Photocatalytic degradation of Acid Red 4 using a titanium dioxide membrane supported on a porous ceramic tube

Wen-Yu Wang\textsuperscript{a}, Agus Irawan\textsuperscript{b}, Young Ku\textsuperscript{b, c,}* \\
\textsuperscript{a}Department of Environmental Engineering and Management, Chaoyang University of Technology, 168 Jifong E. Road, Wufong Township, Taichung County, Taiwan \\
\textsuperscript{b}Department of Chemical Engineering, National Taiwan University of Science and Technology, 43 Keelung Road, Section 4, Taipei 106, Taiwan

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\textbf{a b s t r a c t}

A photocatalytic membrane supported on a porous ceramic tube was described, in which permeation of solutes through the membrane and tube and photocatalytic reaction occur simultaneously. In this photocatalytic membrane reactor, TiO\textsubscript{2} catalyst was coated on the surface of a porous ceramic tube and all experiments were conducted in one pass dead-end system. The objectives of this study are to demonstrate the predominance of dead-end operation and to determine the reaction kinetics model of the photocatalytic reaction. Acid Red 4 (AR 4) dye was used as a model pollutant. A detailed study of physical parameters including flow configurations (dead-end and cross-flow), flow rate, initial dye concentration, light intensity and catalyst loading has been performed to obtain the reaction kinetics. The simultaneous effect of light intensity and catalyst loading was also determined experimentally. Experiments were also conducted to compare the photocatalytic degradation of AR 4 in the dead-end and cross-flow system. 

The major findings of this study are: (1) the decomposition ratios for dead-end system were three and five times higher than cross-flow system at flow rates of 6.67 \texttimes 10^{-4} and 4.00 \texttimes 10^{-4} m^3/s, respectively. (2) The decomposition ratio increased with increasing catalyst loading and light intensity, but remained constant at higher catalyst loading. (3) The decomposition ratio was found to be decreased with increasing flow rate.

1. \textbf{Introduction}

In the past decade, considerable attention has been focused on using nanocrystalline TiO\textsubscript{2} as a photocatalyst for the degradation of organic pollutants (Blake, 2001). The photocatalyst titanium dioxide is a wide bandgap (3.2 eV) semiconductor, corresponding to radiation in the near-UV range. An electron-hole pair formation occurs within the conduction and valence bands of TiO\textsubscript{2} after the absorption of UV radiation. The positive hole is apparently able to oxidize a water molecule to hydroxyl radical (Fujishima and Honda, 1972). The hydroxyl radical, in turn, is a powerful oxidant. The oxidation of organic contaminants seems to be mediated by a series of reactions initiated by hydroxyl radical on the TiO\textsubscript{2} surface. However, recombination of the separated electron and hole can occur either in the volume or on the surface of the semiconductor particle accompanied with heat releasing (Linsebigler et al., 1995). For the photooxidation reaction to occur, both TiO\textsubscript{2} and an UV light source are necessary.

The semiconductor catalyst can be employed as in the form of colloid or as an immobilized film. The types of photoreactors include slurry reactor (Puma and Yue, 2001),
immobilized reactor system (Fabiyi and Skelton, 2000; Noorjahani et al., 2004; Gao and Liu, 2005; Kanki et al., 2005; Lee et al., 2004; Li et al., 2005), fixed/fluidized bed reactor (Sengupta et al., 2001), fiber reactor (Lin and Valsaraj, 2005) and some other designs such as spinning disc reactor (Yatmaz et al., 2001) or multiple tube reactors (Ray, 1999).

In photoreactors operated with slurry system, the reaction rate is predominantly determined by the light intensity, the quantum efficiency of the catalyst and the adsorption properties of both the reacting and non-reacting components in solution. However, this slurry system generates other problems such as the requirement of the separation and recycling of the ultra fine catalyst from the treated liquid and therefore can be an inconvenient, time consuming expensive process. In addition, the depth of UV light penetration is limited because of strong absorptions by both catalyst and dissolved organic species. The above problems could be avoided in photoreactors if the catalyst particles are immobilized, but immobilization of a semiconductor on a support generates another unique problem. The reaction which occurs at the interface of liquid–solid and mass transfer from the bulk liquid to the catalyst surface will play an important role in determining the overall rate (Ray, 1998).

This study was to utilize porous TiO₂ membranes in which the titanium dioxide itself is immobilized in the form of a porous membrane which is capable of a photocatalytic reaction. The major objectives of this study are to demonstrate the predominance of dead-end operation in the permeable photocatalytic reactor and to determine the reaction kinetics model of the photocatalytic reaction. It is proposed that the oxidation reaction occurs both on the surface and inside the porous TiO₂ membranes in the dead-end operation. Two different flow configurations in the permeable photocatalytic reactor were illustrated in Fig. 1(a) and (b), and described in Section 2.

2. Experimental

The solutions used in experiments were prepared from certified reagent grade chemicals with double distilled water. The chemical structure of Acid Red 4 (AR 4, Acros) was presented in Fig. 2. AR 4 is an anionic dye and its pKₐ is 6.5 (Ku et al., 2005). The concentrations of AR 4 were determined by a Shimadzu UV-160A spectrophotometer. Degussa P-25 was used as a photocatalyst and coated on the inner surface of a porous ceramic membrane (20.0 mm inside diameter, 29.5 mm outside diameter, 146.0 mm length and 0.1–1.0 mm pore size). A mixture containing 10 wt% of catalyst was prepared by dissolving 100 g of P-25 powder catalyst into 900 g of pure water and then followed by the addition of 0.02 g of dioctyl sulfo succinate into the mixture as a dispersant. This suspension was then stirred with a magnetic stirrer for 12 h followed by ultrasonication in ultrasonic bath to obtain a milky solution that can be kept stable for weeks.

After TiO₂ catalyst was prepared, the next step is to coat the ceramic tube with TiO₂ catalyst with following procedure. The outside surface of ceramic tube was first covered with Parafilm since only the inner surface of ceramic tube was needed to be coated with TiO₂ catalyst. The ceramic tube was then coated with catalyst by the dip-coating technique. The catalyst coating was dried in room temperature for about 15 min and then above procedure was repeated several times depending on the desired mass of coated catalyst. Finally, the coated ceramic membrane tube was calcined in a furnace by raising the temperature gradually in two stages. The first stage is to raise the temperature gradually from room temperature at a rate of 1 C/min to 150 C and held there for 3 h. The second stage is to raise the temperature from 150 C to 500 C and held there for 5 h with the same rate of 1 C/min. After that, the coated ceramic membrane was flushed about 30 min with water by letting the water to penetrate through the ceramic membrane. The total mass of catalyst deposited was determined by weighing the ceramic tube before catalyst coating and after the ceramic membrane was calcined in furnace.

As illustrated in Fig. 1(a) and (b), the photocatalytic membrane reactor consisted of a fixture made entirely of stainless steel. A bundle (one to three lamps) of blacklight cathode lamps (UV-A, peak wavelength 365 nm) were shielded by a quartz tube (12.0 mm outer diameter and 10.0 mm inner diameter) and placed in the center of the porous ceramic tube along the coaxial direction. The UV light intensity was measured by an International Light’s IL1400 digital

![Fig. 1 – Feeding modes used in photocatalytic membrane (a) cross-flow and (b) dead-end system.](image-url)
pass cross-flow operation, dye solution flowed tangentially and no dye solution permeated through the catalyst membrane and ceramic tube. In one pass dead-end operation, dye solution fully permeated through the catalyst membrane and ceramic tube while without any retentate. Furthermore, there was not any observable flux decline in all experiments.

The experimental procedures to study the kinetic degradation of AR 4 were as follows. The feed solution was agitated using a magnetic stirrer at a speed of about 250 rpm and was then pressurized using a gear pump into the membrane reactor system while the temperature of the feed solution was kept at 25 °C using a water bath. The dye solution was then collected in a reservoir tank. For all experiments, samples were taken after 45 min (time needed for the system to reach stable condition). These aliquots of solution were then sampled periodically for analysis purpose by using UV spectrophotometer. The same procedures were carried out for different initial feed concentrations (0.013, 0.026 and 0.052 mol/m$^3$), different flow rates (6.67 $10^{-8}$, 1.33 $10^{-7}$, 2.67 $10^{-7}$ and 4.00 $10^{-7}$ m$^3$/s), different catalyst loadings (0.03, 0.13, 0.29 and 0.44 g) and also different light intensities (1.1, 4.0 and 6.0 mW/cm$^2$).

From preliminary experiments, it was found that the flow rate of dye solution was not affected by both solution pH and dye concentrations. While, from dark adsorption experiments (in the presence of TiO$_2$ and in the absence of UV light), it was found that AR 4 was weakly adsorbed on the surface of TiO$_2$, which is about 3% adsorption after 6 h. When the direct photolysis experiment (in the presence of UV light and in the absence of TiO$_2$) was conducted, the result showed that almost no photodegradation was happened, which is about 2% degradation after 6 h. Both dark adsorption and photolysis experiments indicated that significance photodegradation of AR 4 was only happened in the presence of both UV light and TiO$_2$ catalyst. It was also found that the catalyst membrane and the ceramic tube were fully permeable to the dye molecules. There was not any observable flux decline in all experiments. In the absence of UV light, the concentration of dye solution in the inner side of the reactor tube was the same as that in the outer side. Preliminary experiments’ results also showed the optimum pH for photocatalytic reaction was 5, and therefore all experimental results presented in Section 3 were carried out in pH 5.

3. Results and discussion

The effects of operational parameters such as flow configuration (dead-end and cross-flow), light intensity and catalyst loading were examined using the reaction set and followed the procedures described above.

3.1. Comparison between dead-end and cross-flow

One of the purposes of this study is to compare the performance for photocatalytic degradation of organic pollutant in a dead-end system or cross-flow system. In cross-flow system (Fig. 3(a)) the solution is allowed to flow only on the surface of catalyst layer, while in dead-end system (Fig. 3(b)) the solution is flowing through the catalyst layer. Both cross-flow and

![Diagram of reactor configurations](image-url)
dead-end systems were conducted at the same circulation flow rates (same residence time in the reactor) of $6.67 \times 10^{-8}$, $1.33 \times 10^{-7}$, $2.67 \times 10^{-7}$ and $4.00 \times 10^{-7}$ m$^3$/s while the initial dye concentration was $0.026$ mol/m$^3$.

Fig. 4 shows that for dead-end system the decomposition ratio is 3–5 times higher than for cross-flow system at the same residence time. It was also observed that for dead-end system, the decomposition ratio decreases rapidly with increasing flow rate rather than for cross-flow system.

In dead-end system, the pollutant transported from the bulk solution through a boundary layer (liquid-film mass transfer resistance), outer catalyst layer and finally reaches the inner layer of catalyst bed. At the same time, UV light first reaches the outer layer and then penetrates into the depth of catalyst layer, independence of flow system whether it is dead-end or cross-flow. UV light not only illuminates the outer surface of catalyst but also can penetrate deep in the catalyst layer. In dead-end system, the pollutant will be transported through the catalyst layer to locate the active sites not only at the outer layer but also the active sites at the inner layer of catalyst. While in cross-flow system the pollutant can only contact with catalyst located at the outer surface but it cannot contact active sites in the inner layer. Therefore the decomposition ratio of AR 4 observed in dead-end system was higher than cross-flow system.

Low decomposition ratio in cross-flow system is probably influenced by different factors: (1) there is no mechanical mixing applied inside the reactor, (2) the catalyst is immobilized only on the inner surface of ceramic tube, therefore not all of the reactant can contact with the catalyst (stagnant region/dead zone is encountered), (3) the flow rates studied in this system are within the laminar region therefore there is no turbulence mixing happened inside the reactor, (4) a combination of all of the above. For dead-end flow system, although there is no mechanical mixing and flow rates are in the laminar region but all of the solution is forced to flow through the catalyst layer therefore it can further minimize the presence of stagnant region (dead zone).

A proposed photocatalytic reaction model by Tsuru et al. (2003) is also found to be consistent with the present system. They proposed that the oxidation reaction occurs both on the surface and inside the porous TiO$_2$ membranes. The advantages of this system are (1) the forced transport of reactants by convection into the TiO$_2$ membranes, (2) the oxidation reaction which occurs on the outer and inner layer of the TiO$_2$ membranes where high concentrations of OH radicals would be expected, and (3) the potential for obtaining a permeate stream oxidized with OH radicals after permeation through the TiO$_2$ membranes.

The benefits of the photocatalytic reactor using a titanium dioxide membrane supported on a porous ceramic tube in a dead-end system are: (1) no requirement of the separation and recycling of ultra fine catalyst from the treated solution, (2) higher photocatalytic degradation rate than non-permeable thin film fixed bed photocatalytic reactor system.

3.2. Effect of light intensity

It is obvious that light intensity has great effect on photocatalytic reaction rate. The reaction rate constant usually follows power-law dependence on light intensities. It has been found that the reaction rate constant is proportional to the square root of the light intensity at high intensity, while at a sufficiently low intensity the reaction rate constant follows first-order dependence (Zhou and Ray, 2003).

In order to investigate the relationship between the reaction rate and light intensity, and also to determine the intrinsic kinetic rate constant, a series of experiments have been conducted at different light intensities and initial dye concentrations. The experiments were conducted in a one pass dead-end system with light intensities of 1.1, 4.0 and 6.0 mW/cm$^2$ while initial dye concentrations are 0.013, 0.026 and 0.052 mol/m$^3$.

The combined effect of the initial dye concentration and light intensity on the photocatalytic degradation rate is shown in Fig. 5. This figure shows that the decomposition ratio increases sharply initially with an increase of the light intensity, and then the rise becomes less gradual at light intensity of 6.0 mW/cm$^2$. Decomposition ratio is defined as 1 minus the ratio of the permeate concentration to the feed concentration or $1 - \frac{C_p}{C_{t,0}}$. It also can be seen from this figure that the decomposition ratio decreases with the increase of initial pollutant concentration as commonly happened in photocatalytic reaction.

The rate equation for photodegradation of AR 4 is proposed as follows:

$$\frac{dC_a}{dt} = k_0 C_a$$

(1)

where $n$ is kinetic order with respect to dye concentration and $k_0$ is global rate constant which is a function of catalyst loading ($W$) and light intensity ($I_0$) as follows:

\[ k_0 = \frac{1.1 \times 10^{-4}}{W} \times \frac{1}{100} \times \frac{1}{I_0} \]
which with values then intensity calculated reactor A0 integrated intensity parameter where the system.

Fig. 5 – Effect of light intensity and initial concentration on the decomposition ratio of AR 4 for one pass dead-end system.

\[ k_0 = \frac{k_w t^n}{1 \cdot \rho \cdot a \cdot W} \]  

(2)

where \( k_w \) is the intrinsic rate constant and \( a \) and \( b \) are kinetic parameters with respect to catalyst loading and incident light intensity, respectively. If the kinetic order \( n \) was not equal to one (indicating not first-order process), then Eq. (1) can be integrated and gives:

\[ k_0 \cdot t^{\frac{1}{n}} = k_\text{f0} \cdot \ln \left( \frac{C_i}{C} \right) \]  

(3)

Here \( t \) is residence time in the reactor calculated by dividing reactor volume with flow rate. The global rate constants were calculated by first assuming that the kinetic order is equal to one with respect to \( C_0 \). The calculation result showed that the values of global rate constants increase with increasing light intensity and initial concentration. Since the global rate constants should not be affected by initial dye concentration, then the kinetic order \( n \) might not equal to one, therefore the values of \( k_0 \) were then recalculated for kinetic order not equal to one. The value of \( n \) for each light intensity was calculated by trial and error method until the global rate constants give constant value for whole range of initial dye concentration studied. The calculation by trial and error method gave \( n = 0.3 \) for the whole range of light intensities studied and the result is shown in Fig. 6.

Fig. 6 clearly shows that the global rate constants increase with the increase of light intensities. The kinetic parameter with respect to incident light intensity \( b \) is found equal to 0.5 which is obtained by fitting the obtained experimental results with rate equation proposed in Eqs. (1) and (2) by first taking natural logarithmic on both sides as shown in Eq. (4) below.

\[ \ln(k_0 \cdot t^{\frac{1}{n}}) = \ln \left( \frac{k_w}{1 \cdot \rho \cdot a \cdot W} \right) + b \cdot \ln I_o \]  

(4)

Mehrotra et al. (2005) in their study also concludes that at low light intensities (catalyst dependent, surface reaction limited) the rate is linearly proportional to the light intensity, while at medium–high values, the rate becomes proportional to the square root of the light intensity and at higher values, the rate would not be affected by the increase of the light intensity (zero order). The transition points between these regimes, however, will vary depending on the system. At lower illumination intensities, the photon flux is insufficient to excite all of the available active TiO₂ sites on the surface of ceramic membrane. Hence, too few electron-hole pairs are generated to degrade all of the dye adsorbed on the active catalyst surface. An increase in the light intensity leads to more excitation and more electron-hole pair generation (Choi et al., 2000), along with the corresponding increase in OH species creation and in the dye degradation rate. However, as the light intensity increases, it should enhance the recombination processes (second-order) faster than oxidation processes (first-order in excited oxidant), regardless of the photochemistry involved (Oliss et al., 1991). Under these conditions, the degradation rate becomes independent of light intensity, and both reaction rate and rate constant reach a constant value.

3.3. Effect of catalyst loading

Different amounts of TiO₂ were coated on the inner surface of the ceramic membrane to determine the effect of increased
catalyst loading. The experiments were conducted in one pass dead-end system at various amounts of TiO$_2$ of 0.03, 0.13, 0.29 and 0.44 g, while initial dye concentrations used were 0.013, 0.026 and 0.052 mol/m$^3$.

Fig. 7 showed that for whole range of initial dye concentrations studied, the decomposition ratio increased with the catalyst loading until a saturation value was reached at 0.29 g of TiO$_2$. The global rate constants were then calculated by using the same equation as was shown in Eq. (3) and the results were presented in Fig. 8 as a function of catalyst loading.

The value of n for each catalyst loading are again calculated by trial and error method until the global rate constants give constant value for whole range of initial dye concentration studied. The calculation by trial and error method also gives n = 0.3 for the whole range of catalyst loading studied. The obtained experimental results were then fitted with rate equation proposed in Eq. (2) by first taking its reciprocal as shown in Eq. (5) below.

$$\frac{1}{k_0} = \frac{1}{k_e} + \frac{1}{W} \frac{a}{k_n}$$

The calculated result from Eq. (5) gives 18.1/g for the value of a, while the value of k$_n$ is found to be 0.0024. Therefore, rate equation as shown in Eq. (1) for degradation of AR 4 can be written as follows:

$$r_A = \frac{0.0024W^{0.5}}{1 + 18.1W} C_A^{0.3}$$

(6)

The catalyst layer thickness (amount of catalyst) is one of the important parameters in photocatalytic degradation. As in slurry system, there also exists an optimal catalyst dosage for fixed catalyst system. This is due to the increase of internal (inter-particle agglomeration) mass transfer resistance and light shielding effect, which can further result in the decrease of overall reaction rate at very high catalyst loading (Mehrotra et al., 2005). Subsequently, Chen et al. (2000) reported detailed analysis of the effect of mass transfer and catalyst layer thickness on photocatalytic degradation rate.

When the TiO$_2$ loading increases, the decomposition ratio increases because the surface area available for reaction also increases. On the other hand, as the catalyst loading increases, the thickness of the film increases, and further decreases the transparency of the film. When the film thickness increases, it will increase the surface area available for the reaction, but since the photon flux remains the same, therefore the available electron-hole will decrease. These factors are the reasons for the observed saturation value where no further increase in decomposition ratio is observed at higher catalyst loading.

It can be seen from Fig. 8 that the global rate constants increase as the catalyst loading increase until reaching some constant value at higher catalyst loading. This could be happened mainly because the light cannot penetrate deep into the catalyst layer and cannot activate the whole inner surfaces, but only can penetrate into certain depth. Therefore any additional catalyst only slightly improves both the decomposition ratio and global rate constants.

3.4. Combined effect of light intensity and catalyst loading

In order to check whether rate equation shown in Eq. (6) has a good agreement with experimental results, the experiments
were again conducted at different light intensity and catalyst loading. Experiments have been done in one pass dead-end system when the catalyst loading was varied between 0.03 and 0.44 g while the range of light intensity used was between 1.1 and 6.0 mW/cm². The results are shown in Fig. 9 as a function of catalyst loading (W). Fig. 9 clearly shows that at any particular light intensity the decomposition ratio is almost constant when the catalyst loading is greater than 0.29 g.

The global rate constants calculated from the experiment are shown in Fig. 10 and marked as symbols while the value of global rate constants calculated from rate Eq. (2) with kinetic parameters shown in Eq. (6) is marked as solid lines.

Fig. 9 shows that decomposition ratio goes through a saturation value at an optimum catalyst loading (0.29 g) irrespective of incident light intensity. In immobilized catalyst system, the pollutant is transported from the bulk solution through a boundary layer (liquid-film mass transfer resistance) to reach the liquid–catalyst interface. The reactant will then diffuse through the catalyst layer to locate active sites where they get adsorbed and react. At the same time, UV light must also reach the catalyst surface to activate the catalyst. The decomposition ratio increases as the light intensity increases due to more available catalyst surface sites since higher light intensity causes the light to penetrate deeper into the catalyst layer.

Fig. 10 reveals that the global rate constants increase as the catalyst loading and light intensity increase. Within the bulk of the catalyst film, the extinction of light follows the exponential decay (Chen et al., 2000). Fig. 10 indicates that the rate constant reaches a saturation value at 0.29 g as the catalyst layer thickness increases. This can be understood because when the catalyst film is thin, the light could penetrate into the deepest layer, and consequently, the catalyst layer can be active to its highest possible level. As the film thickness increases, at some point the penetration depth of light will be limited to certain depth only and the photocatalytic decomposition ratio tends to remain constant at this point. With further increase in the film thickness (thicker film), the light cannot penetrate into deeper layer, and consequently, some part of TiO₂ catalyst cannot be activated. Therefore, a further increase of film thickness may not increase the photocatalytic reaction rate. It is also shown that rate equation proposed in Eq. (6) has a good agreement with experimental result as indicated in Fig. 10.

4. Conclusion

Photocatalytic degradation of Acid Red 4 (AR 4) dye solution has been studied in a photocatalytic membrane reactor system where Degussa P-25 catalyst was immobilized on the surface of ceramic filter tube. The decomposition ratio and rate constant of AR 4 increase with increasing light intensity where the kinetic order with respect to light intensity was found to be 0.5. The decomposition ratio went through a saturation value at catalyst loading of 0.29 g. The global rate constant was found to increase with increasing catalyst loading and a rate equation has been proposed to describe the photodegradation of AR 4. The combined effect of the catalyst loading and light intensity on the photocatalytic degradation of AR 4 showed that both decomposition ratio and global rate constant increase with increasing light intensity and catalyst
loading. The rate equation proposed was in a good agreement with the experimental results. The effect of the flow rate on the photocatalytic degradation in one pass dead-end system showed that the decomposition ratio decreases as the flow rate increases. The permeate concentrations coming out from the reactor at varying flow rates were successfully correlated by the photocatalytic model developed in this study. It was also found that degradation rate of AR 4 was higher in the dead-end system rather than in cross-flow system.

references


