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A KINETIC MODEL FOR PHOTOCATALYTIC DEGRADATION OF ORGANIC CONTAMINANTS IN A THIN-FILM TiO₂ CATALYST

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Abstract—The thin-film technique is becoming a standard for the preparation of TiO₂-based photocatalysts for organic degradation. The catalyst alleviates the drawback of poor settleability associated with the powder TiO₂ traditionally used. In addition, the thin-film catalyst can be connected to an external power source to **reduce the recombination of UV-activated electrons and holes, thereby increasing the quantum efficiency**. The immobilization of TiO₂ on a solid carrier as a thin-film catalyst introduces several mechanisms not normally found in conventional TiO₂ slurry process. These mechanisms have been identified to include at least liquid–film transfer, adsorption, diffusion and photocatalytic reaction in a thin-film. **A mathematical model was developed to incorporate these mechanisms for the photodegradation of organic molecules in a batch reactor. The model was verified using the data of 4-chlorophenol degradation obtained from the literature.** The thin-film photocatalytic model was then used to **investigate the effect of catalyst properties on the photodegradation of organics**. The properties investigated included adsorption capacity, diffusion in the catalyst, UV attenuation and film thickness. The results of model simulation show that the effects of catalyst properties on the degradation of organics are highly nonlinear. There is an optimal film thickness that yields a maximum rate of photodegradation. The model not only provides insights into the effect of these underlying mechanisms but also can be used as a tool to assist the design of a thin-film photocatalyst. © 1999 Elsevier Science Ltd. All rights reserved

Key words—photocatalysis, thin-film catalyst, kinetic modeling, organic degradation

NOMENCLATURE

A area of catalyst exterior surface (cm²)
A matrix operator for second derivative in space
b coefficient for Langmuir–Hinshelwood isotherm (L/mg)
B matrix operator for first derivative in space
D_s effective diffusivity of molecules in catalyst (cm²/day)
I UV intensity in catalyst (W/cm²)
I₀ intensity of irradiating UV (W/cm²)
k rate constant for photocatalytic reaction (cm^{2m} mg¹⁻ⁿ gⁿ⁻¹ day^{m-1} W^{-m})
k_f liquid–film transfer coefficient (cm/day)
H thickness of catalyst thin-film (cm)
m reaction order with respect to UV intensity (variable)
M_p mass of molecules destroyed by photocatalytic reaction (mg/g)
M₀ mass of molecules initially in reactor (mg/g)
M₁ mass of molecules in bulk liquid (mg/g)
M_q mass of molecules adsorbed in catalyst (mg/g)
n reaction order with respect to solid-phase concentration (variable)

q solid-phase concentration of molecules in catalyst (mg/g)
q₀ initial solid-phase concentration in catalyst (mg/g)
q_{max} coefficient for Langmuir–Hinshelwood isotherm (mg/g)
ρ_p wet density of thin-film catalyst (g/cm³)
S₀ initial concentration of molecules in bulk liquid (mg/L)
S_b **concentration of molecules in bulk liquid (mg/L)**
S_w liquid-phase concentration of molecules on catalyst surface (mg/L)
t time (s)
V volume of bulk liquid in reactor (mL)
W_i weights for numerical quadrature
X_i coordinate of collocation points
z distance from carrier surface (cm)
α coefficient of UV attenuation in catalyst (μm⁻¹)

INTRODUCTION

The photocatalytic process is emerging as a promising technology for the oxidation/degradation of organic contaminants in environmental control. In this process a semiconductor activated by ultra-

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violet (UV) radiation is used as a catalyst to destroy organic contaminants. The process has several advantages when compared to biological and traditional chemical oxidation processes. First, the photocatalytic reaction is not specific and, therefore, is capable of destroying a spectrum of organic chemicals. These compounds include hydrocarbon fuels, halogenated solvents, surfactants, pesticides and many hazardous organic chemicals (Venkatadri and Peter, 1993; Hoffmann *et al.*, 1995). Second, the process is very powerful, often achieving a complete mineralization of organics. Third, the process is immune to organic toxicity. This advantage makes the photocatalytic process particularly attractive for the degradation of recalcitrant and toxic xenobiotic compounds. Fourth, the process can be applied equally well to liquid (e.g. wastewater and contaminated groundwater) and gaseous streams (e.g. VOC emission). Finally, there is a potential to utilize sunlight instead of an artificial light as an UV source, thereby reducing the energy cost for the process (Pruden and Ollis, 1983; Kormann *et al.*, 1991; Crittenden *et al.*, 1997).

In conventional photocatalytic processes, powder titanium dioxide (TiO_2) was used as the catalyst for organic destruction. These fine particulates, with an average diameter of $0.2 \mu\text{m}$, were added to the waste stream that was placed under an UV irradiation (Ollis, 1985; Ollis *et al.*, 1991). The powder catalysts, however, suffer two serious drawbacks which limit its practical applications. First, the settling velocity of powder TiO_2 is very slow requiring a long retention time in the clarifier. Second, as the dosage of TiO_2 is increased in order to increase the photocatalytic rate, the high turbidity created by the high TiO_2 concentration can actually decrease the depth of UV penetration. This "shadowing effect" can drastically lower the rate of photocatalytic reaction on a unit TiO_2 weight basis. To eliminate the need for a follow-up clarifier, techniques were developed to immobilize TiO_2 on a solid carrier.

Among these immobilization methods, the thin-film technique appears to be the most promising in terms of practical applications. A thin-film catalyst is normally prepared using a sol-gel technique (Kim and Anderson, 1994). TiO_2 powder is mixed in a gel-like solution containing mineral oxides. A solid carrier such as a glass slide or stainless steel plate is then submerged in the gel. The carrier coated with TiO_2 gel is then airdried and baked at $200\text{--}600^\circ\text{C}$ for about one hour. The resulting thin-film is a porous construct of TiO_2 powder about $0.2\text{--}0.5 \mu\text{m}$ thick. The coating-drying-baking procedure can be repeated several times to increase the thickness of the film. The carrier coated with thin-film TiO_2 can then be mounted in a reactor to receive UV irradiation for the destruction of organic contaminants (Hidaka *et al.*, 1995; Kim and Anderson, 1996). The immobilization of TiO_2 as a

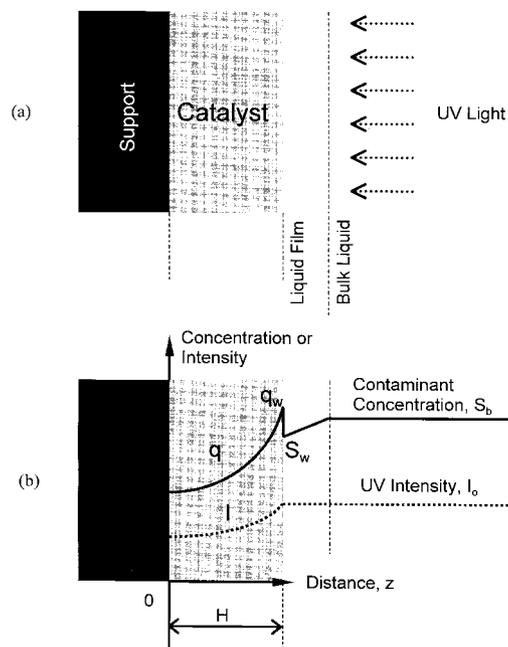


Fig. 1. Conceptual model for photocatalytic reaction in thin-film catalyst: (a) system configuration and (b) coordinate system and concentration profile.

thin-film also added a major advantage to the photocatalytic process; the carrier can be connected to an external power source to draw electrons excited by UV away from the catalyst. The result is a reduction of the recombination of electrons and holes and an increase in quantum efficiency (Vinodgopal *et al.*, 1993, 1994).

Although thin-film TiO_2 provides several advantages over its traditional powder form, the technique introduced several variables that can potentially limit the rate of photocatalytic reaction in a thin-film. For example, the diffusion of organic molecules in the film may be so slow that not enough molecules are available inside the catalyst for degradation. Or, UV intensity may be attenuated by the catalyst so much that photocatalytic degradation inside a thick catalyst can become very limited. The effects of these variables are not well understood. In addition, it still lacks of reliable model to simulate experimental results so far. The purpose of this study is to develop a mathematical model to incorporate mechanisms underlying the photocatalytic destruction of organic molecules in a thin-film catalyst. The model will be used to investigate the effect of important process variables on the destruction of organic molecules.

MODEL DEVELOPMENT

A batch photocatalytic model will be developed for this study. The model development focuses primarily on the transport and degradation of parent contaminant. Although the production of by-pro-

ducts can potentially affect the behavior of parent compound, their impacts are beyond the scope of this study. The conceptual basis for organic destruction by a thin-film TiO₂ photocatalyst is depicted in Fig. 1.

Fig. 1(a) shows that a thin layer of TiO₂ catalyst is immobilized on an inert carrier. The thin-film-carrier assembly is submerged in a solution containing organic molecules. An UV light source is positioned on the right side to provide a uniform irradiation on the surface of catalyst. The UV attenuates as it penetrates into the catalyst layer. It is assumed that UV attenuation by the bulk liquid is negligible, as compared with the TiO₂ thin-film. Organic molecules in the bulk liquid migrate to the surface of catalyst and diffuse into the catalyst layer. The diffusing molecules are destroyed photocatalytically by the radicals generated by UV penetrating the catalyst. As a result of these sequence of events, a concentration profile for organic molecules and a intensity profile for UV radiation is established (see Fig. 1(b)). The physical model described above provides a basis for the development of a mathematical model.

A Cartesian coordinate is defined in the thin-film catalyst to allow the description of contaminant and UV profiles (see Fig. 1(b)). The origin of the coordinate ($z = 0$) is located at the surface of inert carrier. The simultaneous diffusion and photocatalytic destruction of organic molecules is described by the following equation.

$$\frac{\partial q}{\partial t} = D_s \frac{\partial^2 q}{\partial z^2} - kI^m q^n \quad 0 \leq z \leq H \quad (1)$$

In the above equation, q is the sorbed concentration of molecules in the catalyst (mg/g), D_s is the effective diffusivity of molecules in the catalyst (cm²/day), k is the rate constant for the photocatalytic reaction, I is the intensity of UV in the catalyst (W/cm²), H is the thickness of catalyst (cm), z is the distance from the carrier surface (cm), t is the reaction time (s) and m, n are reaction order constants.

In Eq. (1), the diffusion of molecules in the catalyst is described by Fick's second law (Bird *et al.*, 1960). The second term on the right hand side describes the photocatalytic destruction of organic molecules. The rate of destruction is assumed to be proportional to the m th order of UV intensity (I) and the n th order of sorbed organic concentration (q). Although several studies have been devoted to determine the rate of photocatalytic destruction (Crittenden *et al.*, 1996; Hong *et al.*, 1996), no generally accepted rate expressions are yet available in the literature. The rate term in Eq. (1) can be modified easily once a valid rate expression becomes available.

Several studies have shown that photocatalytic destruction is preceded by the adsorption of organic molecules onto the catalyst surface (Ollis *et al.*,

1991; Hoffmann *et al.*, 1995). The adsorption could form a maximum of single layer of molecules on the surface. This adsorption is depicted as a "jump" in the concentration of organic molecules in Fig. 1(b). The Langmuir-Hinshelwood isotherm, which is based on monolayer coverage of molecules, is selected to describe this adsorption step.

$$q|_{z=H} = \frac{q_{\max} b S_w}{1 + b S_w} \quad (2)$$

In this equation, $q|_{z=H}$ and S_w are respectively the sorbed and liquid phase concentration of contaminant molecules on the catalyst surface. q_{\max} (mg/g) and b (L/mg) are the coefficients for Langmuir-Hinshelwood isotherm. q_{\max} represents the maximum adsorption capacity when a complete monolayer coverage is achieved.

The attenuation of UV in the catalyst is a function of UV wavelength and the optical properties of the catalyst. The attenuation is described by a Beer-Lambert expression that follows an exponential decay law (Schwarzenbach *et al.*, 1993).

$$I = I_0 \times 10^{-\alpha(H-z)} \quad 0 < z < H \quad (3)$$

I_0 is the intensity of incident UV (W/cm²) and α is the attenuation coefficient for UV in the catalyst (cm⁻¹).

Eqs.(1)–(3) describe the fundamental mechanisms underlying the process of photodegradation of organic molecules in a thin-film catalyst. The equations must be coupled to a reactor model to completely define a photocatalytic process model. As described previously in the sequence of events, organic molecules disappear from the bulk liquid because of their migration into the catalyst. This migration flux can be described using Fick's first law.

$$\frac{dS_b}{dt} = -\frac{A}{V} k_f (S_b - S_w) \quad (4)$$

In the equation, A is equal to the exterior surface area of thin-film catalyst (cm²); V is the volume of wastewater in the reactor (cm³); and k_f is the coefficient of film-transfer across the boundary layer (cm/s). To completely describe the performance of a batch photocatalytic reactor, two initial conditions (ICs) and two boundary conditions (BCs) are required.

$$\text{IC1: } S_b = S_0 \quad \text{at } t < 0 \quad (5)$$

$$\text{IC2: } q = q_0 \quad \text{at } t < 0 \quad (6)$$

$$\text{BC1: } \left. \frac{\partial q}{\partial z} \right|_{z=0} = 0 \quad \text{at } t > 0 \quad (7)$$

$$\text{BC2: } \rho_p D_s \left. \frac{\partial q}{\partial z} \right|_{z=H} = k_f (S_b - S_w) \quad \text{at } t > 0 \quad (8)$$

S_0 and q_0 are equaled to the initial concentration of organic molecules in the bulk liquid and catalyst, respectively. ρ_p is the density of thin-film TiO₂ catalyst (g/cm³). **BC1 is a no-flux condition at the catalyst-carrier interface. BC2 specifies the continuity of mass flux on the liquid-catalyst interface.** The flux continuity, rather than a mass conservation, must be used because molecules are destroyed in the catalyst.

Eqs. (1)–(8) constitute a process model for photocatalytic reaction in a batch reactor employing a thin-film TiO₂ catalyst. **The equations were solved using a combination of the orthogonal collocation method (OCM) (Finlayson, 1972) and Gear's method (Hindmarsh, 1987), as described in the next section.**

MODEL SOLUTION

The first step in orthogonal collocation is the normalization of catalyst domain. This was achieved by first defining the following variable.

$$z^* = \frac{z}{H} \quad \text{for } 0 \leq z^* \leq 1 \quad (9)$$

The dimensionless variable z^* was then substituted into Eqs. (1)–(8) to obtain a set of normalized equations. **The second step of OCM was the selection of an orthogonal polynomial to approximate the concentration of contaminant in the catalyst.** In the case of thin-film catalyst, the concentration profile has a zero gradient at the carrier surface, i.e. it is symmetrical with respect to $z^*=0$. This feature suggests the selection of a symmetrical polynomial such as Legendre polynomial.

Another consideration in OCM is the selection of the number of **collocation points**. Generally, the accuracy of OCM approximation increases with an increase in the number of collocation points. However, this increase leads to an increase in the computation time. It has been shown that the use of **six internal collocation points can yield accurate results for diffusional problems in activated carbon (Crittenden *et al.*, 1980) and in biofilm systems (Chang and Rittmann, 1987).** Hence, a **sixth order Legendre polynomial** was selected for this study.

The application of OCM resulted in the replacement of first and second derivative with collocation matrix \mathbf{A} and \mathbf{B} , respectively. The coordinate z^* was also replaced by collocation points X_i . The new equations for photocatalytic model are presented as follows.

$$\frac{dq_i}{dt} = \frac{D_s}{H^2} \sum_{j=1}^{\text{NR}} \mathbf{B}_{i,j} q_j - k I_i^n q_i^n \quad \text{for } i = 1, \dots, N \quad (10)$$

$$q_{\text{NR}} = \frac{q_{\text{max}} b S_w}{1 + b S_w} \quad (11)$$

$$I_i = I_0 \times 10^{-\alpha H(1-X_i)} \quad \text{for } i = 1, \dots, \text{NR} \quad (12)$$

$$\text{IC2: } q_i = q_0 \quad \text{for } i = 1, \dots, \text{NR} \quad (13)$$

$$\text{BC2: } \frac{\rho_p D_s}{H} \sum_{j=1}^{\text{NR}} \mathbf{A}_{\text{NR},j} q_j = k_f (S_b - S_w) \quad (14)$$

The equation for bulk concentration (Eq. (4)) did not change because it is not dependent on the z variable. Boundary condition (BC1) on the carrier surface (Eq. (7)) was satisfied automatically by the **Legendre polynomial** and was eliminated safely. Consequently, the point on the carrier surface ($z^*=0$) is not a collocation point. In the above equations, N is the number of internal collocation points, which is equaled to 6 in this study. Collocation point $i = \text{NR}$ ($=N + 1$) is located on the surface of the thin-film.

Eq. (14) was rearranged as follows to obtain an expression for q_{NR}

$$q_{\text{NR}} = \frac{1}{\mathbf{A}_{\text{NR},\text{NR}}} \left(\frac{H}{1000(\text{mL/L})\rho_p D_s} k_f (S_b - S_w) - \sum_{j=1}^{\text{NR}} \mathbf{A}_{\text{NR},j} q_j \right) \quad (15)$$

The factor 1000 mL/L in the denominator was introduced to keep the units consistent in the equation. Langmuir-Hinshelwood isotherm was also rearranged as follows.

$$S_w = \frac{q_{\text{NR}}}{(q_{\text{max}} q_{\text{NR}}) \times b} \quad (16)$$

Eq. (16) was substituted into Eq. (15) to obtain an implicit equation that was solved for q_{NR} iteratively. The values for q_{NR} and S_w , obtained from Eq. (16), were then substituted into Eqs. (4) and (10) during the numerical integration. This approach ensures that both isotherm and flux continuity were satisfied on the catalyst surface. The system of seven ($=N + 1$) ordinary differential equations were integrated using a package subroutine — LSODE — which is based on Gear's method (Hindmarsh, 1987).

The solution of thin-film photocatalytic model yields **the concentration of contaminant in the catalyst (q_i) and in the bulk liquid (S_b).** In light of the two possible removal mechanisms in the process — adsorption and photocatalysis — bulk concentration alone is not a suitable measurement for the photocatalytic degradation of organic molecules. The amount of contaminant removed by adsorption

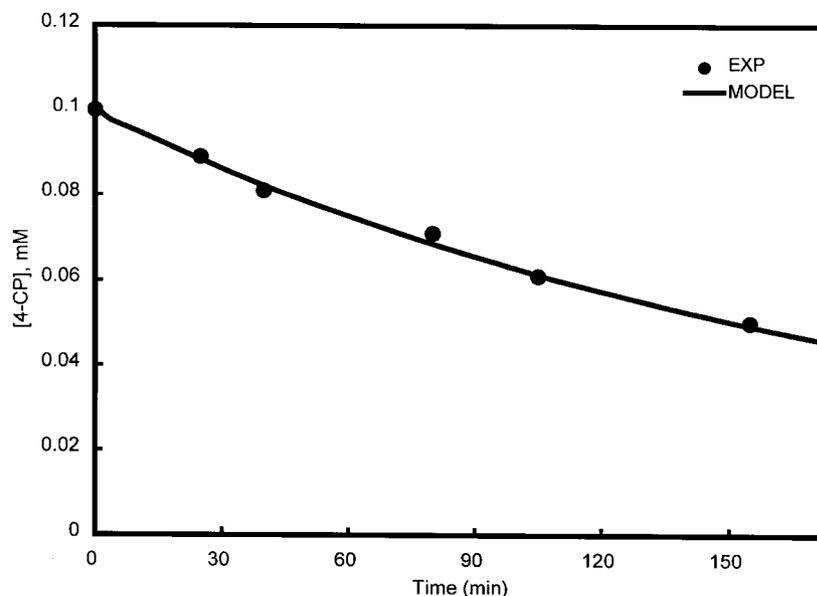


Fig. 2. Model simulation and experimental data for 4-chlorophenol degradation in a batch reactor.

and photocatalysis can be calculated separately from the model using the following equations. The mass of molecules adsorbed (M_q) was obtained by integrating the solid-phase concentration (q) throughout the entire catalyst.

$$M_q = A \rho_p \int_0^H q dz \quad (17)$$

The integral in the above equation was evaluated using the quadrature in OCM, as shown below.

$$M_q = A \times H \times \rho_p \times \sum_{j=1}^{NR} (W_j \times q_j) \quad (18)$$

In the above equation, W is a vector of the weights for numerical quadrature. The mass of molecules removed by the photocatalytic reaction (M_p) was then calculated by subtracting the mass adsorbed and the mass remaining in bulk liquid (M_l) from

the mass initially present in the reactor (M_0).

$$M_p = M_0 - M_l - M_q \quad (19)$$

Written in an explicit form

$$M_p = \frac{V}{1000(\text{mL/L})} (S_0 - S_b) - A \times H \times \rho_p \times \sum_{j=1}^{NR} (W_j \times q_j) \quad (20)$$

The solution for the photocatalytic model was coded in a FORTRAN program. The verification of the model is presented next.

MODEL VALIDATION

The thin-film photocatalytic model derived in this study was validated using data obtained from the

Table 1. Model parameters used to simulate the experimental data of Vinodgopal *et al.* (1993)

Symbol	Parameter description (unit)	Value
a	specific surface area of catalyst (cm^{-1})	0.011
α	UV attenuation coefficient in catalyst (μm^{-1})	20
b	Langmuir–Hinshelwood isotherm coefficient (L/mg)	0.2
D_s	effective diffusivity in thin-film catalyst (cm^2/day)	9.5×10^{-5}
I_0	intensity of incident UV (W/cm^2)	114
k	rate constant for photodegradation ($\text{cm}^{2m} \text{g}^{n-1} / \text{W}^{-m} \text{mg}^{n-1} \text{day}$)	1.0
k_f	liquid–film transfer coefficient (cm/day)	700
H	thickness of catalyst (μm)	1.0
m	reaction order with respect to UV intensity	1.0
n	reaction order with respect to solid-phase concentration	1.0
q_0	initial concentration of organic compound in catalyst (mg/g)	0.0
q_{max}	Langmuir–Hinshelwood isotherm coefficient (mg/g)	0.215
ρ_p	density of catalyst (g/cm^3)	3.2
S_0	initial concentration of 4-CP (mg/L)	12.85
V	liquid volume in reactor (mL)	200.0

Table 2. Parameters used for base case model simulation

Symbol	Parameter description (unit)	Value
a	specific surface area of catalyst (cm^{-1})	0.011
α	UV attenuation coefficient in catalyst (μm^{-1})	1.0
b	Langmuir–Hinshelwood isotherm coefficient (L/mg)	2.3
D_s	effective diffusivity in thin-film catalyst (cm^2/day)	9.5×10^{-5}
I_0	intensity of incident UV (W/cm^2)	114
k	rate constant for photodegradation ($\text{cm}^{2m} \text{g}^{n-1} / \text{W}^{-m} \text{mg}^{n-1} \text{day}$)	1.0
k_f	liquid–film transfer coefficient (cm/day)	700
H	thickness of catalyst (μm)	1.0
m	reaction order with respect to UV intensity	1.0
n	reaction order with respect to solid-phase concentration	1.0
q_0	initial concentration of organic compound in catalyst (mg/g)	0.0
q_{max}	Langmuir–Hinshelwood isotherm coefficient (mg/g)	0.215
ρ_p	density of catalyst (g/cm^3)	3.2
S_0	initial concentration of contaminant (mg/L)	12.85
V	liquid volume in reactor (mL)	200.0

literature. Vinodgopal *et al.* (1993) used a thin-film TiO_2 coated on a glass slide to study the photocatalytic degradation of 4-chlorophenol (4-CP) in an aqueous solution. The thin-film TiO_2 with a thickness of $1 \mu\text{m}$ was prepared using a sol–gel technique. The slide-supported film catalyst was mounted in a solution containing 12.85 mg/L 4-CP. Samples were taken at different times to monitor the degradation of 4-CP. The experimental results are presented in Fig. 2 as solid circles. Although Vinodgopal *et al.* (1993) conducted several experiments, no mathematical models were developed to describe the data.

The parameters required for the simulation of Vinodgopal's data were extracted from the paper (Vinodgopal *et al.*, 1993). However, not all the parameters could be found in the paper, especially the mass transfer coefficients. For example, the diffusivity of 4-CP had to be assumed to have the same

value as its isomer 2-CP (Wu, 1999). Coefficients for liquid–film transfer and Langmuir–Hinshelwood isotherm were also assumed to have a reasonable value as its isomer 2-CP. Several parameters were then varied to obtain a good fit of the experimental data. The parameters used in the final simulation are presented in Table 1 and the results are plotted in Fig. 2.

Fig. 2 shows that the thin-film photocatalytic model developed in this study simulates the degradation of 4-CP very well. Although not all the parameters were measured independently, the fact that model simulation matches experimental data indicates the key mechanisms governing the thin-film photocatalytic process were captured in the model. These mechanisms include liquid–film transfer, adsorption, diffusion and photocatalytic degradation of organic molecules. **The model presented above is used next to investigate the effect of these**

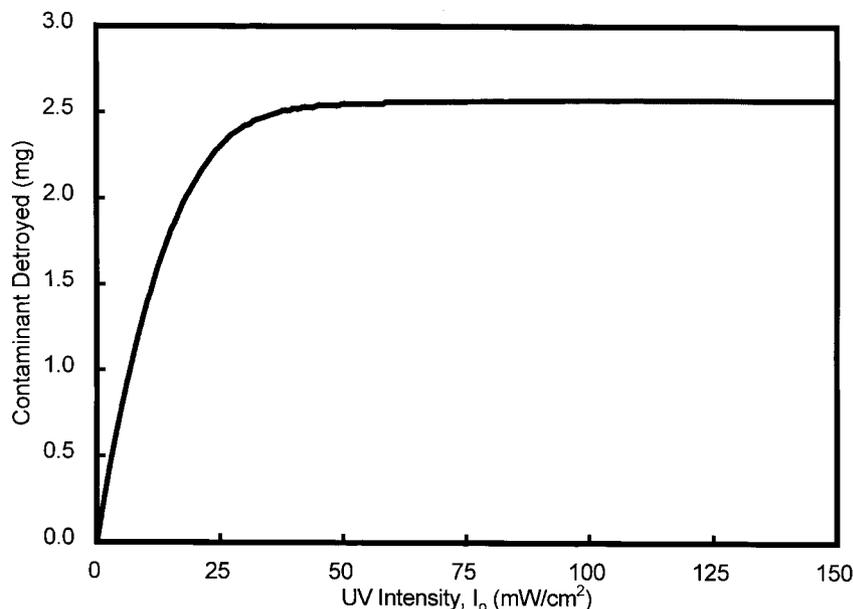


Fig. 3. Effect of UV intensity on the amount of contaminant destroyed.

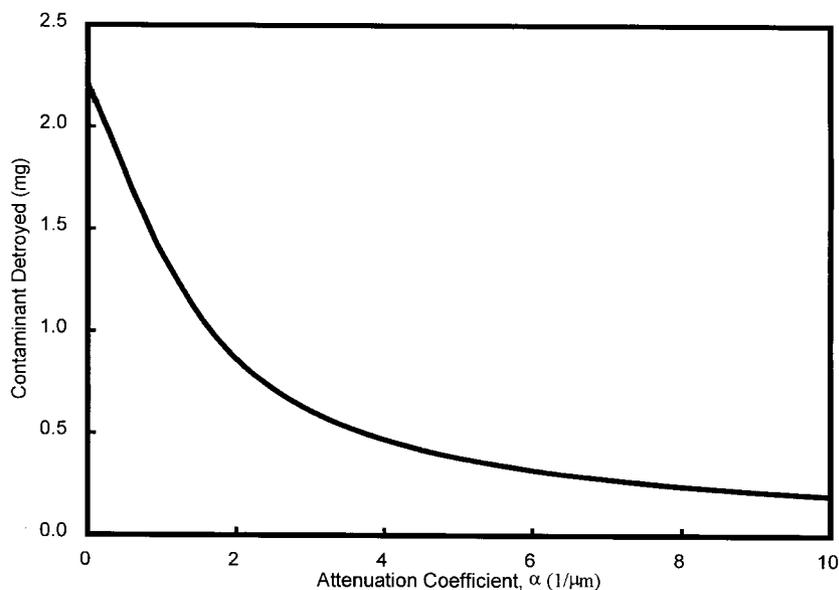


Fig. 4. Effect of UV attenuation.

mechanisms on the performance of a thin-film TiO_2 catalyst.

MODEL SIMULATIONS

The parameters used in the base case simulation of a photocatalytic process are presented in Table 2. The values of parameters are basically the same as those used in model verification in order to simulate a realistic process. The only exceptions are the isotherm coefficients, q_{max} and b . These coefficients were changed to the values for phenol, a common environmental pollutant.

The effect of the intensity of irradiating UV (I_0) on the photodegradation of phenol is presented in Fig. 3. The figure shows the amount of phenol destroyed at the end of simulation at 160 min, calculated using Eq. (20), as a function of the UV intensity. It is clear that the amount of phenol destroyed increases initially with an increase in the UV intensity. This is reasonable because the stronger the UV irradiation, the more the penetration of UV light into the catalyst. As a result, the degradation of phenol is also increased (see Eq. (1)). However, as the intensity of UV was increased to about $50 \text{ mW}/\text{cm}^2$, the amount of phenol destroyed

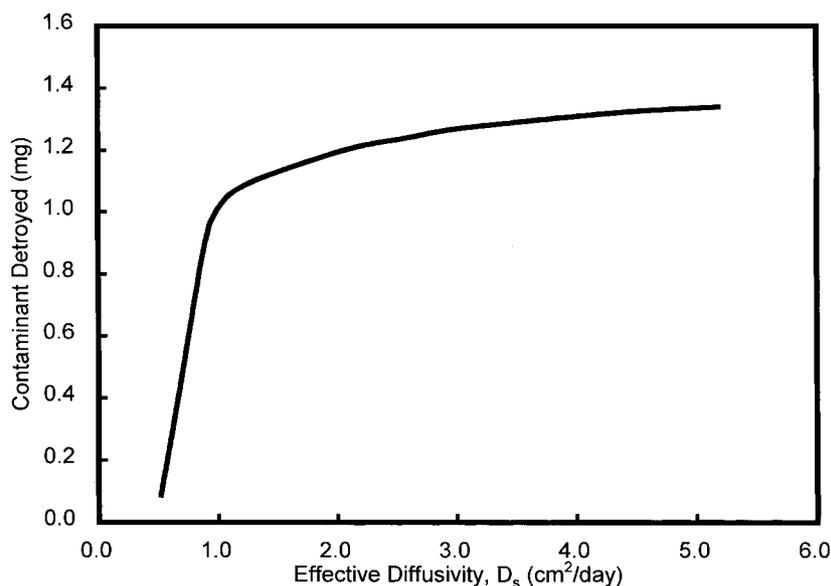


Fig. 5. Effect of diffusion in the thin-film catalyst on the amount of contaminant destroyed.

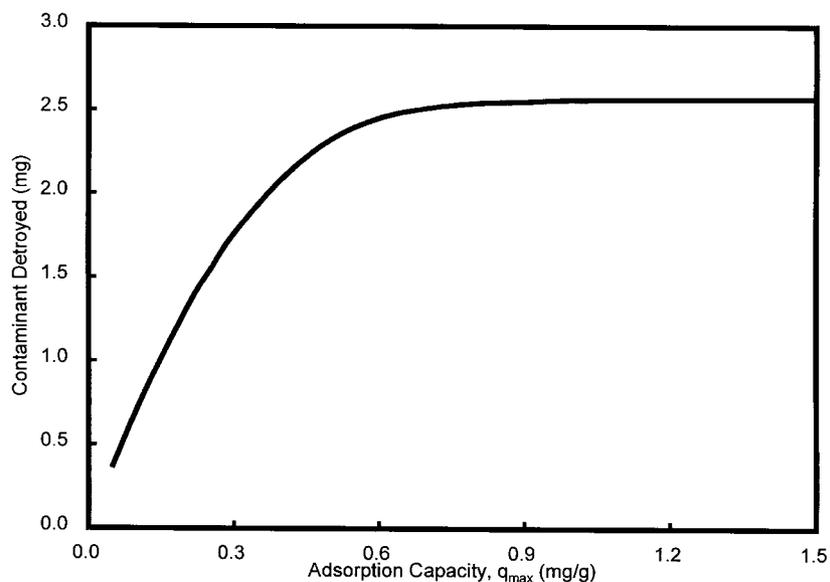


Fig. 6. Effect of adsorption capacity on the amount of contaminant destroyed.

reaches a plateau. Further increase in UV intensity could not increase the degradation of phenol. Apparently, the degradation of phenol is limited by other variables perhaps diffusion, liquid–film transfer, or phenol adsorption. To increase the amount of phenol destruction, one or more of these factors must be identified and alleviated.

The large number of parameters for a thin-film photocatalytic process can be grouped into two categories: operational and catalyst properties. The intensity of irradiating UV used in the above simulation belongs to one of the operation parameters. Since the objective of this study is to develop a thin-film photocatalyst, the following simulations will focus on the effect of catalyst properties on the degradation of phenol.

Fig. 4 shows the effect of the UV attenuation coefficient (α) on the amount of phenol destroyed. The coefficient represents one of the optical properties that can be manipulated during the manufacturing of a thin-film catalyst. A $1\ \mu\text{m}$ thick catalyst was used in the simulation to accentuate the effect of a large α . Fig. 4 shows that at small α the amount of phenol destroyed decreases quickly with an increase in α . The decrease in phenol destroyed was caused by a decrease in the intensity of penetrating UV irradiation at a high α , thereby giving a smaller photodegradation rate (see Eq. (1)). As the value of α is increased to about $20\ \mu\text{m}^{-1}$ the amount of phenol destroyed begins to level off and approaches zero gradually. This result indicates that at very high values for α , the UV irradiation can be attenuated so much that the degradation of phenol has essentially stopped. In other words, UV irradiation is essentially blocked out of the catalyst. The result of this simulation demonstrates that it is advantageous to pre-

pare a thin-film catalyst with a high transparency (i.e. low attenuation) for UV.

The effect of molecular diffusion (D_s) on the amount of phenol destroyed is depicted in Fig. 5. The diffusivity of molecules in the catalyst is a function of the pore structure of the catalyst and the dimension of the molecules. The value of D_s can be increased, to a limited extent, by increasing the porosity of the catalyst during its manufacturing. Fig. 5 shows that initially the amount of phenol destroyed increases quickly with an increase in diffusivity. This is reasonable because molecules can move into the catalyst faster, thereby increasing the rate of photodegradation. As the diffusivity is increased to about $1.5 \times 10^{-4}\ \text{cm}^2/\text{day}$, the degradation of phenol reaches a plateau of about 1.42 mg. Further increase in diffusivity cannot increase the amount of phenol destroyed. The plateau represents a condition where phenol has fully penetrated the catalyst. The rate of phenol degradation may be limited by one or more of the following factors: UV intensity, adsorption and liquid–film transfer rate. More studies are required to identify the limiting factor(s).

As discussed previously in the sequence of events, the photocatalytic reaction in a thin-film catalyst is preceded by adsorption. The effect of adsorption can be evaluated using this photocatalytic model by changing the value of the Langmuir coefficients. Fig. 6 shows the effect of adsorption capacity, represented by coefficient q_{max} , on the amount of phenol destroyed. The figure shows that the amount of phenol destroyed increases almost linearly from zero with an increase in the adsorption capacity. This is reasonable because the more phenols are adsorbed, the more phenols are available for photocatalytic destruction. However, as the adsorption

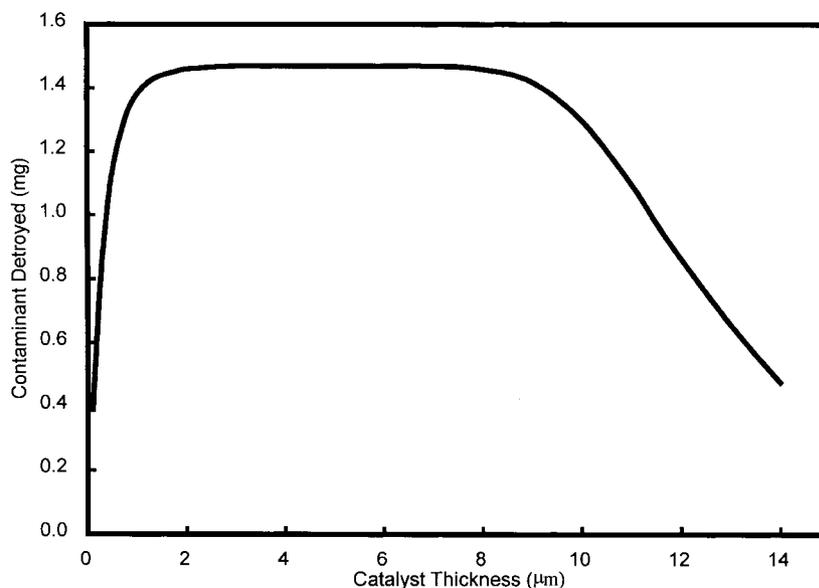


Fig. 7. Effect of catalyst thickness on the amount of contaminant destroyed.

capacity increases to about 1 mg/g, the amount of phenol destroyed reaches a plateau of 2.5 mg. The capacity has become so high that the catalyst is essentially saturated with phenol molecules. This condition is similar to those fully penetrated conditions discussed in Fig. 5, although the causes are completely different.

The adsorption of molecules from an aqueous solution is controlled by the hydrophobicity of the molecules and the selectivity of the catalyst. Although the properties of molecules are dictated by the type of wastewater, the selectivity of the catalyst may be manipulated. For example, a sorptive material such as SiO_2 may be added to the gel in the preparation of the thin-film TiO_2 catalyst. Being a hydrophobic material (Ruthven, 1984), SiO_2 can adsorb hydrophobic compounds preferentially and possibly increase the rate of photodegradation.

One of the properties of a thin-film catalyst that can be changed easily is its thickness. The effect of film thickness (H) on the amount of phenol destroyed is presented in Fig. 7. Fig. 7 shows that at small thickness, the amount of phenol destroyed increases with an increase in the film thickness. This increase in phenol degradation can be attributed to an increase in the amount of catalyst available to be activated by UV for the photodegradation. As the thickness is increased to about $2 \mu\text{m}$, the amount of phenol destroyed reaches a maximum of 1.5 mg. This result indicates that a thin-film catalyst thicker than $2 \mu\text{m}$ provides no additional photocatalytic power. It appears that the interior of the catalyst simply serves as an inert support. There are two possible explanations. First, a slow diffusion is limiting the number of molecules reaching the interior of the catalyst. Second, the strong attenuation

is limiting the intensity of UV reaching the interior of the catalyst. Either one or both of these factors can render the interior of the catalyst photocatalytically inert.

Fig. 7 also shows that as the thickness of the catalyst is increased to beyond $8 \mu\text{m}$ the amount of phenol destroyed starts to decrease. In other words, the amount of phenol destroyed by thin-film catalyst reaches a maximum with respect to the thickness of the catalyst. This trend has been observed in several other studies. Termakone *et al.* (1997) observed that the degradation of carbofuran by a thin-film TiO_2 catalyst reached a maximum at about 20 coatings ($\sim 6 \mu\text{m}$). Kim and Anderson (1994) used a TiO_2 -coated glass slide to degrade formic acid in an aqueous solution. They found that the amount of acid destroyed increased with an increase in the number of TiO_2 coatings until a maximum was reached at 7 layers. A similar result was observed by Ha and Anderson (1996) who used a TiO_2 thin-film supported on a stainless steel plate to degrade formic acid. Although it is possible that phenol molecules are sorbed in the interior of the thick catalyst, this scenario can only provide a partial explanation for the effect of film thickness. It is likely that more than one factor is affecting the decrease of phenol destroyed. More studies are required to elucidate the mechanisms underlying this phenomenon.

SUMMARY AND CONCLUSIONS

A kinetic model describing the photocatalytic degradation of organic molecules by a thin-film TiO_2 catalyst has been developed in this study. The model simulated the experimental data of 4-CP

degradation obtained from the literature very well. This result indicated that the model has captured the fundamental mechanisms underlying the thin-film photocatalytic process including adsorption, diffusion, liquid-film transfer, UV attenuation and photocatalytic reaction. The model was used to evaluate the effects of these mechanisms on the photodegradation of organic molecules.

The results of model simulation show that increasing the intensity of incident UV can increase the rate of photodegradation until a maximum rate is reached. At maximum rate, the catalyst may be fully penetrated by UV and the rate of photodegradation may be limited by liquid-film transfer, diffusion, adsorption, or a combination of these three factors. The model was then used to investigate the effect on organic degradation by the following catalyst properties: UV attenuation, diffusivity, adsorption capacity and film thickness. The results show that there exists a highly nonlinear relationship between each of these properties and the rate of photocatalytic degradation. Among these properties, film thickness shows the most interesting effect. The amount of molecules photodegraded shows a maximum for a medium range of film thickness. At a greater thickness the amount of photodegradation actually decreases indicating there exists an optimal thickness for the system studied. The thin-film photocatalytic model developed in this study can be used to gain insights into the effect of catalyst properties, and also as a tool to assist the design of a thin-film catalyst.

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