Mass Transfer Effect on the Photocatalytic Activity of UV/TiO₂ Packed-Bed System

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Abstract: Effects of mass transfer on photocatalytic activity were investigated using a recirculated feed solution (20 – 500 mL/min) in a UV/TiO₂ packed-bed photoreactor. The rate of phenol disappearance was significantly increased as the recirculation rate was raised up to 300 mL/min and reached a plateau beyond 400 mL/min. We confirmed that the degradation rate was influenced by the convective mass transfer of phenol from the bulk solution to the external surface of the catalysis particles. Other factors, such as solution pH and initial concentration, exhibited clear influences on the photocatalytic activity of the UV/TiO₂ packed-bed system. Assuming a constant intrinsic kinetic coefficient, the ratio of effective catalyst surface area to reactor volume, \( a_\text{exp} \) (cm²/cm³), was estimated to be on the order of \( 10^3 \) by the resistance-in-series model of rate constants. The obtained low \( a \) values indicate that only a small fraction of the surface area was effectively illuminated by the radiant source in the present reactor configuration and that improving the \( a \) value should be considered as one of the parameters for optimizing photoreactor design.

Keywords: mass transfer, packed-bed, UV/TiO₂, photocatalysts, phenol

Introduction

A photocatalytic reactor is suitable for the treatment of wastewater containing toxic organic pollutants [1-3]. Semiconductor catalysts can be employed, either in a slurry state or in a fixed form on a support. The former type is known to exhibit an outstanding reaction rate that is due to the dispersion of small particles that have high surface areas. A slurry-type configuration, however, presents some limitations, such as a low light-utilization efficiency that is due to the absorption and scattering of the light into an aqueous suspension of illuminated powders. Furthermore, a practical limitation is the post-process filtration required to separate the catalyst after the photocatalytic reaction is completed. Such problems associated with the use of catalyst suspensions can be circumvented by using catalysts immobilized on an appropriate support [4].

For this purpose, Serpone and coworkers [5] and Matthews [6] have utilized TiO₂ supported on glass beads and glass surfaces; these catalysts have proved to be both stable and effective for the photodegradation of dilute organic compounds. The supported catalysts, however, bear an intrinsic mass transfer resistance and, thus, their reaction rates show a dependence on the flow rate. In addition, a complexity problem exists in elucidating the influences of diffusional and other kinetic processes on an observed reaction rate [7].

According to the schematic illustration in Figure 1, there are essentially two consecutive mass transport steps associated with the oxidative reaction using the catalytic particles [8]. The bulk transport of solute in the solution phase is usually rapid because of mixing and convective flow. The film transport involves diffusion of the solute through a hypothetical boundary layer film, where the diffusion process controls the transfer of solute through the boundary layer immediately adjacent to the external surface of the particles. The overall observed reaction rate over the immobilized photocatalysts is strongly influenced by the mass transfer rate as well as by the surface reaction rate [9,10].

In this study, the effects of mass transfer on the photocatalytic activity of a UV/TiO₂ packed-bed system

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were investigated by varying the feed flow rates, solution pH, and initial concentration. TiO$_2$ was used as the photocatalyst of the stationary phase; it was immobilized on the surface of spherical glass beads (5 mm diameter). Phenol was used as a model component to measure the photocatalytic activity of the UV/TiO$_2$ system. The complexity confronted in the kinetic studies of the liquid-solid interface was minimized by fixing many variables, such as the surface area of the photocatalysts, the dissolved O$_2$ concentration (under atmospheric condition), the temperature, and the reactant concentration; this situation allowed us to envisage the behavior of the diffusion rate from a well-mixed liquid phase to the catalyst surface.

**Experimental**

**Materials**

TiO$_2$ colloidal sol (STS-02, Ishihara Co., Japan) was immobilized on the external surface of glass beads (dia. 5 mm) by using a successive impregnating method. The resulting coated fraction of TiO$_2$ on the glass beads was ca. 0.05 wt%. The coated glass beads were calcined at 550°C for 2 h under atmospheric conditions. Phenol (laboratory reagent grade) was used without further purification. TiO$_2$ granules (ST-B01, Ishihara Co., Japan) were also used in a spherically pelleted form for the photocatalytic degradation of phenol.

As shown in Figure 2, the reactor was designed as a cylindrical vessel (10 cm height; 2.2 cm diameter) packed with spherical beads through which the upward flow passed. The photoreactor was surrounded externally by an 80 W/cm$^2$ high-pressure mercury UV lamp (24 mm dia; 230 mm length) that emits radiation over the range 300–425 nm. The radiation intensity entering the cylindrical reactor vessel, equipped with a back aluminum reflector, was measured to be ca. 17 mW/cm$^2$ using a Model 380 radiometer (UVX, UVP Co., UK). Tygon tubing was fitted to the inlet and outlet ports to allow circulation of the solution through the reactors.

**Photol Degradation**

Experiments for phenol degradation were conducted in...
the packed-bed photoreactor operating in a continuous recirculation mode; 500 mL of a solution containing phenol was pumped at a pre-determined flow rate (20~500 mL/min). A peristaltic pump circulated the solution between the fluid reservoir and the photochemical reactor. Aliquots were retrieved from the feed tank at certain time intervals during each run; the degradation of phenol was analyzed by determining the concentration of unreacted phenol by measuring UV absorbance at 269 nm. The reaction temperature was maintained at 40°C as a result of the radiant heat from the UV lamp.

Results and Discussion

Effect of Flow Rate on Photocatalytic Reaction

The effect of mass transfer from the bulk phase to the external surface of the catalyst was investigated by varying the recirculation rate. As shown in Figure 3, an enhancement of phenol disappearance is clearly observed when the recirculation rate was increased from 50 to 300 mL/min. The increase of degradation rate at a higher flow rate indicates that the photocatalytic kinetics are influenced strongly by the external mass transfer rate, and that there existed a significant mass transfer limitation. The Reynolds number for the aqueous phase, whose flow rates are in the range 10~500 mL/min, nominally corresponded to a laminar flow regime.

The photocatalytic decomposition of phenol was assumed to follow the first-order reaction kinetics [11,12]. Thus, a plot of ln(C/C₀) versus irradiation time resulted in an approximate straight line whose slope we considered as the apparent first-order rate constant. Application of the least-squares method to estimate Kₐ values gave correlation coefficients > 0.99 in all cases, which validates our assumption of first-order kinetics.

\[ \ln(C/C_0) = K_a t \]  

(1)

To quantify the mass transfer rate in the photocatalytic reaction, Kₐ values were determined under various recirculation rates. The overall rate constants, Kₐ, with respect to the flow rate, are plotted in Figure 4. This figure demonstrates that the degradation rate increased almost linearly as the flow rates increased up to 300 mL/min, followed by an asymptotic approach to a plateau at ca. 400 mL/min. The photocatalytic activity of granular TiO₂ beads was higher than that of the TiO₂-coated glass beads; i.e., the Kₐ values of granular type were greater than those of the TiO₂-coated beads. The higher activity of the former type may be contributed in part by the dispersion of attrited particles from the granular beads that is caused by the shearing force of the flowing fluids. In addition, the amount of TiO₂ coated on to the surfaces of the glass beads does not seem to be high enough for efficient photoactivation via absorption of illuminated lights [13]. Both types of immobilized beads, however, clearly exhibit significant increases of their Kₐ values upon increasing the flow rates under all of the conditions used in this study; this observation provides a strong clue for the existence of an external mass-transfer limitation.

The overall reaction rate on supported nonporous photocatalysts can be governed, in general, by the surface reaction rate, the mass transfer rate, or a combination of the two. It is evident that when the packed-bed system incorporating the TiO₂ beads is employed, the forced convective mass transport of reactants from a well-mixed liquid phase to the catalyst surface plays an important role. Indeed, the increase of the flow rate through the reactor caused a significant increase in the rate of photocatalytic degradation by mitigating the resistance of external mass transfer in the diffusive film layer.
Effect of Reynolds Number on Mass Transfer Coefficients
At a steady state, all of the rates involved in the photocatalytic degradation can be correlated by the equation [14,15]

$$N_A = K_o(C_o - 0) = k_o a(C_o - C) = k_o aC_s$$

(2)

where $N_A$ is the disappearing flux of the reactant; $C_o$ and $C$ are the concentrations of the solute in the bulk phase and on the catalyst surface, respectively; $K_o$ is the experimentally observed overall rate constant; $a$ is the effectively illuminated surface area of the catalyst particles inside the reactor volume; $k_o$ is the mass transfer coefficient, which is a function of diffusivity, particle size, and flow rate; $k_i$ is the first-order reaction rate constant on the surface, which is a function of pH, the surface structure of the catalyst, and $O_2$ concentration.

For a fixed-bed reactor packed with spherical particles of 40~45% void fraction, the mass transfer coefficient can be correlated well in terms of the Sherwood number ($N_S\rho$), the Reynolds number ($N_Re$), and the Schmidt number ($N_Sc$) [15].

$$N_S = 1.17 N^{2/3} Re^{5/6} S^{1/2} = \frac{k_o d_p}{D}$$

(3)

$$N_Re = \frac{u_o d_p}{\mu (1 - \varepsilon)}$$

$$N_Sc = \frac{u_o}{\rho D}$$

Here, $d_p$ is the particle diameter; $u_o$ is the feed flow rate; $\rho$ is the density of the solution; $\mu$ is the viscosity of the solution; $\varepsilon$ is the void fraction of the packed-bed reactor; $D$ is the diffusivity of a solute in the aqueous phase.

The diffusivity of an organic component in a dilute solution can be estimated by the Wilke-Chang’s empirically modified Stokes- Einstein equation [17].

$$D_{AB} = 7.4 \times 10^{-9} \frac{(\phi B M_b)^{1/2} T}{\mu B V_A^2}$$

(4)

where $D_{AB}$ is the mutual diffusion coefficient of a very dilute solute $A$ (phenol) in solvent $B$ (water); $T$ is the absolute temperature; $\mu$ is the viscosity of the pure solvent; $M_b$ is the molecular weight of solvent $B$; $V_A$ is the molar volume of solute $A$ at its normal boiling point; $\eta_B$ is the association factor of solvent $B$ (Table 1).

The values of the parameter listed in Table 1 were used to deduce the mass transfer coefficient, $k_m$, by semi-empirical expressions that for Sherwood number and the diffusion coefficient using Equations (3) and (4). Figure 5 shows a gradual monotonic increase of $k_m$ with respect to the Reynolds number; this finding clearly indicates that the overall reaction rate is limited by the mass transfer, which is strongly dependent on the flow rates of the feed.

**Estimation of Model Parameters**
According to Equation (2), the relationship between the observed rate, $K_o$, the mass transfer controlled rate, $k_m$, and the intrinsic kinetic controlled rate, $k_s$, can be ex-

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**Table 1. Parameter Values Used in the Mathematical Models**

<table>
<thead>
<tr>
<th>Parameter Values</th>
<th>Parameters Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_o$ 100 [ppm]</td>
<td>$\rho$ 0.992 [g/cm']</td>
</tr>
<tr>
<td>$d_p$ 0.5 [cm]</td>
<td>$\mu_B$ 0.715 [cp]</td>
</tr>
<tr>
<td>$M_B$ 18 [g/mol]</td>
<td>$\varepsilon$ 0.4</td>
</tr>
<tr>
<td>$T$ 313 [K]</td>
<td>$\phi$ 0.01</td>
</tr>
<tr>
<td>$V_A$ 97.9 [cm³/mol]</td>
<td>$\eta_B$ 2.6</td>
</tr>
</tbody>
</table>
Figure 5. The variation of mass transfer coefficient, \(k_m\), with respect to Reynolds number in the bed packed with spherical beads of 5 mm diameter.

Figure 6. The linear plot of \(1/k\alpha\) vs. \(1/K_o\) (intercept = \(1/k\alpha\), slope = \(a\)).

Table 2. The Estimated Parameter Values

<table>
<thead>
<tr>
<th>Photocatalysts</th>
<th>(k\alpha)</th>
<th>(a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO(_2) granular beads</td>
<td>0.309</td>
<td>6.23x10(^4)</td>
</tr>
<tr>
<td>TiO(_2)-coated beads</td>
<td>0.046</td>
<td>5.23x10(^4)</td>
</tr>
</tbody>
</table>

pressed as Equation (5) [10]:

\[
\frac{1}{k_{m}} = \frac{a}{K_o} - \frac{1}{k_s} \tag{5}
\]

Based on the assumption of a constant intrinsic rate coefficient, the values of \(1/k\alpha\) and \(a\) were fitted, as intercept and slope, respectively, of Equation (5) by plotting \(1/K_o\) versus \(1/k_m\) (Figure 6). The estimated parameter values are summarized in Table 2.

The variations of \(K_o\), \(k_m\), and \(k_s\) values are plotted as a function of Reynolds number in Figure 7. This figure indicates that the values of the mass transfer coefficient are ca. one-tenth of the values of the surface reaction rate values; This finding exhibits quantitatively that the overall measured rate was mainly governed by the mass transfer rate.

In this study, the values of \(a\) we obtained were in the range \(10^{4} \sim 10^{5}\). The value of \(a\) can be interpreted as the effectiveness of the photoreactor in utilizing the incident rays or the effectively illuminated surface area of the TiO\(_2\)-immobilized substrate to carry out the photocatalytic reaction. Therefore, \(a\) can be expressed as the following equation:

\[
da (cm^{2}/cm^{3}) = n \times A \times \frac{K'}{V}
\]

where, \(K' = \eta \times \Phi (0 \leq \eta \leq 1)\) [18]

where \(n\) is the number of spherical beads packed in a cylindrical reactor; \(A\) is the surface area of a spherical bead; \(V\) is the reactor volume; \(K'\) is the effective fraction of the illuminated surface area that is actively participating in the photocatalytic activity; \(\Phi\) is the quantum yield that is related to the efficiency of the catalyst to generate active radicals for degradation of molecules; \(\eta\) is the so-called effective configuration factor, which depends on the reactor geometry, catalyst type, and radiation field. Thus, the effective fraction of the illuminated surface area, \(K'\), cannot exceed the quantum yield, \(\Phi\), because the geometrical restrictions of the reactor do not allow the maximum utilization of the UV irradiation.

In the present study, the value of \(\eta\) obtained by setting \(\eta = 1.0\) (i.e., \(K' = \Phi\)) in Equation (6). Then, we used 0.01 as the value of \(\Phi\); it is the quantum yield of phenol at 400 nm
Effect of Other Factors

The photocatalytic reaction was conducted at different values of pH. The flow rate was maintained at 400 mL/min and the total solution volume was 500 mL. As shown in Figure 8, the residual concentration of phenol decreased rapidly upon lowering the solution pH. Over the range of values of pH we studied, acidic conditions were more effective at increasing the photocatalytic degradation of phenol over UV/TiO₂ packed-bed system. The trends of decreasing reaction rates with rising values of pH are probably caused by the decrease in the number of adsorption sites of phenol on the surface of the titanium dioxide [22].

It is well known that the photocatalytic degradation of phenol follows Langmuir-Hinshelwood kinetics and that the overall rate constant can be described as follows [12]:

$$K_o = \frac{k_1 k_2 C_o}{1 + k_2 C_o}$$

(7)

where $k_1$ and $k_2$ are proportionality constants for the solute and $C_o$ is the initial concentration of the reactant. According to Langmuir-Hinshelwood kinetics, the overall rate constant, $K_o$, is supposed to decrease upon increasing the initial concentration. The reaction was conducted to investigate the effect of initial concentrations on the photocatalytic degradation of phenol; We found that the degradation rate increased when the initial concentration of phenol decreased, but there was no clear difference between the reaction rates when the initial concentration was < 50 ppm.

Conclusions

The effect of mass transfer on the photocatalytic activity was investigated by varying the feed flow rates (20~500 mL/min) in a UV/TiO₂ packed-bed system. The degradation rate of phenol increased almost linearly with respect to the flow rates, reaching a plateau at 400 mL/min. Our results indicate clearly that the overall reaction rate is governed by mass transfer resistance in the external boundary layer. We have also confirmed that other factors, such as solution pH and initial concentration, exhibit a clear influence on the photocatalytic activity of UV/TiO₂ packed-bed system.

The magnitude of the value of the mass transfer coefficient was ca. one-tenth of that of the surface reaction rate. The ratio of the effective catalyst surface area to the reactor volume, $a_{exp}$ (cm²/cm³), of the current configuration was evaluated to fall in the range $10^4$~$10^5$, which implies that only a small fraction of the external surface of the photocatalysts are activated effectively by the UV irradiation source. Thus, the value of $a$
should be considered as one of the optimizing parameters for photoreactor design to improve treatment effectiveness.

**Nomenclature**

- $C_o$: Concentration in the bulk (mol/cm$^3$)
- $C_s$: Concentration in the catalyst surface (mol/cm$^3$)
- $D$: Diffusivity of solute in the aqueous phase (cm$^2$/sec)
- $D_{AB}^\prime$: Mutual diffusivity (cm$^2$/sec)
- $d_p$: Particle diameter (cm)
- $K^\prime$: Effective fraction of illuminated surface area of the photocatalysts
- $K_o$: Overall rate coefficient (hr$^{-1}$)
- $k_m$: Mass transfer coefficient (cm/sec)
- $k_s$: Surface reaction rate coefficient (cm/sec)
- $M_B$: Molecular weight of solvent
- $N_A$: Molar flux of reactant (mol/cm$^2$-sec)
- $T$: Temperature (K)
- $u_o$: Feed flow rate (mL/min)
- $V$: Volume of reactor
- $V_A$: Molar volume of solute at normal boiling point (cm$^3$/mol)
- $\exp$: Experimentally obtained values

**Greeks**

- $\alpha$: Effective catalyst surface area to reactor volume (cm$^2$/cm$^3$)
- $\epsilon$: Void fraction of the packed bed
- $\mu$: Viscosity (cp)
- $\rho$: Density of solution (g/cm$^3$)
- $\psi_B$: Association factor
- $\phi$: Quantum yield
- $\eta$: Effectiveness configuration factor of $K^\prime$

**References**

15. Patent WO97/3793 (PCT/NL&/00173)