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Effect of Diffusional Film on Formation of Hydrogen Peroxide in Photocatalytic Reactions

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We recently found that photocatalytic reactions produce H_2O_2 at a concentration level of ppm (parts per million) from water. For some reason, however, other researchers have paid little attention to the formation of H_2O_2 in this reaction. Of course, one of the reasons is due to low sensitivities of the conventional methods employed to measure the H_2O_2 concentration. However, we suppose that there is another reason which makes it difficult to measure it. To elucidate this reason, therefore, an effect of linear liquid velocity on the photocatalytic formation of H_2O_2 from water is experimentally investigated, and an explanation for the experimental result is made using a mathematical model that takes into consideration the formation and decomposition of H_2O_2 and its diffusion through a film in the neighborhood of the photocatalyst surface into a bulk liquid. This effect is also discussed on the formation of H_2O_2 from an aqueous solution of formic acid. As a result, it is concluded that the diffusion film is responsible for the reduction in the H_2O_2 concentration.

1. Introduction

A photocatalytic reaction is constituted by the formation of several kinds of radicals.[1−3,4] The mechanism of this reaction includes the formation of hydrogen peroxide, H_2O_2.[5−7] In fact, it is known that the photocatalytic reactions using TiO_2,[8,9] TiO_2−Co^{II}TSP,[9] ZnO,[8] and so forth produce H_2O_2. We also have recently found that the photocatalytic reactions using TiO_2 and Pd−TiO_2 produce H_2O_2 at a concentration level of ppm (parts per million) from water,[10] and the initial rates of formation of H_2O_2 are in proportion to the initial rates of decomposition of formaldehyde (HCHO) and formic acid (HCOOH), i.e., the photocatalytic activities. For example, Pd−TiO_2 decomposed several organic compounds and produced H_2O_2 more quickly than did TiO_2.[11] Thus, it is clear that the photocatalytic activity is closely related to the formation of H_2O_2.

For some reason, however, other researchers have paid little attention to the formation of H_2O_2 in the photocatalytic reaction. Of course, this is first due to the fact that the conventional methods employed to measure the concentration of a trace of H_2O_2 formed during the photocatalytic reaction were insensitive. Fortunately, we could successfully measure the time course of the H_2O_2 concentration by use of the enzyme *peroxidase* that catalyzes a coloring reaction.[10] On the other hand, we suppose that there is another reason which makes it difficult to measure the H_2O_2 concentration in the photocatalytic reaction.

In the present work, therefore, we first investigate experimentally an effect of linear flow velocity on the photocatalytic formation of H_2O_2 from water and then attempt to explain the experimental result using a mathematical model that takes into consideration the formation and decomposition of H_2O_2 and its diffusion through a film formed in the neighborhood of the photocatalyst surface into a bulk liquid. Similarly, a formation of H_2O_2 from an aqueous solution of HCOOH is investigated.

2. Theory

2.1. Photocatalytic Formation of H_2O_2 from H_2O. A mass-transfer limitation to the photocatalytic reaction has first been invoked experimentally by Matthews[12] and then commented by Turchi and Ollis[13] from the standpoint of photocatalytic reactor design. However, no detailed procedure for mathematical analysis is available so far.

Let us consider the following reaction that produces H_2O_2 from H_2O on the photocatalyst surface:

$$H_2O + \frac{1}{2}O_2 \xrightarrow{k_1} H_2O_2 \qquad (1)$$

Assuming that the dissolved oxygen concentration in the water is sufficiently high and kept constant because of continuous supply from the air in a batch-recirculation reactor, the rate of formation of H_2O_2 on the photocatalyst surface, $r_{H_2O_2,i}$ (mol m^{-2}-surface min^{-1}), is expressed as

$$r_{H_2O_2,i} = \frac{k_1 K_H C_{H_2O,i}}{1 + K_H C_{H_2O,i}} \qquad (2)$$

where k_1 (mol m^{-3} min^{-1}) is the kinetic constant, K_H is the adsorption equilibrium constant (mol^{-1} m^3), and $C_{H_2O,i}$ is the concentration of H_2O at the photocatalyst surface (mol m^{-3}). For convenience, we will express the concentration of a given chemical substance at the photocatalyst surface in units of moles per volume. Since the concentration of H_2O is extremely high, eq 2 is simplified to

$$r_{H_2O_2,i} \simeq k_1 \qquad (3)$$

which means that the formation of H_2O_2 proceeds with zeroth-order kinetics.

On the other hand, when conducting the photocatalytic reaction in an aqueous solution, a diffusion film is commonly formed in the neighborhood of the photocatalyst surface, as illustrated in Figure 1. Reactant molecules must diffuse through the film to the photocatalyst surface, which lowers the rate of the photocatalytic reaction. Therefore, the overall rate of the photocatalytic reaction must be described by taking into consideration the effect of film-diffusional resistance. Moreover,

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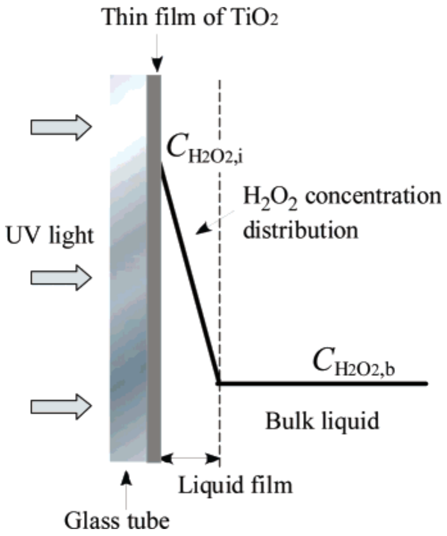

Figure 1. Distribution of hydrogen peroxide concentration in neighborhood of photocatalyst surface.

the decomposition of H_2O_2 proceeds in parallel with its formation in the very neighborhood of the photocatalyst surface where various kinds of radical species exist at high concentrations. Consequently, we simply describe the formation and decomposition of H_2O_2 as

$$H_2O + \frac{1}{2}O_2 \underset{k_2}{\overset{k_1}{\rightleftarrows}} H_2O_2 \tag{4}$$

When the system is at equilibrium, the rate of formation of H_2O_2 on the photocatalyst surface, $r_{H_2O_2,i}$ is identical to the rate of diffusion of H_2O_2 through the film, $N_{H_2O_2}$ (mol m^{-2}-surface h^{-1}), so that[14]

$$N_{H_2O_2} = k_L(C_{H_2O_2,i} - C_{H_2O_2,b}) = k_1 - k_2C_{H_2O_2,i} = r_{H_2O_2,i} \tag{5}$$

where $C_{H_2O_2,i}$ and $C_{H_2O_2,b}$ express the concentrations of H_2O_2 (mol m^{-3}) at the photocatalyst surface and in the bulk liquid, respectively, and k_L is the mass-transfer coefficient (m h^{-1}). Solving eq 5 with respect to $C_{H_2O_2,i}$ leads to

$$C_{H_2O_2,i} = \frac{C_{H_2O_2,b} + k_1/k_L}{1 + k_2/k_L} \tag{6}$$

Therefore, the rate of formation of H_2O_2 on the photocatalyst surface is described as a function of only $C_{H_2O_2,b}$ by

$$r_{H_2O_2,i} = \frac{k_1 - k_2C_{H_2O_2,b}}{1 + k_2/k_L} \tag{7}$$

Consequently, when a reaction mixture with a liquid volume of V_L (m^3) is treated by the photocatalyst with an external surface of S (m^2-surface) irradiated with UV light, the rate of photocatalytic reaction on a liquid volume basis, $r_{H_2O_2,L}$ (mol m^{-3}-liquid min^{-1}), is given as

$$r_{H_2O_2,L} = \frac{dC_{H_2O_2,b}}{dt} = (S/V_L)\frac{k_1 - k_2C_{H_2O_2,b}}{1 + k_2/k_L} \tag{8}$$

2.2. Method for Determination of Kinetic Parameters and Mass-Transfer Coefficient. Before calculating the time course of the H_2O_2 concentration in the photocatalytic reaction, it is necessary to determine the kinetic parameters and mass-transfer coefficient involved in eq 8 from the experimental data. As described later, we conducted a series of the photocatalytic reaction experiments in a batch-recirculation reactor, as described elsewhere,[10,15] where the reactant mixture was recirculated at a constant flow velocity between the annular-flow reactor and perfectly mixed flow vessel. In the following, therefore, we will describe the method for determination of kinetic parameters and mass-transfer coefficient on the assumption of using the experimental data obtained in the batch-recirculation reactions.

From eq 8, it is obvious that the initial rate of formation of H_2O_2 from H_2O is written as

$$r_{H_2O_2,L}|_{t=0} = \left.\frac{dC_{H_2O_2,b}}{dt}\right|_{t=0} = (S/V_L)\left.\frac{k_1 - k_2C_{H_2O_2,b}}{1 + k_2/k_L}\right|_{t=0} = (S/V_L)\frac{k_1}{1 + k_2/k_L} \tag{9}$$

Since the mass-transfer coefficient increases toward the infinity as the recirculation flow rate (or linear velocity) increases, eq 9 becomes

$$r_{H_2O_2,L}|_{t=0} = (S/V_L)k_1 \tag{10}$$

which indicates that the initial rates of formation of H_2O_2 measured at different linear velocities become constant at a sufficiently large linear velocity. Consequently, the value of k_1 can be determined from the measured values.

Similarly, when H_2O_2 is added to H_2O to decompose under irradiation with UV light recirculating the solution at a sufficiently high linear velocity, eq 8 gives the rate of the decomposition as

$$-r_{H_2O_2,L} = -\frac{dC_{H_2O_2,b}}{dt} = (S/V_L)(k_2C_{H_2O_2,b} - k_1) \tag{11}$$

which gives the following relationship between the initial rate of decomposition of H_2O_2 and the initial concentration of H_2O_2.

$$-r_{H_2O_2,L}|_{t=0} = -\left.\frac{dC_{H_2O_2,b}}{dt}\right|_{t=0} = (S/V_L)(k_2C_{H_2O_2,b0} - k_1) \tag{12}$$

Thus, the initial rates of photocatalytic decomposition of H_2O_2 are measured at different initial concentrations of H_2O_2, and these values and the value of k_1 already determined are applied to eq 12. As a result, the value of k_2 is obtained.

Furthermore, solving eq 9 for k_L leads to

$$k_L = \frac{r_{H_2O_2,L}|_{t=0}\,k_2}{(S/V_L)k_1 - r_{H_2O_2,L}|_{t=0}} \tag{13}$$

Therefore, the values of k_1 and k_2 determined above and the values of $r_{H_2O_2,L}|_{t=0}$ measured at different linear velocities, u_z (m h^{-1}), are applied to eq 13. The values of k_L thus calculated are plotted against their respective linear velocities. In general, the relationship between k_L and u_z is expressed as[16,17]

$$k_L = a{u_z}^b \tag{14}$$

Thus, eq 14 is applied to the plotted data in order to determine the parameter values by the least-squares method.

3. Experimental Section

3.1. Materials and Reagents. Titanium tetraisopropozide (TIP) was purchased from Katayama Chemicals Co., Ltd.

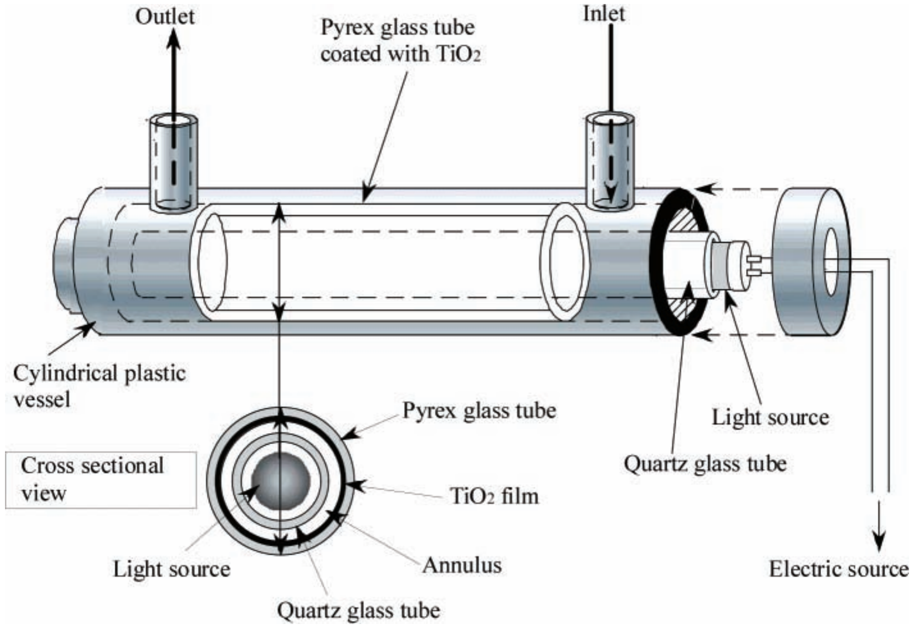

Figure 2. Annular-flow photocatalytic reactor.

(Tokyo). Isopropyl alcohol (IPA) was obtained form Wako Pure Chemical Industries Ltd. (Osaka). A 31% (v/v) aqueous H_2O_2 solution was a product of Mitsubishi Chemical Co., Ltd. (Tokyo). Glucose B test Wako (Wako Pure Chemical Industries Ltd.) was used to measure the H_2O_2 concentration. Two kinds of 6 W UV lamps were used as a light source; black light blue fluorescent lamp (FL6BL-B; Matsushita Denki, Tokyo) and germicidal lamp (GL-6; Sankyo Denki, Tokyo). The wavelength distributions of UV lights emitted from these lamps are available elsewhere.[18,19]

3.2. Operational Method of the Photocatalytic Reactor. Amorphous titanium dioxide was prepared from TIP and used to coat the surface of a glass tube according to the procedure described elsewhere.[20,21] As illustrated in Figure 2, the photocatalytic reactor has an annular structure,[21−23] consisting of a light source protected by a quartz glass tube (24 mm in outer diameter and 220 mm long) centered along the main axis of a plastic cylinder and a Pyrex glass tube (28 mm in inner diameter, 140 mm long, and 1.8 mm in thickness), whose inner surface is coated with a thin film of photocatalyst (surface area 0.0123 m^2), which is inserted and fixed so as to closely contact with the outer surface of the plastic cylinder. A reactant mixture was allowed to flow through the annulus of 2 mm in width between the quartz and Pyrex glass tubes. The inlet volume of the reactor was about 7×10^{-5} m^3.

The photocatalytic reactor was circularly connected with a mixed-flow vessel and a peristaltic pump (RP-1000; EYELA, Tokyo), as shown in Figure 3. Distilled water of 3.0×10^{-4} m^3 with or without formic acid was poured into the mixed-flow vessel and circulated at a constant flow rate. The light source was switched on to start the photocatalytic reaction and a small amount of reaction mixture was withdrawn at appropriate intervals from the mixed-flow vessel. All the experiments were conducted by placing the experimental apparatus in a constant-temperature chamber to keep the liquid temperature constant (21 °C) and to shut out all unnecessary light.

3.3. Measurement of H_2O_2 Concentration. Glucose B Test Wako (3.0×10^{-6} m^3) was added to the reaction mixture (2.0×10^{-6} m^3) withdrawn from the mixed-flow vessel to cause a coloring reaction. After 20 min, the absorbance of the solution was measured at 505 nm with a spectrophotometer (UV-240; Shimazu, Tokyo) to determine the H_2O_2 concentration.

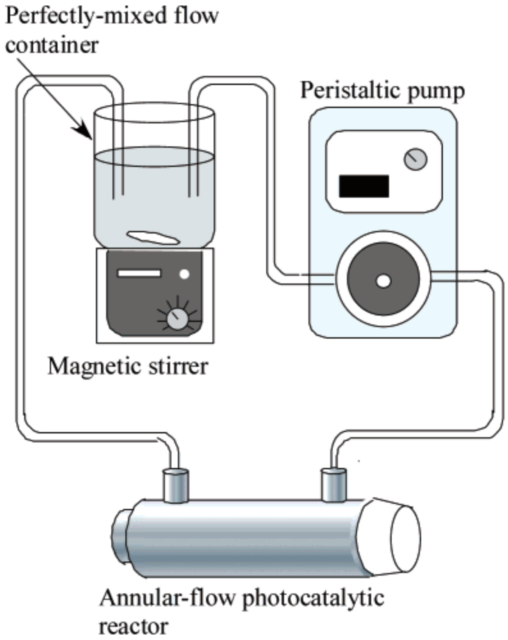

Figure 3. Batch-recirculation reactor system.

4. Results and Discussion

4.1. H_2O System. *4.1.1. Relationship between the Initial Rate of Formation of H_2O_2 and Linear Velocity.* Table 1 summarizes the kinetic scheme of the photocatalytic reaction described in a number of papers.[5−7] There exist two elementary reactions that produce H_2O_2. We experimentally elucidated that the photocatalyst can produce H_2O_2 from distilled water. However, the rate of its formation sooner or later slowed and became constant, suggesting that the decomposition of H_2O_2 takes place in parallel with its decomposition.

It is considered that this decomposition is caused by the highly active radicals formed during the photocatalytic reaction as well

TABLE 1: Formation of Radicals in a Photocatalytic Reaction

$TiO_2 \xrightarrow{h\nu} TiO_2(e^- + h^+)$	
$H_2O + h^+ \rightarrow HO\bullet + H^+$	$O_2^-\bullet + HO_2\bullet \rightarrow HO_2^- + O_2$
$OH^- + h^+ \rightarrow HO\bullet$	$HO_2\bullet + H^+ \rightarrow H_2O_2$
$O_2 + e^- \rightarrow O_2^-\bullet$	$H_2O_2 + e^- \rightarrow HO\bullet + OH^-$
$O_2^- g + H^+ \rightarrow HO_2\bullet$	$H_2O_2 + O_2^-\bullet \rightarrow HO\bullet + OH^- + O_2$
$HO_2\bullet + HO_2\bullet \rightarrow H_2O_2 + O_2$	$H_2O_2 \xrightarrow{h\nu} 2HO\bullet$
$HO\bullet + H_2O_2 \rightarrow HO_2\bullet + H_2O$	

as the UV light, which terminates increasing concentration of H_2O_2 at a certain low level. As a result, it becomes difficult to monitor the time course of the H_2O_2 concentration in the photocatalytic reaction. According to our measurement,[21] the concentration of H_2O_2 formed is on the order of 10^{-4}−10^{-3} mol m^{-3} at the maximum. We were able to accurately measure the concentration of H_2O_2 at such a low level by introducing an enzymatic method. Another advantage of using this enzymatic method is the substrate specificity of the enzyme, in which the enzyme acts on only H_2O_2. Thus, the true concentration can be measured. However, would the low sensitivities of the measurement methods be only a reason for the fact that little measurement of H_2O_2 has been done in the past photocatalytic reaction studies? A comparison shows that most of the photocatalytic reaction experiments reported by other researchers have been performed at low linear velocities compared with our experiment, so that we suppose that this experimental condition may cause a difficulty in the measurement of H_2O_2 concentration in the photocatalytic reaction. In the following, therefore, the effect of linear velocity on the photocatalytic reaction will be investigated both experimentally and theoretically.

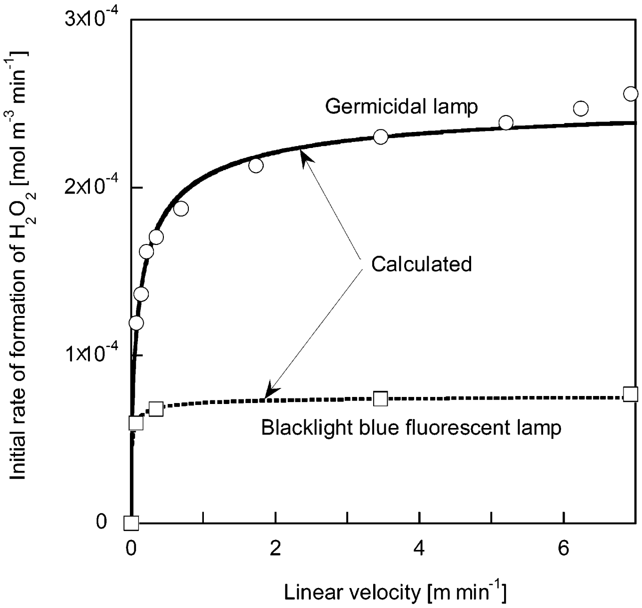

Figure 4. Effect of linear velocity on initial rate of formation of hydrogen peroxide.

Figure 4 shows the relationship between the initial rate of formation of H_2O_2 and the linear velocity when the surface of the photocatalyst immersed in the distilled water was irradiated with the UV light from a black light fluorescent lamp and germicidal lamp. The initial rate of formation of H_2O_2 initially increases linearly with the linear velocity and then plateaus. The Reynolds number [24] in the present system lies in the range of 66.7−233 for the linear velocity of 2−7 m min^{-1}, indicating that the liquid flow in the photocatalytic reactor is a laminar flow. A comparison at the same linear velocity indicates that the germicidal lamp, emitting more powerful UV light with a shorter wavelength, can produce H_2O_2 more rapidly than does the black light blue fluorescent lamp. The initial rate of formation of H_2O_2 with the black light blue fluorescent lamp plateaus in the region of lower linear velocity because of its lower rate of formation.

Since the thickness of the film formed in the very neighborhood of the photocatalyst surface decreases with the increase of the linear velocity,[17] we suppose that the film must have strongly affected the amount of H_2O_2 produced. In the following, therefore, this will be undertaken to explain using the mathematical model described above.

4.1.2. Determination of Kinetic Parameters and Mass-Transfer Coefficient. Figure 4, where the germicidal lamp was employed as a light source, clearly indicates that the initial rate of formation of H_2O_2 becomes almost constant above a certain value of linear velocity. From the initial rate of formation in this region, the value of k_1 was determined to be 6.24×10^{-6} mol m^{-2} min^{-1}. When decomposition of H_2O_2 in an aqueous solution by UV light is carried out at a sufficiently large linear velocity, the initial rate of decomposition is expressed by eq 12, which takes into consideration the decomposition of H_2O_2 in the film. Therefore, H_2O_2 at an initial concentration of 3.21×10^{-2} mol m^{-3} was decomposed using the photocatalyst irradiated with the UV light from the germicidal lamp. The result is shown in Figure 5. From these experimental data, the initial rate of decomposition, $r_{H_2O_2,L}|_{t=0}$, was determined to be 2.93×10^{-4} mol m^{-3} min^{-1}. Furthermore, this value and the value of k_1 determined above were applied to eq 12, so that k_2 was determined to be 4.17×10^{-4} mol m^{-2} min^{-1}. The values of k_1 and k_2 and the experimental data in Figure 4 were further applied to eq 13 to obtain the value of k_L for each linear velocity. The values of k_L thus determined are plotted against their respective linear velocities, as shown in Figure 6. Equation 14 was applied to the data in Figure 6 and the parameters included in the

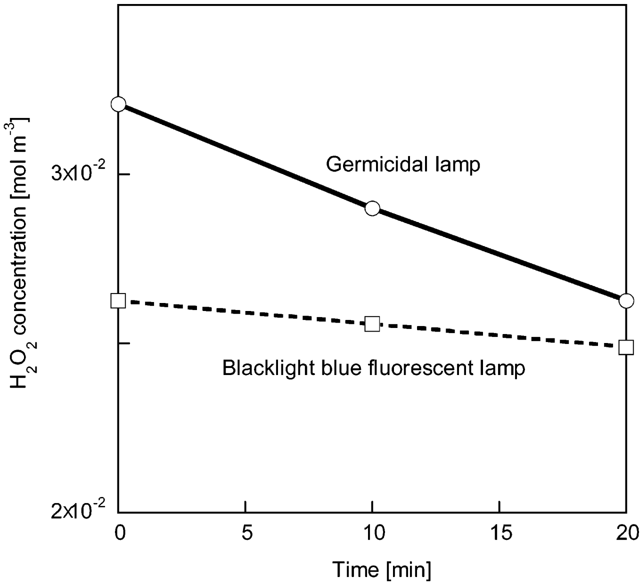

Figure 5. Time courses of hydrogen peroxide concentration in decomposition of hydrogen peroxide by UV lights.

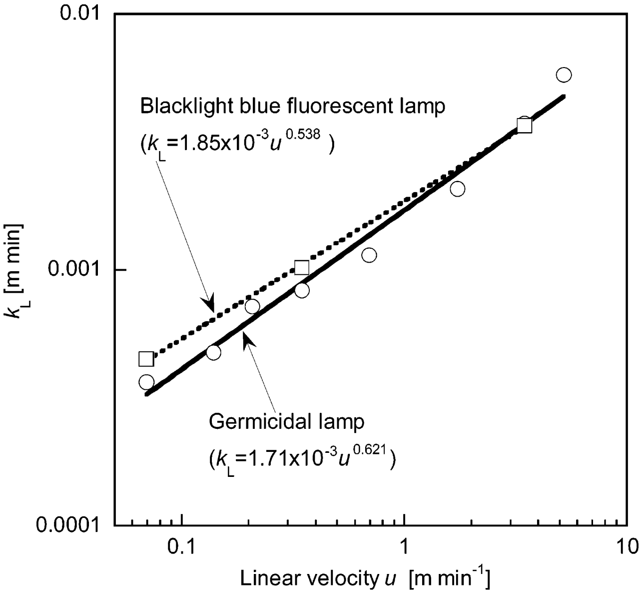

Figure 6. Effect of linear velocity on mass-transfer coefficients determined from experimental data of photocatalytic reactions.

TABLE 2: Kinetic Constants and Equations of Mass-Transfer Coefficient

	germicidal lamp	black light blue fluorescent lamp
k_1 (mol m^{-2} min^{-1})	6.24×10^{-6}	1.87×10^{-6}
k_2 (mol m^{-2} min^{-1})	4.17×10^{-4}	1.29×10^{-4}
k_L (m min^{-1})	$1.71 \times 10^{-3}\ u^{0.621}$	$1.85 \times 10^{-3}\ u^{0.538}$

equation were determined by the least-squares method. As a result, the following equation was obtained.

$$k_L = 1.71 \times 10^{-3} u^{0.621} \tag{15}$$

The same procedure was applied to the experimental data in Figure 4, where the black light blue fluorescent lamp was used as a light source, and the value of k_1 was determined to be 1.87×10^{-6} mol m^{-2} min^{-1}. From the experimental result for the decomposition of H_2O_2 at an initial concentration of 2.63×10^{-2} mol m^{-3} (Figure 5), the value of $r_{H_2O_2,L}|_{t=0}$ was determined to be 6.17×10^{-5} mol m^{-3} min^{-1}. Furthermore, this value and the value of k_1 determined above was applied to eq 12 and the value of k_2 was determined to be 1.29×10^{-4} mol m^{-2} min^{-1}. The values of k_1 and k_2 and the data in Figure 4 were further applied to eq 13 in order to determine the value of k_L for each linear velocity. The values of k_L thus determined are plotted against their respective linear velocities, as shown in Figure 6. Equation 14 was therefore applied to the data in Figure 6 and the parameters involved in the equation were determined by the least-squares method. As a result, the following equation was obtained.

$$k_L = 1.85 \times 10^{-3} u^{0.538} \tag{16}$$

The parameter values and mass-transfer coefficients for the two light sources are compared in Table 2. The kinetic constant for the formation of H_2O_2, k_1, with the germicidal lamp is 3.3 times larger than that with the black light blue fluorescent lamp. Similarly, the kinetic constant for the decomposition of H_2O_2, k_2, with the germicidal lamp is 3.2 times larger than that with the black light blue fluorescent lamp. In eq 8, the denominator on the right-hand side can be approximately written as $1 + k_2/k_L \simeq 1$, and therefore, the apparent rate of formation of H_2O_2 on the photocatalyst irradiated with the UV light from the germicidal lamp is three times larger throughout the whole reaction time. It should be noted that the parameter values in the equations of mass-transfer coefficient for the germicidal lamp and black light blue fluorescent lamp are almost the same. This result is reasonable because the same reactor with either black light blue fluorescent lamp or germicidal lamp was used to carry out the photocatalytic reactions under the same liquid flow condition so that the mass-transfer coefficients must be fundamentally the same.

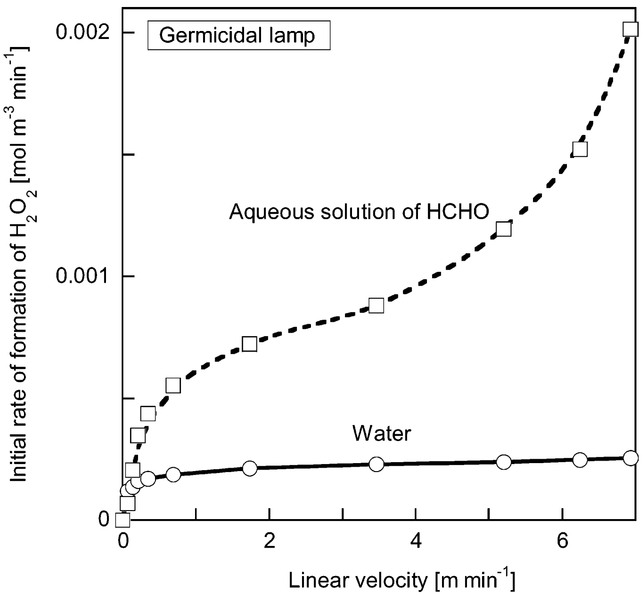

Figure 7. Comparison between initial rates of formation of hydrogen peroxide from water and an aqueous solution of formic acid (light source: germicidal lamp).

4.1.3. Comparison of the Calculated Results. The kinetic parameters and mass-transfer coefficients determined above were applied to eq 9 in order to determine the relationship between the kinetic parameters and mass-transfer coefficients. The calculated results for the germicidal lamp and black light blue fluorescent lamp are shown by solid and broken lines, respectively, in Figure 4. The calculated lines are in good agreement with their respective experimental values, indicating that there is a close relationship between the film formed in the neighborhood of the photocatalyst surface and the observed result that the initial rate of formation of H_2O_2 initially increases with the linear velocity and then plateaus.

4.2. Formic Acid−H_2O System. In a previous paper,[21] we have revealed that H_2O_2 is also formed in the process of the photocatalytic decomposition of formic acid. Therefore, the H_2O_2 concentration becomes higher in the photocatalytic treatment of H_2O containing formic acid than in the photocatalytic treatment of H_2O alone. Figures 7 and 8 show the relationships between the initial rate of formation of H_2O_2 and the linear velocity when H_2O containing formic acid at an initial concentration of 0.45 mol m^{-3} was photocatalytically treated using the germicidal lamp and black light blue fluorescent lamp, respectively. For comparison, each figure also includes the initial rate of formation of H_2O_2 in the photocatalytic treatment of H_2O alone. It is clear that despite the kind of the light source, the initial rate of formation is remarkably increased in the presence of formic acid. This is explained as follows. The intermediate product HCOOH is known to be a scavenger of the hole h^+ in the recombination reaction described as $h^+ + e^- \rightarrow$ heat and causes the competitive reaction described as $h^+ + HCOO^- \rightarrow HCOO^\bullet$, leading to the formation of a larger amount of H_2O_2

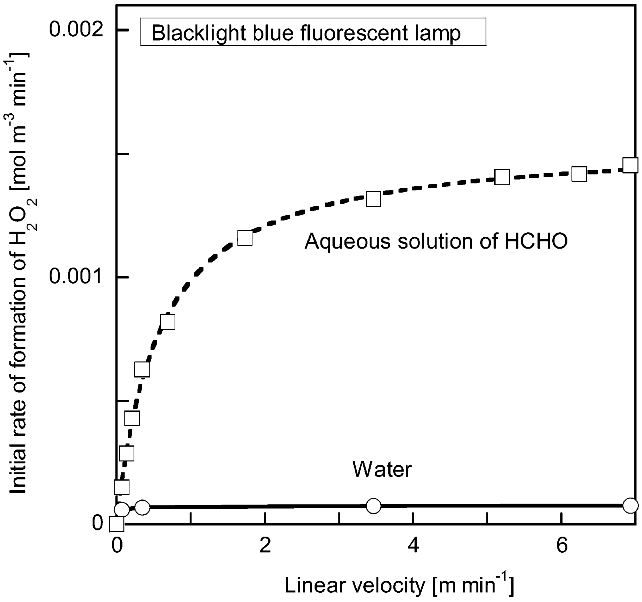

Figure 8. Comparison between initial rates of formation of hydrogen peroxide from water and an aqueous solution of formic acid (light source: black light blue fluorescent lamp).

according to the subsequent reactions described as $e^- + O_2 \rightarrow O_2^{-\bullet} \rightarrow \cdots\cdot \rightarrow H_2O_2$.

Interestingly, the initial rate of formation of H_2O_2 for the germicidal lamp is lower than that for the black light blue fluorescent lamp in the region of low linear velocity, rapidly increasing with the increase of linear velocity and finally becoming higher. Considering the fact that the germicidal lamp emits more powerful UV light than does the black light blue fluorescent lamp, the experimental result is evidently contradictory. This can be explained as follows. When the linear velocity is low and the film is relatively thick, the H_2O_2 produced on the photocatalyst surface must move slowly by diffusion through the film to the bulk liquid. As a result, H_2O_2 is exposed for a longer time to a highly reactive circumstance in the film, crowded by a larger amount of radicals produced under irradiation with the UV light from the germicidal lamp, and the majority of H_2O_2 is quickly decomposed in the film. In the region of high linear velocity, however, the thickness of the film is thin and the H_2O_2 produced can quickly move out of the film or is withdrawn from the film into the bulk liquid by the recirculation flow passing through the neighborhood of the photocatalyst surface, thereby increasing the H_2O_2 concentration in the bulk liquid. Even when the film becomes very thin due to a higher linear liquid velocity and the system is reaction-controlled, H_2O_2 is decomposed by the radicals that are continuously produced on the photocatalyst surface and by the UV light in the bulk liquid. Consequently, the H_2O_2 concentration in the bulk liquid takes a constant value at a point where the rate of formation of H_2O_2 is equal to the rate of decomposition of H_2O_2.

5. Conclusion

In the present work, we investigated the relationship between the rate of formation of H_2O_2 and the recirculation flow rate (linear velocity) in the photocatalytic reaction using a batch recirculation reactor to elucidate the effect of film formed in the neighborhood of the photocatalyst on the photocatalytic reaction. As a result, we obtained the following conclusions.

(1) The rate of formation of H_2O_2 in the photocatalytic reaction apparently increases with the increase of the linear velocity.

(2) This is probably because the thickness of the film becomes thin with the increase of the linear velocity and the H_2O_2 formed on the photocatalyst surface can easily move through the film to the bulk liquid.

(3) This phenomenon can successfully be explained by using a mathematical model for the overall photocatalytic reaction that takes into consideration the diffusion of H_2O_2 through the film.

(4) One of the reasons other researchers could not detect H_2O_2 in the photocatalytic reaction is that the reaction experiments were performed under the conditions where H_2O_2 formed on the photocatalyst was so quickly decomposed in the film that the H_2O_2 concentration in the bulk liquid did not become high.

(5) As a result, it is concluded that a diffusion film formed in the neighborhood of the photocatalyst surface is responsible for a reduction in the H_2O_2 concentration.

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