs concentration in catalyst (mg/g)
C_{max}	adsorption capacity of Langmuir–Hinshelwood isotherm (mg/g)
C_0	initial concentration of VOCs in TiO_2 catalyst (mg/g)
D_t	effective diffusivity in TiO_2 catalyst (m^2/s)
F_p	source term
H	thickness of TiO_2 catalyst film (μm)
I	UV light intensity (μW/cm^2)
I_0	intensity of incident UV light (μW/cm^2)
k	Langmuir–Hinshelwood isotherm coefficient (mg/m^3)
k_f	convective mass transfer coefficient (m/s)
K	coefficient of photocatalytic reaction (cm^2/μW s)
l	characteristic length (m)
m	exponent
M_{ad}	VOCs mass degraded by adsorption (mg)
M_p	VOCs mass degraded by photocatalysis (mg)
M_0	initial VOCs mass (mg)
M_1	VOCs mass at the end of time τ (mg)
n	exponent
Q_a	VOCs concentration in the reactor (mg/m^3)
Q_w	VOCs concentration at the surface of TiO_2 (mg/m^3)
Q_0	initial concentration of VOCs in the reactor (mg/m^3)
r	photocatalytic degradation rate (mg/m^3 s)
Re	Reynolds criterion
Sc	Schmidt criterion
Sh	Sherwood criterion
u	flow rate through TiO_2 catalyst (m/s)
V	volume of the reactor (m^3)
x	coordinate (m)

Greek letters

ε	UV light attenuation coefficient in TiO_2 catalyst (μm^{-1})
ν	dynamic viscosity (m^2/s)
ρ_p	density of TiO_2 catalyst (g/cm^3)
τ	time (s)

catalyst due to the UV light intensity attenuation by the catalyst. The VOCs molecules diffusion in the catalyst can be very slow so that there are not enough molecules available for degradation inside the catalyst. The effects of these parameters are not well understood and they are not easy to be understood by experimental approach in some sense. In this study, a mathematical model for the non-steady photocatalytic degradation process of VOCs using thin film nano-TiO_2 is developed. The model is verified by experimental results and then employed to study the effects of important factors on the photocatalytic degradation process of VOCs.

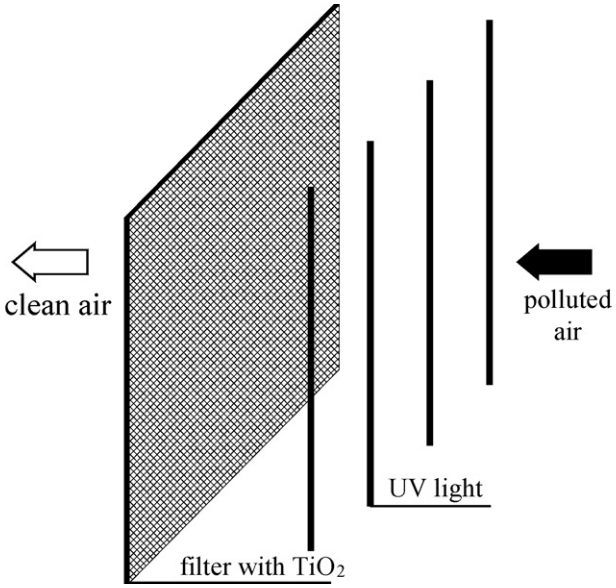

Fig. 1. Schematic of the plane plate photocatalytic reaction set-up.

2. Model development

VOCs photocatalytic reaction can be divided into five processes: (1) mass transport of contaminant from the bulk air to the surface of catalyst; (2) adsorption of the contaminant at the surface of catalyst; (3) photochemistry reaction in the catalyst; (4) desorption of the by-products from the surface of catalyst; (5) mass transport of the by-products from the surface of catalyst to bulk air. The photocatalytic model focuses mainly on the processes (1, 2, 3) of parent contaminant. Although the by-products can potentially affect the behavior of parent contaminant, their impacts are beyond the scope of this study. The model is based on a plane plate photocatalytic reaction set-up as shown in Fig. 1. The thin film catalyst can be considered as a kind of porous media composed of nano-TiO_2 and fiber. And polytetrafluoroethylene (PTFE) acts as the substrate of the catalyst. Mass transport between air and TiO_2 particle will occur when air-containing VOCs passes through the catalyst. VOCs molecules adsorbed on TiO_2 particles provide the reactants for the photocatalytic reaction as shown in Fig. 2.

The mathematic model is based on the following assumptions: (1) Fick's law can be employed to describe the mass

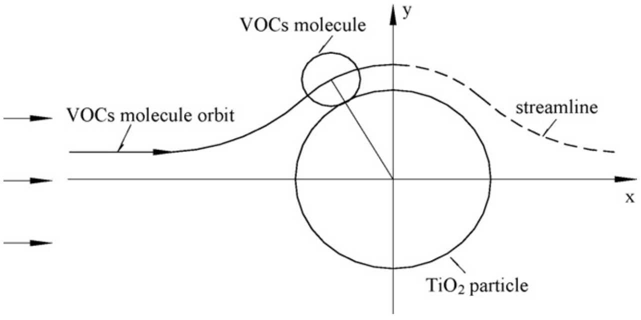

Fig. 2. Mass transport between gas and TiO_2 particle.

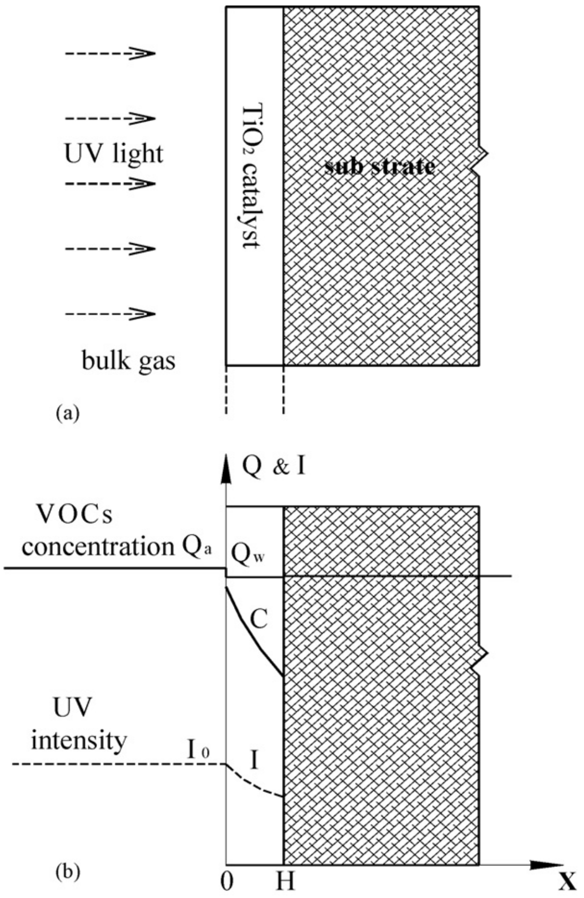

Fig. 3. Conceptual model for photocatalytic reaction in TiO_2 catalyst: (a) system configuration and (b) concentration profile.

transport processes both in air and in solid. The diffusion of air containing VOCs in TiO_2 thin film is a continuous process that satisfies diffusion equation; (2) TiO_2 thin film is homogeneous; the effective diffusivity of VOCs in TiO_2 and the mass transfer coefficient between air and TiO_2 are constant; (3) due to the very small thickness of TiO_2 thin film (in the range of micron), the degradation process of VOCs is assumed to be one dimensional; (4) the attenuation of UV light in air is ignored compared to that in catalyst; (5) the generated heat during adsorption process is ignored owing to the small concentration of VOCs in air; (6) the effects of by-products produced in photocatalytic reaction are neglected; (7) the adsorption effect of PTFE substrate on VOCs can be ignored compared to that of TiO_2 photocatalysis and then the VOCs concentration in PTFE is assumed to be constant [21]. The system configuration of TiO_2 thin film and PTFE substrate is shown in Fig. 3(a) and the VOCs concentration profile in TiO_2 is illustrated in Fig. 3(b). The VOCs concentration in air is expressed using Q (mg/m^3). The VOCs concentration in catalyst is denoted using C (mg/g).

2.1. Governing equation

The fluid can be considered as incompressible because of the low operating pressure. Therefore, the mass conservation equation for incompressible Newton fluid in Cartesian coordinates can be written as

$$\frac{\partial u_i}{\partial x_i} = 0 \tag{1}$$

According to assumption (3), the flow is one dimensional. Therefore, after integration, Eq. (1) can be rewritten as

$$u = \text{const} \tag{2}$$

where u is the flow rate (m/s). In accordance with assumption (1), the governing equation for the photocatalytic reaction of VOCs in TiO_2 thin film can be expressed as

$$\frac{\partial C}{\partial \tau} + u\frac{\partial C}{\partial x} = D_{\mathrm{t}}\frac{\partial^2 C}{\partial x^2} + F_{\mathrm{p}} \tag{3}$$

where C is the concentration (mg/g), τ the time (s), x the coordinate (m), D_{t} the effective diffusivity (m^2/s), and F_{p} is the source term. The value of F_{p} is equal to that of the photocatalytic degradation rate (r) of VOCs.

2.1.1. Source term

The degradation rate (r) is affected by UV light intensity, reactant concentration, diffusion rate, flow rate, temperature and humidity. In this study, the effects of temperature and humidity are covered by the coefficient of photocatalytic reaction. And also, the effect of flow rate has been reflected in governing Eq. (3). Accordingly, the effect of flow rate is not considered in the source term. The degradation rate is assumed to be proportional to the mth order of UV light intensity (I, W/cm^2) and the nth order of sorbed VOCs concentration (C) [22]. Although several studies have been devoted to determine the rate of photocatalytic degradation, no generally accepted rate expressions are yet available in the literature [23]. According to the experiments performed for TiO_2 photocatalytic degradation of VOCs [21], the author found that the degradation rate increases almost linearly with the concentration and UV light intensity. Therefore,

$$r \propto C^n, \quad n = 1 \tag{4}$$

$$r \propto I^m, \quad m = 1 \tag{5}$$

from Eqs. (4) and (5), the degradation rate, r can be expressed as

$$r = KIC \tag{6}$$

where K is the coefficient of photocatalytic reaction (cm^2/μW s). Consequently, the source term F_{p} in Eq. (3) can be written as

$$F_{\mathrm{p}} = -KIC \tag{7}$$

where "−" means that the photocatalytic reaction makes the VOCs concentration decrease. Therefore, the governing Eq. (3) can be expressed as

$$\frac{\partial C}{\partial \tau} + u\frac{\partial C}{\partial x} = D_{\mathrm{t}}\frac{\partial^2 C}{\partial x^2} - KIC \tag{8}$$

2.2. Boundary conditions

For the convective mass transfer between fluid and TiO_2 particle, due to the very small film thickness, the mass transfer between the fluid and the surface of TiO_2 thin film can be approximately considered the same as that between the fluid and the entire TiO_2 thin film. Accordingly,

$$-\rho_p D_t \left.\frac{\partial C}{\partial x}\right|_{x=0} = k_f(Q_a - Q_w) \tag{9}$$

where ρ_p is the density of TiO_2 thin film (g/m^3), k_f the convective mass transfer coefficient (m/s) between fluid and TiO_2 thin film, Q_a the VOCs concentration in fluid, and Q_w is the VOCs concentration at the surface of TiO_2 thin film. According to porous media mass transfer theory, there exists a correlation (10) for the mass transfer between single spherical particle and fluid [24].

$$Sh = 2 + 0.6Sc^{1/3}Re^{1/2} \tag{10}$$

where Sh is the Sherwood criterion, $Sh = k_f l/D_t$; Sc the Schmidt criterion, $Sc = \nu/D_t$; Re is the Reynolds criterion, $\mathrm{Re} = \mu l/\nu$.

Correlation (10) is used to determine the convective mass transfer coefficient k_f.

A number of studies have shown that photocatalytic degradation is preceded by the adsorption of VOCs molecules onto the catalyst surface [25,26]. The adsorption could form a maximum of single layer of molecules on the surface. This is depicted as a "jump" in the VOCs concentration in Fig. 3(b). The Langmuir–Hinshelwood isotherm, which is based on monolayer coverage of molecules, is employed to describe this adsorption step.

$$M_i^{\text{ads}} = \frac{M_i^{\max} k_i Q_i}{1 + k_i Q_i} \tag{11}$$

where Q_i is the gas concentration of i material, M_i^{ads}, $M_i^{\max}$ the adsorption mass and maximum adsorption capacity of i material after the time of τ, and k_i (m^3/mg) is the coefficient for Langmuir–Hinshelwood isotherm. Due to the small value of VOCs concentration in catalyst (Q_w), Eq. (11) can be simplified as

$$C|_{x=0} = C_{\max} k Q_w \tag{12}$$

where $C_{\max}$ (mg/g) is the maximum adsorption coefficient (adsorption capacity) of Langmuir–Hinshelwood isotherm.

According to assumption (7), the VOCs concentration in PTFE substrate is assumed to be constant. Therefore, at the interface between TiO_2 catalyst and PTFE substrate ($x = H$), there exists

$$-D_t \frac{\partial C(H, \tau)}{\partial x} = 0 \tag{13}$$

The attenuation of UV light in the catalyst is a function of UV light wavelength and the optical properties of the catalyst. The attenuation is described by a Beer–Lambert expression that follows an exponential decay law [27].

$$I = I_0 \times 10^{-\varepsilon x} \tag{14}$$

where I_0 is the intensity of incident UV light and ε is the attenuation coefficient for UV light in the catalyst (m^{-1}).

Eqs. (8)–(13) describe the fundamental mechanisms underlying the process of photocatalytic degradation of VOCs molecules in TiO_2 thin film catalyst. The equations must be coupled to a reactor model to completely define a photocatalytic process model. As described previously, VOCs molecules disappear from the bulk gas because of their mass transfer into the catalyst. The concentration variation of VOCs in the reactor can be described using Fick's first law.

$$\frac{\mathrm{d}Q_a}{\mathrm{d}\tau} = -\frac{A}{V} k_f(Q_a - Q_w) \tag{15}$$

where A is the surface area of thin film catalyst (m^2) and V is the volume of the reactor (m^3).

2.3. Initial conditions

For the non-steady photocatalytic reaction, the initial conditions are

$$C(x, 0) = C_0 \tag{16}$$

$$Q_a = Q_0 \tag{17}$$

where C_0 (mg/g) is the initial concentration of VOCs in TiO_2 thin film. Its value is zero in the computation. Q_0 (mg/m^3) is the initial concentration of VOCs in the reactor.

3. Computation

The governing equation and boundary conditions are discretized using finite difference method and the solution for the photocatalytic model is coded in a Visual Fortran program. The solution of the model yields the concentration of VOCs in the catalyst (C_i) and in the bulk gas of the reactor (Q_a). The initial VOCs mass is assumed to be M_0. It changes into M_1 at the end of time τ. The masses of VOCs molecules degraded by adsorption and photocatalysis are denoted by M_{ad} and M_p, respectively. Therefore,

$$M_0 - M_1 = M_{ad} + M_P \tag{18}$$

The mass of VOCs molecules degraded by adsorption M_{ad} is obtained by integrating the VOCs concentration (C) throughout the entire catalyst.

$$M_{ad} = A\rho_p \int_0^H C \ \mathrm{d}x \tag{19}$$

Consequently,

$$M_P = M_0 - M_1 - M_{ad} = V(Q_0 - Q_a) - A\rho_P \int_0^H C \ \mathrm{d}x \tag{20}$$

4. Model validation

The photocatalytic model developed in this study is validated using the experimental data from Ref. [21]. Formaldehyde is chosen as the target pollutant, which is one of the major VOCs of indoor air pollution. The experimental set-up is shown in Fig. 4.

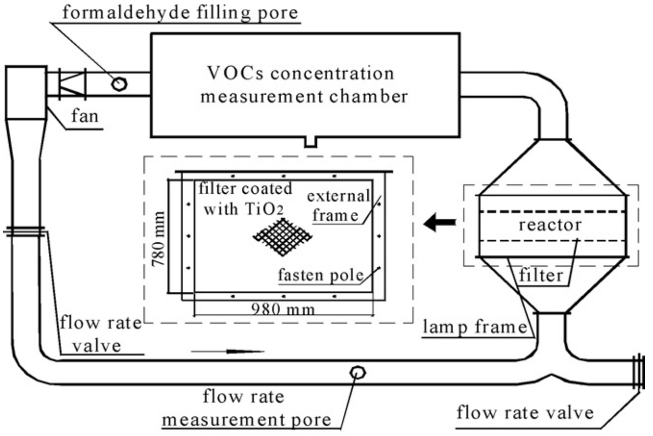

Fig. 4. Schematic of experimental set-up.

The set-up is a closed air-recirculation system. The sizes of the measurement chamber are 1500 mm × 1500 mm × 2000 mm (L × W × H), where the formaldehyde concentration is measured using a formaldehyde detector with a precision of 0.01 ppm. The catalyst is obtained by dip-coating PTFE filter inside nano-TiO_2 (anatase) sol with the spherical particle size of 30–60 nm. The PTFE filter coated with nano-TiO_2 and UV lamp frame are installed inside the photocatalytic reactor with the dimensions of 500 mm × 1000 mm × 800 mm (L × W × H). The conditions in that experiment are same as those in the model. The parameters used in the computation are presented in Table 1. According to Ref. [28], for small molecule organic compounds, for instance formaldehyde, the effective diffusivity can be generally selected as 10^{-8} m^2/s. The Langmuir–Hinshelwood isotherm coefficient and adsorption capacity for formaldehyde adsorption on TiO_2 surface are obtained from Ref. [29]. The density of TiO_2 catalyst is taken from Ref. [22] with a value of 3.2 g/cm^3. The convective mass transfer coefficient between fluid and TiO_2 is computed form Eq. (10). The amount of TiO_2 catalyst can be calculated using the data in Table 1 and the resulting value is 2.56 g.

Table 1
Parameters used for the computation

Symbol	Parameter description (unit)	Value
ε	UV light attenuation coefficient in TiO_2 catalyst (μm^{-1})	0.1
k	Langmuir–Hinshelwood isotherm coefficient (m^3/mg) [29]	0.0042
D_t	Effective diffusivity in TiO_2 catalyst (m^2/s) [28]	1.0×10^{-8}
I_0	UV light intensity ($\mu m/cm^2$)	250
K	Coefficient of photocatalytic reaction ($cm^2/\mu W\,s$)	1.2×10^{-1}
H	Thickness of TiO_2 catalyst film (μm)	1.0
u	Flow rate through TiO_2 catalyst (m/s)	0.0768
Q_a	Formaldehyde concentration in the reactor (mg/m^3)	1.17
C_{max}	Adsorption capacity of Langmuir–Hinshelwood isotherm (mg/g) [29]	0.742
ρ_p	Density of TiO_2 catalyst (g/cm^3) [22]	3.2
V	Gas volume in reactor (m^3)	6.258
A	Surface area of TiO_2 catalyst film (m^2)	0.8
k_f	Convective mass transfer coefficient between fluid and TiO_2 thin film (m/s)	16.6

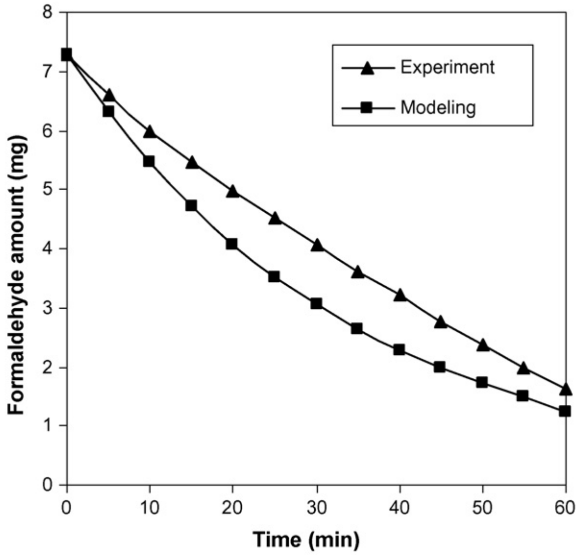

Fig. 5. Comparison between modeling and experimental data.

The model is first validated with the degradation amount versus time as shown in Fig. 5 and further validation with independent parameters will be presented below. As can be seen in Fig. 5, the data from the model computation match experimental data well. This indicates that the key mechanisms governing the photocatalytic process are captured in the model. These mechanisms include gas-film mass transfer, adsorption, diffusion and photochemistry. The model presented above is used next to investigate the effects of these mechanisms on the performance of the TiO_2 photocatalytic degradation.

5. Computation results

5.1. *Effect of UV light intensity*

UV light intensity is an important factor in photocatalytic reaction. The effect of the UV light intensity on the degradation of formaldehyde is illustrated in Fig. 6. The figure shows the degradation amount of formaldehyde at the time of 60 min, calculated using Eq. (20). It can be seen that the degradation amount increases with the increase of UV light intensity from 0 $\mu W/cm^2$ to about 200 $\mu W/cm^2$. This is reasonable because the stronger the UV light intensity, the more the penetration of UV light into the catalyst. Consequently, the degradation amount also increases. However, when the UV light intensity is over 200 $\mu W/cm^2$, the degradation amount reaches a plateau. Further increase in UV light intensity cannot increase the degradation amount any more. The reason is that the degradation amount is also limited by other variables such as diffusion, mass transfer, or adsorption.

Fig. 7 shows the comparison between modeling and experiment at different UV light intensities, where the experiment is performed using the set-up shown in Fig. 4 with UV light intensity ranging from 50 to 250 $\mu W/cm^2$. The trends between modeling and experiment curves are similar. The minimum difference is 5.6% at 250 $\mu W/cm^2$ and the maximum difference is

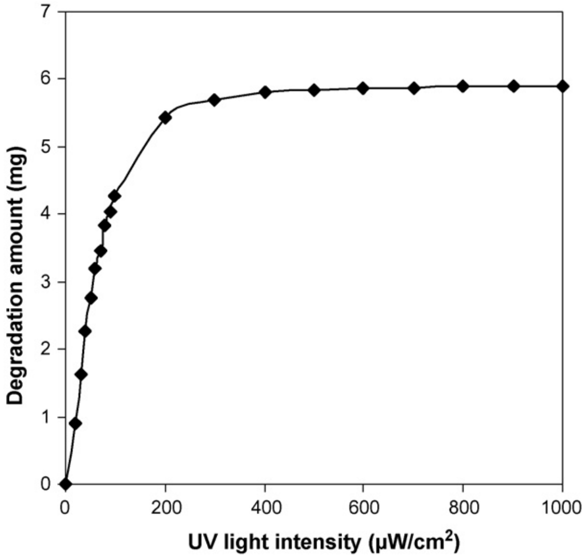

Fig. 6. Effect of UV light intensity on degradation amount.

17.6% at 50 μW/cm^2. Generally, photocatalytic reaction occurs in two regimes with UV light intensity: first-order regime and half-order regime. In the first-order regime, the electron–hole pairs are consumed more rapidly by chemical reactions than by recombination reaction. Nevertheless, in the half-order regime, the recombination rate is dominant. In the first-order regime, the degradation rate increases almost linearly with UV light intensity. In the half-order regime, the degradation rate increases with the square root of UV light intensity. The model here is mainly developed to assist the design of VOCs photocatalytic reactor for technical applications in heating, ventilation, and air conditioning (HVAC) air purification systems. Normally, for this kind of technical applications in HVAC, the photocatalytic reaction is in the first-order regime, which leads to the assumption in Eq. (5). For studying the photocatalytic reaction in high value UV light intensities, the model needs to be improved to include the reaction in the half-order regime.

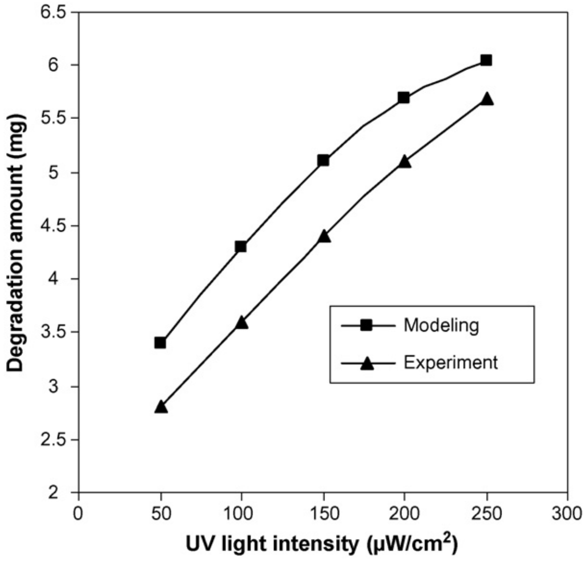

Fig. 7. Comparison between modeling and experiment at different UV light intensities.

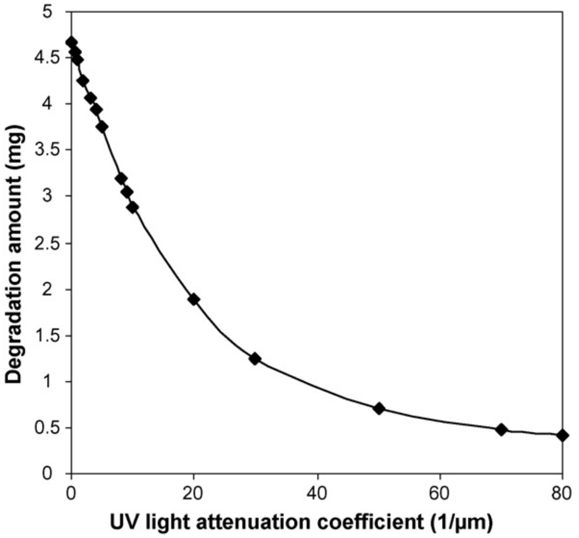

Fig. 8. Effect of UV light attenuation coefficient on degradation amount.

5.2. *Effect of UV light attenuation coefficient*

UV light attenuation coefficient is one of the optical properties of the TiO_2 catalyst. It can be controlled during the catalyst manufacture process. As shown in Fig. 8, the degradation amount of formaldehyde decreases quickly with the increase in attenuation coefficient. The decrease is because of a decrease in the penetrating UV light intensity at a high attenuation coefficient, thus giving a lower degradation rate. As the attenuation coefficient is increased to about 70 μm^{-1}, the degradation amount starts to level off and approaches zero gradually. This indicates that at very high attenuation coefficient, the UV light can be attenuated so much that it is essentially blocked out of the catalyst and the degradation of formaldehyde has essentially terminated. The computation result shows that it is beneficial to realize a TiO_2 catalyst with a low attenuation coefficient for UV light.

5.3. *Effect of adsorption*

The photocatalytic reaction starts with the adsorption of formaldehyde molecules on the surface of TiO_2 catalyst. The effect of adsorption on the degradation amount of formaldehyde is evaluated by changing the value of the Langmuir coefficients. As shown in Fig. 9, the degradation amount increases almost linearly with an increase in the adsorption capacity from 0 to about 0.04 mg/g. This is because the more formaldehyde molecules are adsorbed on the surface of the catalyst, the more formaldehyde molecules are available for photocatalytic degradation. However, as the adsorption capacity increases to about 0.04 mg/g, the degradation amount reaches a plateau of 5 mg. The reason is that the catalyst is essentially saturated with formaldehyde molecules at very high adsorption capacity.

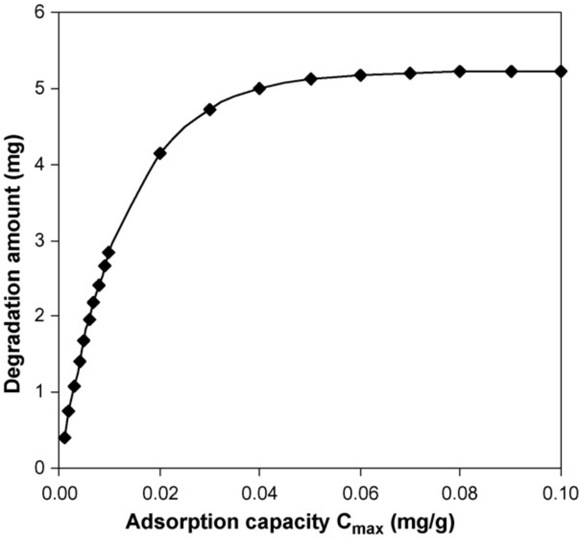

Fig. 9. Effect of adsorption capacity on degradation amount.

5.4. Effect of catalyst thickness

The TiO_2 catalyst film thickness can be controlled easily during the fabrication process. The effect of film thickness on the degradation amount of formaldehyde is shown in Fig. 10. As can be seen, the degradation amount increases from 0.82 to 4.67 mg when the thickness changes from 0.2 to 1.0 μm. This increase is caused by an increase in the catalyst amount available to be activated by UV light for the photocatalytic reaction. However, when the thickness is over 1.0 μm, the degradation amount begins to decrease. This indicates that a thin film catalyst thicker than 1.0 μm provides no additional photocatalytic power. The main reason for this phenomenon is that a slow diffusion is limiting the number of molecules reaching the interior of the catalyst.

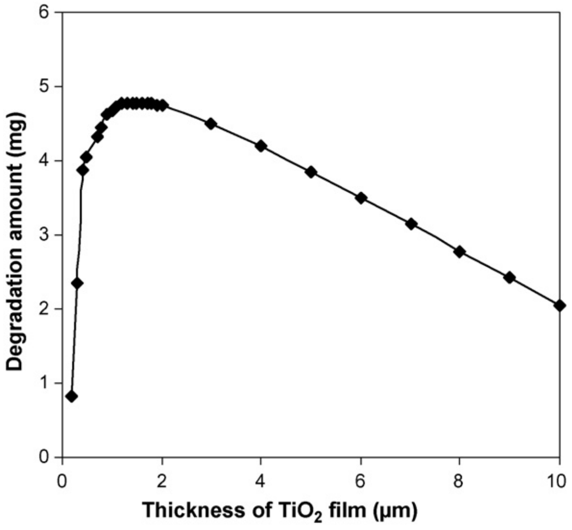

Fig. 10. Effect of catalyst thickness on degradation amount.

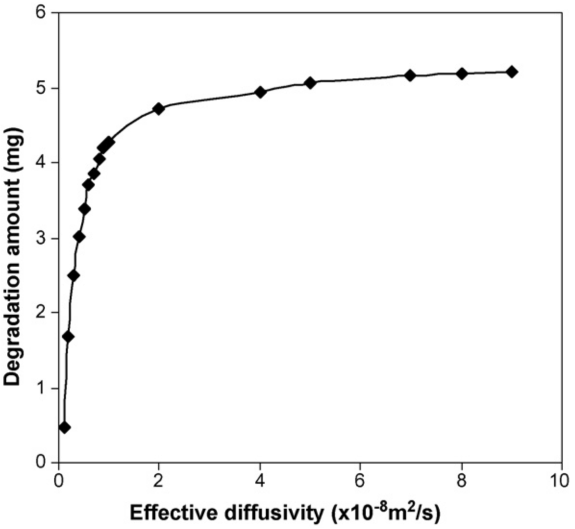

Fig. 11. Effect of effective diffusivity on degradation amount.

5.5. Effect of diffusion

The diffusivity of formaldehyde molecules in the catalyst can be controlled by changing the pore structure of the catalyst. The effect of effective diffusivity on degradation amount of formaldehyde is shown in Fig. 11. The degradation amount increases quickly from 0.47 to 4.72 mg when the effective diffusivity changes from 0.1×10^{-8} to $2.0 \times 10^{-8}\ m^2/s$. This is because formaldehyde molecules can diffuse into the catalyst faster, thus increasing the photocatalytic degradation rate. However, as the diffusivity is more than $2.0 \times 10^{-8}\ m^2/s$, the degradation amount increases very slowly. This indicates that further increase in diffusivity is not beneficial to the increase in degradation amount. The cause for this is that formaldehyde has fully penetrated the catalyst. The degradation amount may be limited by other variables such as adsorption, UV light intensity, and mass transfer rate.

5.6. Effect of flow rate

Flow rate is an important factor that affects photocatalytic reaction by changing the convective mass transfer and diffusion between formaldehyde molecules and TiO_2 catalyst. Fig. 12 shows the effect of flow rate on degradation amount of formaldehyde. When the flow rate increases initially from 0 to 0.0001 m/s, the degradation amount also increases from 5.14 to 5.20 mg. This is because that the increased flow rate improves the photocatalytic reaction by increasing the diffusion between formaldehyde molecules and TiO_2 catalyst. However, as the flow rate increases from 0.0001 to 0.1 m/s, the degradation amount decreases gradually. The reason is that too high flow rate results in shorter residence time, which eventually reduces the degradation amount of formaldehyde by affecting the adsorption of formaldehyde molecules on the surface of TiO_2 and the photocatalytic reaction. Nevertheless, the degradation amount increases again when the flow rate approaches 0.12 m/s. Although too high flow rate results in shorter residence

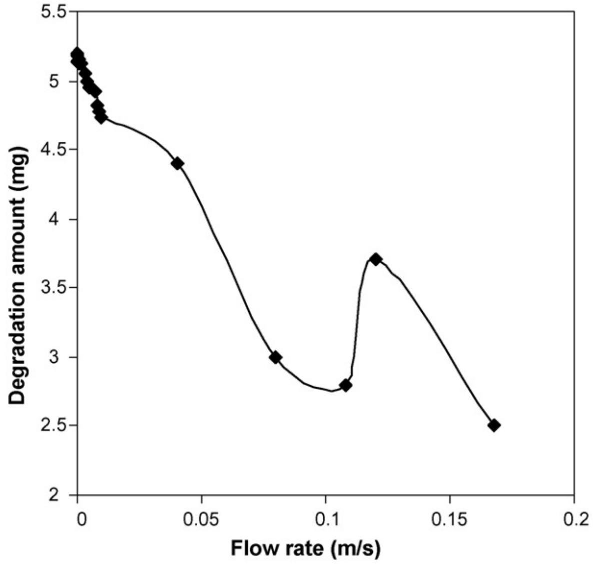

Fig. 12. Effect of flow rate on degradation amount.

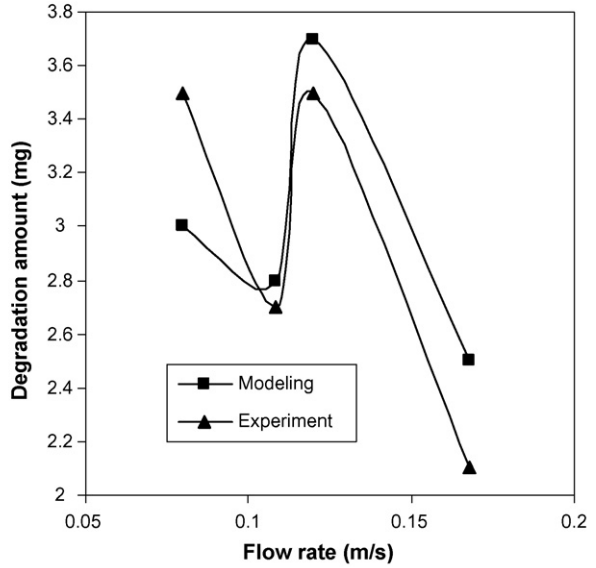

Fig. 13. Comparison between modeling and experiment at different flow rates.

time, it also increases the convective mass transfer between the formaldehyde and TiO_2 according to Eq. (10). This proves that the flow rate has dual effects on the photocatalytic reaction.

The comparison between modeling and experiment at different flow rates is shown in Fig. 13. It can be seen that the modeling results match well those from the experiments with a minimum difference of 3.5% and a maximum difference of 16.7%. The difference between modeling and experiment is mainly caused by experiment uncertainty, the difference in catalyst properties employed in modeling and experiment, and the assumptions in the modeling.

6. Conclusion

A mathematical model is successfully developed for the non-steady photocatalytic degradation process of VOCs using nano-TiO_2 catalyst. The model is validated by experimental data. The controlling mechanisms of the photocatalytic process are found to be mass transfer, diffusion, adsorption and photochemistry. Employing the model, the effects of some key factors on photocatalytic degradation of formaldehyde are investigated. The degradation amount of formaldehyde increases initially and then reaches a plateau with UV light intensity, adsorption capacity, and effective diffusivity. The degradation amount decreases quickly at the early stage and starts to level off and approach zero gradually with the increase in UV light attenuation coefficient. The degradation amount increases initially and then decreases with the increase of catalyst thickness. There is an optimum thickness of 1 μm for this study. The flow rate has dual effects on the photocatalytic degradation of formaldehyde. Finally, the model developed here can be employed to assist the design of VOCs photocatalytic degradation system using thin film nano-TiO_2 catalyst.

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