

Photocatalytic decolorization of azo-dye with zinc oxide powder in an external UV light irradiation slurry photoreactor

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Abstract

Photocatalytic decolorization of azo-dye Orange II in water has been examined in an external UV light irradiation slurry photoreactor using zinc oxide (ZnO) as a semiconductor photocatalyst. The effects of process parameters such as light intensity, initial dye concentration, photocatalyst loading and initial solution pH on the decolorization rate of Orange II have been systematically investigated. A two-stage photocatalytic decolorization of Orange II, the first stage of fast decolorization rate and the subsequent second stage of rather slow decolorization rate, was found. The efficiency of decolorization of Orange II increased as initial Orange II concentration decreased and UV light intensity increased. There was the optimal ZnO concentration being around 1000 mg L⁻¹. The optimal pH was around 7.7, which was at the natural pH of the dye solution. The effect of aeration rate on the decolorization of Orange II has been also investigated and the enhancement of decolorization of Orange II with increasing aeration rate was found. By using a model for the light intensity profile in the external UV light irradiation slurry photoreactor, the simulation model for the decolorization of Orange II with ZnO photocatalyst has been developed. The proposed model in which the slow decolorization in the second stage as well as the initial fast decolorization is also taken into account could simulate the experimental results for UV light irradiation satisfactorily. The proposed simulation model in which the change of light intensity with time due to the decolorization of Orange II and the light scatter due to solid photocatalysts are considered will be very useful for practical engineering design of the slurry photoreactor of wastewater including textile dyes.

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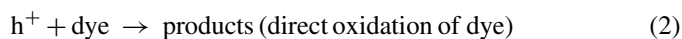
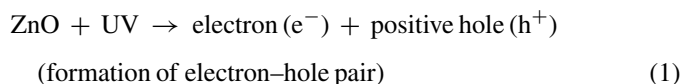
Keywords: Photocatalytic decolorization; Zinc oxide; Azo-dye; External light irradiation; Slurry reactor

1. Introduction

Photocatalytic degradation processes have been widely applied as techniques of destruction of organic pollutants in wastewater and effluents [1,2]. With an appropriate light irradiation, the photocatalyst generates electron/hole pairs with free electrons produced in the empty conduction band leaving positive holes in the valence band. These electron/hole pairs are capable of initiating a series of chemical reactions that eventually mineralize the pollutants. Metal chalcogenide semiconductors such as TiO₂, ZnO, SnO₂, WO₃ and CdS have been attempted for the photocatalytic degradation of a wide variety of environmental contaminants [1]. Titanium dioxide (TiO₂) has been extensively investigated as one of the most active semiconductor

photocatalysts. It has been known that ZnO is a suitable alternative to TiO₂ so far as band gap energy is concerned and in fact higher photocatalytic efficiency compared with TiO₂ have been reported for ZnO [3–5]. Therefore, ZnO powders have recently received much attention and have been well studied.

Degradation may take place either through electron extraction from organic pollutants by the holes of excited ZnO or hydroxide radical mediated decomposition of organic pollutants. When ZnO absorbs a photon of energy equal to or greater than its band gap width (3.2 eV), an electron may be promoted from the valence band to the conduction band leaving behind an electron vacancy or hole in the valence band [1,2,6,7].

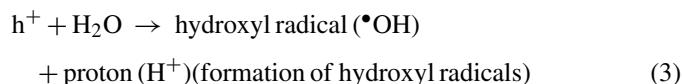


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Nomenclature

a, b, c, d	constants in Eq. (10)
A	cross-sectional area of photoreactor (m^2)
c_z	concentration of ZnO (mg L^{-1} or g L^{-1})
C_S	concentration of Orange II in solution (mg L^{-1} or g L^{-1})
C_{S_0}	initial concentration of Orange II in solution (mg L^{-1} or g L^{-1})
D_I	impeller diameter (m)
I_0	UV light intensity at the photoreactor wall (W m^{-2})
I_{av}	average UV light intensity (W m^{-2})
I_{av_0}	initial average UV light intensity (W m^{-2})
$I(r, \theta)$	local UV light intensity (W m^{-2})
k	pseudo-first-order reaction rate constant (min^{-1})
K	constant in Eq. (10)
l	light path length given by Eq. (13) (m)
N	impeller speed (min^{-1})
Q_g	volumetric gas flow rate (L min^{-1})
r	cylindrical radial coordinate (m)
r_0	distance between light source and external photoreactor surface shown in Fig. 1 (m)
r_1	distance between light source and photoreactor wall (m)
R	radius of photoreactor (m)
s	area (m^2)
S_L	light intensity at light source per unit length (W m^{-1})
t	time (min)
T	light permeation ratio
T_o	light permeation ratio due to absorbance of light by color of Orange II
T_z	light permeation ratio due to absorbance of light by ZnO loading
<i>Greek letter</i>	
θ	cylindrical angular coordinate (radian)

The hole may react with surface-bound H_2O or OH^- to produce the hydroxyl radical which has been suggested to be the primary oxidizing species in the photocatalytic oxidation processes.



The positive holes can be transferred more efficiently to the surrounding water matrix accelerating the $\bullet\text{OH}$ formation. Therefore, the decrease in the recombination of the electrons and positive holes results in an increased decomposition of the dye initiated by h^+ or $\bullet\text{OH}$.

There are still many problems in degrading organic pollutants using ZnO photocatalyst to be elucidated. In particular, only little effort has been made to understand kinetics for photodegradation

of organic pollutants in wastewater and effluents by ZnO photocatalyst. The Langmuir–Hinshelwood and pseudo-first-order model have been used to describe the photocatalytic degradation rate of organic compounds using ZnO [8–11]. However, most of kinetic models do not include the scattering of light which is an important parameter in the modeling of a slurry photocatalytic reactor [2]. There is a significant local light intensity distribution in the slurry photoreactor by reflection and refraction of light due to solids catalysts. Furthermore, in the decolorization of textile effluents the color of the solution changes with time. Due to the complex nature of radiation scattering, the integro-differential equations for radiation transfer in a photoreactor are required to be solved [2]. A simplified radiation emission model of the light source with a radiation absorption–scattering model in the photoreactor is very practical and useful for engineering design and scale-up. As far as our knowledge, the kinetic model for engineering design of an external light irradiation slurry photoreactor with ZnO in which the local light intensity distribution is taken into account has not been proposed.

Synthetic dyes have been extensively used in textile, paper and printing industries and significant losses during manufacture and processing of dyes have been discharged in the effluent. Many of them are very toxic to the surrounding environment and not readily biodegradable. Although decolorization and degradation of azo-dyes such as Methyl Orange, Reactive Red 2 and Procion Red MX-5B have been recently discussed using ZnO (e.g., [6,12–16]), a few studies have been carried out on the kinetics taking account of the light intensity distribution in the photoreactor for degradation of azo-dye by ZnO photocatalyst.

The purpose of this study is to investigate the photodecolorization of Orange II by ZnO powder in an external UV light irradiation photoreactor and to develop the dynamic simulation model for practical engineering design using a model for the light intensity profile in the photoreactor. Orange II which is a typical non-biodegradable azo-dye has been used as a model dye. Effects of operating parameters such as initial dye concentration, photocatalyst loading, light intensity, initial solution pH and aeration rate on the decolorization rate of Orange II have been quantitatively discussed. The mineralization of Orange II has been also examined by total organic carbon (TOC) analysis. The parameters in the proposed simulation model have been assessed using the experimental results obtained by varying the operation conditions.

2. Experimental

ZnO powder (the average particle diameter of $0.8 \mu\text{m}$) and azo-dye Orange II powder ($\text{C}_{16}\text{H}_{11}\text{N}_2\text{SO}_4\text{Na}$) were purchased from Showa Chemical Industries Co. Inc. (Japan) and Sanyo Chemical Industries Co. Inc. (Japan), respectively. These chemicals were used without any further purification. The presence of the sulfonate group causes the good water solubility of Orange II.

Experiments were conducted in a Pyrex glass cylindrical reactor of 0.08 m inside diameter and 0.55 m height (Fig. 1a(1)). The working volume was 2 L. A motor driven disk turbine

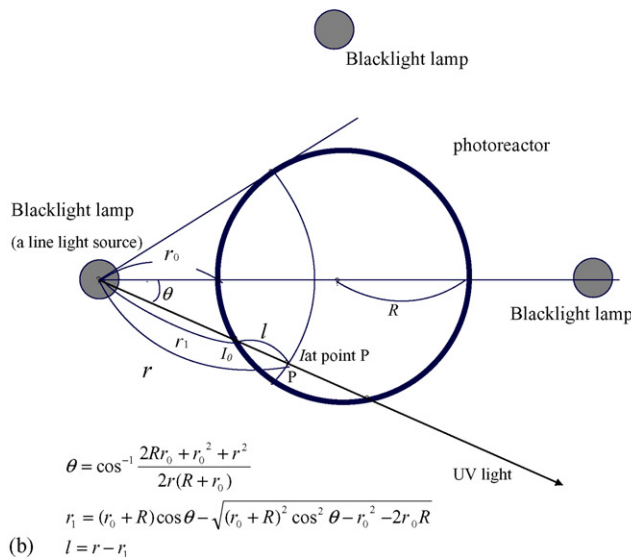
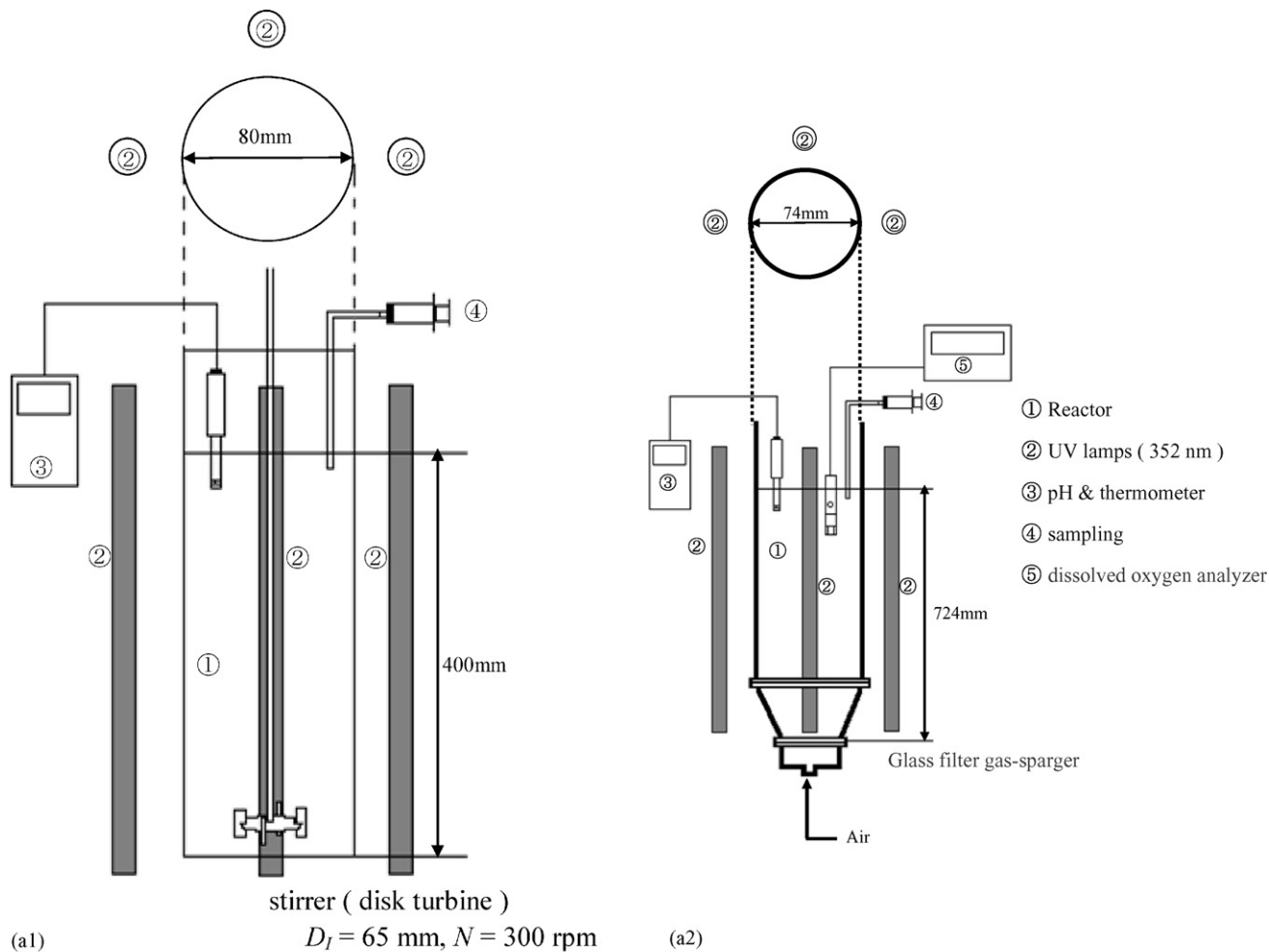


Fig. 1. Schematic diagram of the external UV light irradiation photoreactor: (a) experimental setup— (1) stirred tank and (2) bubble column and (b) model for light intensity in a photoreactor.

impeller (impeller diameter of $D_I = 65 \text{ mm}$) installed at 0.005 m above the reactor bottom was turned on at $N = 300 \text{ rpm}$ to ensure complete suspension of ZnO powder through the photoreactor. In order to examine effects of aeration rate on the decolorization

of Orange II, we used a bubble column of 0.08 m inside diameter and 0.54 m height with a glass filter gas-sparger for aeration instead of the cylindrical photoreactor with the impeller mentioned above (Fig. 1a(2)). Its working volume was also 2 L. All

experiments were performed in a batch mode with respect to liquid phase and at room temperature.

The pH monitoring of the initial solution and the samples was performed using a pH meter (Toa Denpa Co., Japan). As described below, the pH only slightly changed during the period of decolorization without controlling pH. Therefore, all experiments with the exception of experiments evaluating initial solution pH effects were performed at the natural pH of the dye solution without controlling pH.

The UV irradiation sources were three 15 W near-UV fluorescent lamps having the radiation peak at 352 nm (FL15T8BLB, Sankyo Electronics, Co., Japan). They were located around the cylindrical photoreactor and externally irradiated the solution as shown in Fig. 1b. The light intensity at light source per unit length for one UV lamp, S_L , and the distance between the photoreactor surface and the lamps, r_0 , were 6.60 W m^{-1} and 0.025 m , respectively. For the bubble column, three 20 W near-UV fluorescent lamps having the radiation peak at 352 nm (FL20T8BLB, Sankyo Electronics Co.) were used. In this case, the light intensity at light source per unit length for one UV lamp and the distance between the photoreactor wall surface and the lamps are 6.18 W m^{-1} and 0.075 m , respectively. The irradiance was measured by a UV radiometer (UVR-2+UD-36, Topcon Co., Japan). The photoreactor and lamps were completely covered with an aluminum foil.

Samples from the liquid phase were withdrawn at predetermined time intervals using a syringe for the analysis of decolorization and mineralization. In order to remove ZnO powder, the sample was filtrated with a membrane filter (Toyo Roshi Ltd., Japan) before measuring the solution absorbance and total organic carbon. The color of the solution changed from turbid and orange to clear and colorless during the color removal process. A UV-vis spectrophotometer (Hitachi U-1100, Hitachi Co., Japan) was used to determine the absorbance of Orange II at a wavelength of 486 nm. With this method the decrease in the absorbance was directly proportional to the dye concentration reduction. Prior to the measurement, a calibration curve was obtained using standard Orange II solution with the known concentrations. In order to confirm the mineralization of Orange II, the total organic carbon dissolved in the solutions was measured using TOC meter (TOC-VE, Shimadzu Co., Japan).

Distilled, deionized water was used for all solutions. Photodecolorization was initiated by turning on the UV lamp.

3. Results and discussion

Typical data for Orange II decolorization by ZnO photocatalyst with the initial Orange II concentration (C_{S_0}) of 7.31 mg L^{-1} at pH 7.7, the ZnO concentration (c_z) of 500 mg L^{-1} and the total UV light intensity per unit length at light source (S_L) of 19.8 W m^{-1} are illustrated in Fig. 2. In the presence of ZnO photocatalyst and UV light, the significant decolorization of Orange II or decrease in Orange II concentration (C_S) occurred and most of Orange II degraded after 30 min of irradiation. Blank experiments were carried out without UV light or catalyst to verify that the color removal of Orange II was indeed due to photocatalytic reaction. With no light irradiation or in the dark ($S_L = 0 \text{ W m}^{-1}$),

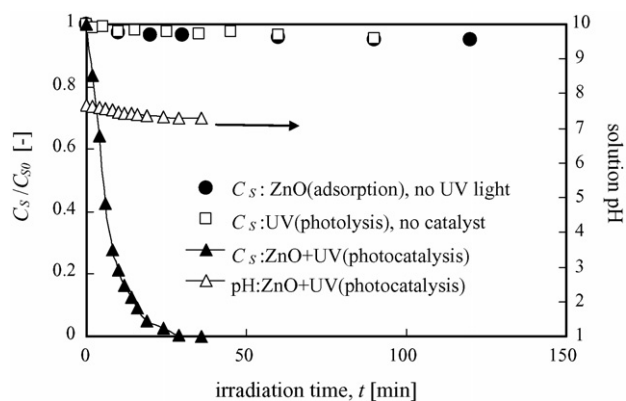


Fig. 2. Decolorization of Orange II: $C_{S_0} = 7.31 \text{ mg L}^{-1}$, $c_z = 500 \text{ mg L}^{-1}$, $S_L = 19.8 \text{ W m}^{-1}$ and initial pH 7.7.

there was practically no decolorization of Orange II. Only 5% of decolorization after 120 min was due to adsorption of Orange II to ZnO powder rather than photodecolorization. Adsorption of dyes to semiconductor photocatalysts such as TiO_2 and ZnO has been reported in the literature (e.g., [9,14,15,17]). As well as the present result at pH 7.7, Wu [15] found no significant adsorption of azo-dye Procion Red MX-5B at pH 7. Furthermore, Fernandez et al. [17] observed adsorption of Orange II to immobilized TiO_2 up to 30% at pH 3.0 but no significant adsorption at pH values of 4.3 and 5.6. They stated that the interaction between the anionic Orange II and the positive form of titania TiOH_2^+ at pH 3 is stronger than at higher pH due to a higher density of acidic positive charges. In the presence of only ZnO, the $\bullet\text{OH}$ radicals oxidizing Orange II might be not generated and as a result only small decolorization of Orange II was observed.

Since some dyes are degraded by direct UV irradiation, it should be examined to what extent Orange II is photolyzed if no photocatalyst was used. In the absence of the catalyst ($c_z = 0 \text{ mg L}^{-1}$), as shown in Fig. 2, Orange II was photolyzed by direct UV radiation only up to 5% in 90 min. This extent is similar to the result for photolysis of Reactive Blue 19 [5]. It is obvious that simultaneous utilization of UV irradiation with ZnO could increase the decolorization rate of Orange II. Incidentally, as illustrated in Fig. 2, the change in the pH of the reaction system without controlling pH was insignificant during the decolorization of Orange II.

3.1. Kinetics for decolorization of Orange II with ZnO

When the initial concentration of organic pollutants is not high, the photocatalytic degradation or decolorization rate of the most organic compounds is described by the pseudo-first-order model [1,2]:

$$-\frac{dC_S}{dt} = kC_S \quad (5)$$

where k is pseudo-first-order decolorization or reaction rate constant and C_S is Orange II concentration. It should be noted here that k represents the apparent decolorization rate constant because it may depend on the conditions of the irradiation field in the photocatalytic reactor as described below. The pseudo-

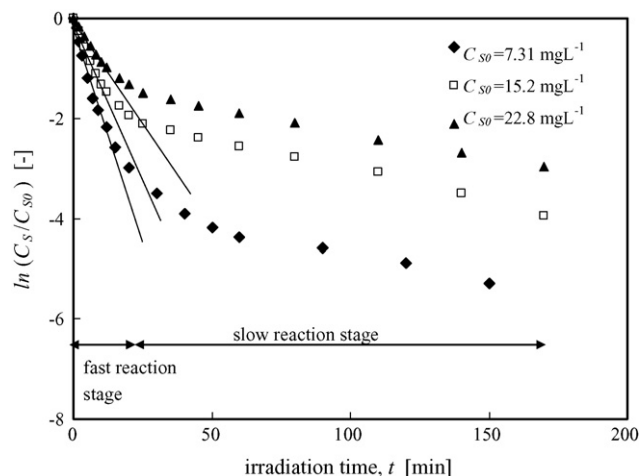


Fig. 3. Typical plots of $\ln(C_S/C_{S_0})$ against irradiation time: $c_z = 500 \text{ mg L}^{-1}$, $S_L = 19.8 \text{ W m}^{-1}$ and initial pH 7.7.

first-order rate constants can be determined from the semi-logarithmic plots of the Orange II concentration as a function of the UV irradiation time, t . When a plot of $\ln(C_S/C_{S_0})$ versus time results in a straight line, its slope is the pseudo-first-order decolorization rate constant. Fig. 3 depicts typical plots of $\ln(C_S/C_{S_0})$ against UV light irradiation time at different three initial Orange II concentrations. A two-stage photodecolorization of Orange II was found. During the first stage of photodecolorization, Orange II was decayed with fast decolorization rate, followed by the second stage which was characterized by a rather slow decolorization rate. As shown in Fig. 3 plots of $\ln(C_S/C_{S_0})$ versus t in the first stage gave straight lines. This indicates that in the first stage the majority of Orange II was rapidly degraded by following pseudo-first-order kinetics, Eq. (5). Its intermediates might be generated in this stage. In the subsequent second stage, the intermediates which were competitive with parent dye molecules in the photocatalytic decolorization process were accumulated and as a result the decolorization rate decreased. It is clear from the figure that in the second stage the experimental data deviated from the straight lines and the actual decolorization rates were rather slower than the first order reaction kinetics. The slow kinetics of azo-dye decolorization in the second stage of decolorization might be due to the difficulty in converting the N-atoms of the dye into oxidized nitrogen compounds [14]. From the slope of a straight line for a plot of $\ln(C_S/C_{S_0})$ versus t in the first stage we determined the pseudo-first-order reaction rate constant, k .

3.2. Effect of initial Orange II concentration

The influence of initial concentration of the dye solution on the photocatalytic color removal is important from the view points of reaction kinetics and photoreactor design. The effect of initial concentration of the dye on the rate of dye decolorization was examined with the Orange II concentration range of $4.08\text{--}27.6 \text{ mg L}^{-1}$. Fig. 4 illustrates the effects of initial Orange II concentration, C_{S_0} , on the decolorization rate constant in the first stage of decolorization, k . All the other operating parameters

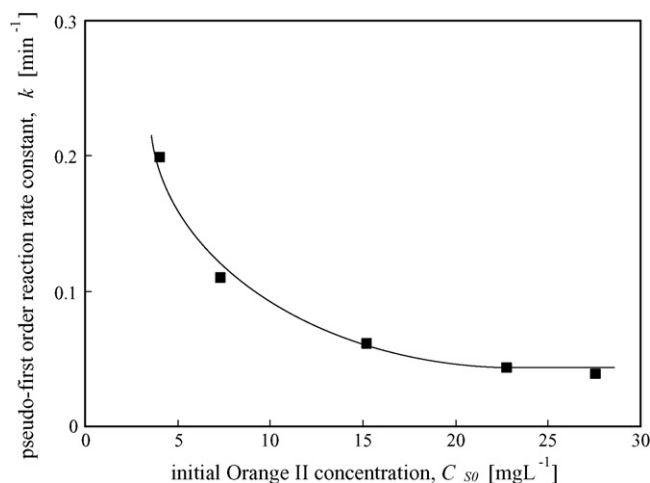


Fig. 4. Effect of initial concentration on the photodecolorization rate of Orange II in the first stage of decolorization: $c_z = 1000 \text{ mg L}^{-1}$, $S_L = 19.8 \text{ W m}^{-1}$ and initial pH 7.7.

were kept on constant and were as follows: the ZnO concentration of $c_z = 1000 \text{ mg L}^{-1}$, the UV light intensity at light source per unit length of $S_L = 19.8 \text{ W m}^{-1}$ and the initial solution pH of 7.7. It can be seen from Fig. 4 that the decolorization rate in the first stage of decolorization sharply decreased with increasing initial Orange II concentration up to 20 mg L^{-1} . When the initial concentration exceeded this value, the pseudo-first-order decolorization rate constant nearly leveled off. This is similar to the results for photodegradation of dyes by ZnO [3,14,18]. The absorbance of UV light by Orange II mainly caused the smaller reaction rate constants at higher Orange II concentrations. The decolorization rate relates to the formation of $\bullet\text{OH}$ radical which is the critical species in the decolorization process. The photons got intercepted before they could reach the catalyst surface. It should be noted that with increasing the initial concentration of the dye the requirement of catalyst surface available for the decolorization increased, whereas the intensity of the UV light source and catalyst loading were constant.

It should be noted that the increase in the average UV intensity with decreasing the color of solution or Orange II concentration caused the enhancement of the decolorization rate during decolorization process. This must be considered in the simulation model of photocatalytic decolorization of Orange II for the whole photodecolorization process as described below.

3.3. Effect of ZnO loading

Catalyst loading is an important factor which can significantly influence the photocatalytic decolorization rate. The increase in the amount of catalyst increased the number of active sites on the photocatalyst surface, which in turn, increased the number of hydroxyl radicals. The effect of initial ZnO concentration on decolorization rate in the first stage of decolorization was investigated by varying its amount from 0 to 5000 mg L^{-1} , keeping all other parameters identical and the results are presented in Fig. 5. The decolorization rate constant in the first stage, k , increased rapidly with the increase in loading of ZnO

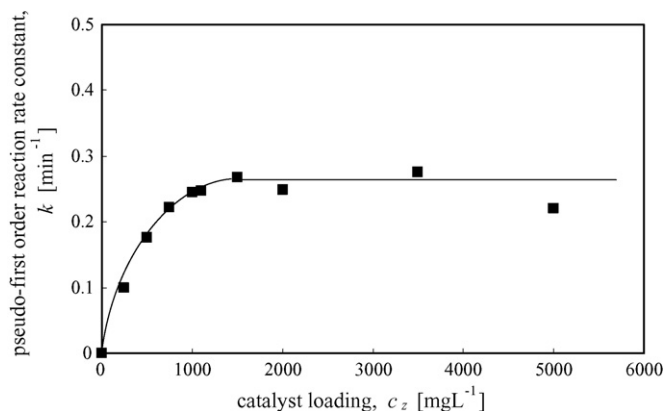


Fig. 5. Effect of catalyst loading on the photodecolorization rate of Orange II in the first stage of decolorization: $C_{S_0} = 7.31 \text{ mg L}^{-1}$, $S_L = 19.8 \text{ W m}^{-1}$ and initial pH 7.7.

for $c_z < 1000 \text{ mg L}^{-1}$. At higher loadings beyond 1500 mg L^{-1} , however, the rate constant reached a constant value, suggesting that an optimal level for catalyst effectiveness exists. This result is similar to the results in the literature [6,8,14,19,20]. Increasing the loading of photocatalyst increased the catalyst surface area and as a result increased the decolorization rate, while it would hinder the transmission of UV light in the photoreactor and consequently decreased the decolorization rate. Until an optimal catalyst loading was achieved, a higher catalyst loading caused a faster color removal of Orange II due to the creation of a higher number of active species. More catalyst would substantially result in more $\bullet\text{OH}$ radicals but above the limiting catalyst loading did not increase the extent of photodecolorization due to the interception of the UV light by ZnO powder suspension. Although the light penetration decreased with increasing ZnO powder loading due to light scattering and shielding, the reaction rate constant was nearly independent of the catalyst concentration for $c_z \geq 1500 \text{ mg L}^{-1}$. When ZnO loading in solution increased the solution became very turbid decreasing the penetration of UV light and as a sequence leading to a decrease in the formation of $\bullet\text{OH}$ radicals. Since the solution was stirred to ensure complete mixing of the ZnO powder by the impeller or aeration, the liquid recirculation induced by the impeller or bubbles periodically transported the ZnO powder to near the photoreactor wall where the UV light adequately permeated. Therefore, further increase in the loading of catalyst caused no significant decrease in the photodecolorization rate. Loss in surface area available for light-harvesting occasioned by agglomeration at higher solid concentration might also resulted in the suppression of photodecolorization rate [14].

3.4. Effect of UV light intensity

The influence of UV light intensity on the rate of dye decolorization was examined at constant initial dye concentration ($C_{S_0} = 7.31 \text{ mg L}^{-1}$, pH 7.7) and catalyst loading ($c_z = 1000 \text{ mg L}^{-1}$). The relationship between the reaction rate constant in the first stage of decolorization and UV light intensity is illustrated in Fig. 6. The UV light intensity at light source per

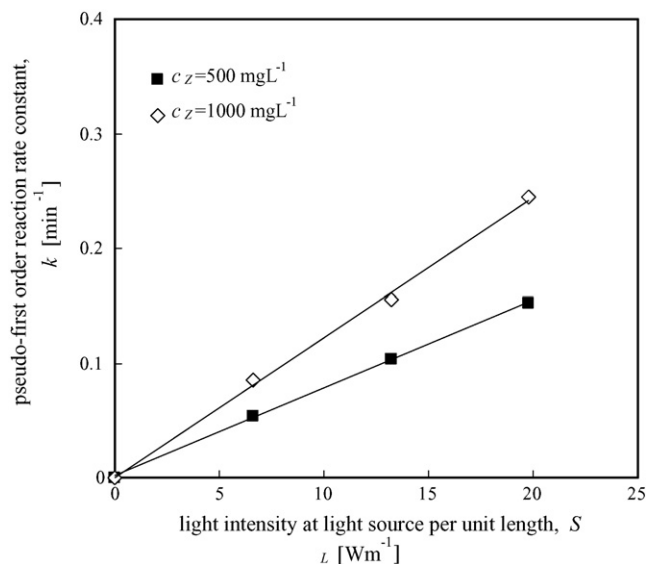


Fig. 6. Effect of UV light intensity on the photodecolorization rate of Orange II in the first stage of decolorization: $C_{S_0} = 7.31 \text{ mg L}^{-1}$ and initial pH 7.7.

unit length, S_L , was varied in the range from 0 to 19.8 W m^{-1} by changing the number of irradiated UV lamps. It can be seen from the figure that the decolorization rate linearly increased with increase in UV light intensity as well as the data for photoassisted Fenton decolorization of Orange II [21]. The dependence of photocatalytic degradation rate on light intensity yields at low and high UV light intensities [22,23]. The linear relationship in Fig. 6 indicates that the UV light intensities used in this study lie within the relatively low UV light intensity range.

3.5. Effects of solution pH

The amount of $\bullet\text{OH}$ radicals produced by UV irradiation is greatly affected by the pH and as a result effective dye decolorization rate is highly dependent on the pH of the solution. In order to investigate the effect of pH on the decolorization kinetics, experiments were conducted at different initial pH values. The initial solution pH was varied from 3 to 11. Fig. 7

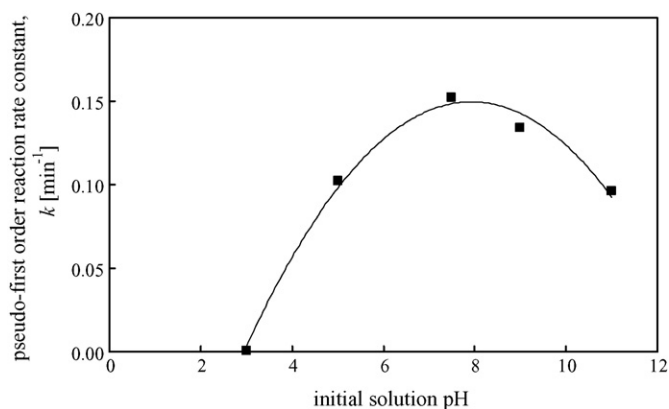
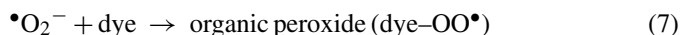
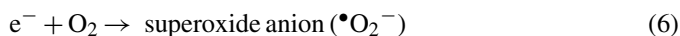


Fig. 7. Effect of initial solution pH on the photodecolorization rate of Orange II in the first stage of decolorization: $C_{S_0} = 10.2 \text{ mg L}^{-1}$, $c_z = 500 \text{ mg L}^{-1}$ and $S_L = 19.8 \text{ W m}^{-1}$.

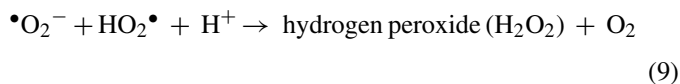
illustrates the decolorization rate constant in the first stage of photodecolorization when different initial pH values were used. The pseudo-first-order reaction rate constant rapidly decreased as the initial solution pH decreased from 7.7 to 3.0. The rate of Orange II decolorization was lower in acidic pH than in neutral or weakly alkaline system. The optimal pH value was around 7.7 which was the natural pH of the dye solution without controlling. Evgenidou et al. [8,10] observed an increase in decolorization rate with increasing pH at acidic pH as well as the present result but the decolorization rate was found to be almost constant at alkaline pH. We observed the complete ZnO dissolution in the solution and the lack of photocatalytic activity of ZnO at pH 3. Evgenidou et al. [10] examined effects of pH on photodecolorization of organophosphorous insecticide dichlorvos with ZnO. They found that the initial photodecolorization rate sharply increased with increasing pH from 2 to 7, the maximum photodecolorization rate was at pH 7 and further increase in pH caused the decrease in the decolorization rate as well as the result obtained in this study. They stated that ZnO reacts with acids to produce the corresponding salt and with bases to form complexes at acidic pH and alkalic pH, respectively. It should be noted that the solution pH insignificantly changed during the period of decolorization without controlling pH at various initial solution pH values.

3.6. Effect of aeration rate

Oxygen supplied to the liquid from air bubbles is expected to scavenge the electrons generated by UV radiation on ZnO surface [4,9,24]. The dissolved oxygen reduces the effect of the recombination of positive holes and electrons being an unfavorable process in photocatalysis. The electron is picked up by dissolved oxygen to generate superoxide radical anion, according to the following reaction:



The superoxide radical anion disproportionates into O_2 and H_2O_2 as follows:



Experiments were carried out in the bubble column photoreactor of 2 L working volume with a glass filter gas-sparger at air flow rates (Q_g) of 1, 2, 3 and 5 $L \text{ min}^{-1}$. Visual observation indicated ZnO powder might uniformly suspend through the column at $Q_g \geq 1 \text{ L min}^{-1}$. Fig. 8 reveals that the pseudo-first-order reaction rate constant in the first stage was found to increase with increasing aeration rate. An increase in the airflow rate increased the supply of oxygen and as a result depressed the decrease in hydroxyl radicals produced following the mechanism described above. A small airflow rate did not supply adequate oxygen in solution to inhibit the recombination of positive holes and

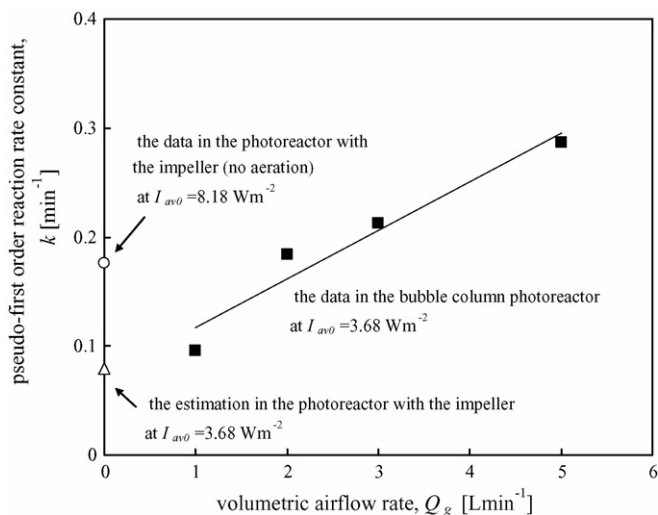


Fig. 8. Effect of aeration rate on the photodecolorization rate of Orange II in the first stage of decolorization: $C_{S0} = 7.31 \text{ mg L}^{-1}$, $c_L = 500 \text{ mg L}^{-1}$ and $S_L = 19.8 \text{ W m}^{-1}$.

electrons. For reference, the result obtained in the photoreactor where the impeller was used to keep the ZnO fine particles in suspension is also plotted in Fig. 8. The initial average UV light intensity in the photoreactor, I_{av0} , was estimated by use of the model described below and their values for the bubble column photoreactor and the photoreactor with the impeller are 3.68 and 8.18 W m^{-2} , respectively. By considering the result for the effect of UV light intensity given above that the decolorization rate linearly depended on the UV light intensity, the pseudo-first-order reaction constant in the photoreactor with the impeller at $I_{av0} = 3.68 \text{ W m}^{-2}$ could be estimated to be 0.0792 min^{-1} . The extent of decolorization in the absence of air injection when the catalyst was kept in suspension by the impeller was about the same for the case where the airflow rate of 1 L min^{-1} was used to supply oxygen in solution and keep the catalyst in suspension. Considering that ZnO powder was kept in uniform suspension at 300 rpm, the enhancement of decolorization rate for $Q_g > 1 \text{ L min}^{-1}$ might be due to the hindrance of the recombination of positive holes and electrons by oxygen.

3.7. Mineralization

The decolorization and mineralization curves of Orange II are presented in Fig. 9. TOC removal indicating the ultimate oxidation of Orange II was much slower than decolorization. The complete decolorization of Orange II occurred in 60 min, whereas for complete mineralization more than 300 min was required. This might be due to the formation of intermediates and its competitiveness with parent dye molecules in the photocatalytic degradation process. However, we did not identify the intermediates in the present work. This is one of our future works.

3.8. Model for design of a slurry photoreactor

For engineering design purposes, it is very useful to find out a simple and easy-to-use photodecolorization rate equation.

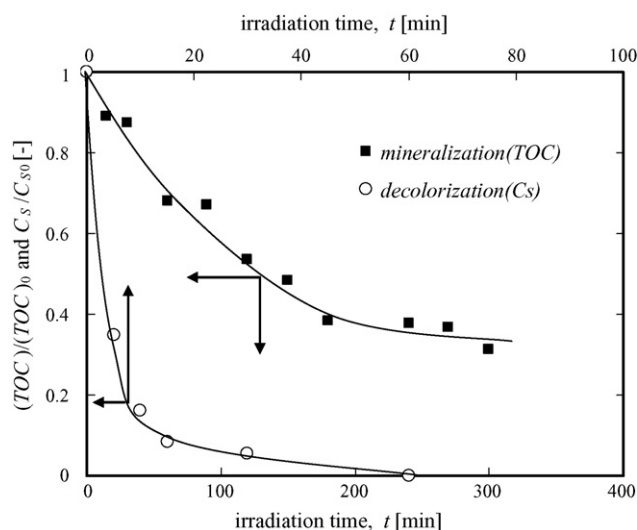


Fig. 9. Mineralization (TOC) and decolorization (C_S) of Orange II: $C_{S_0} = 7.31 \text{ mg L}^{-1}$, $c_z = 1500 \text{ mg L}^{-1}$ and $S_L = 19.8 \text{ W m}^{-2}$.

Based on the experimental results presented above, it is assumed that a pseudo-first-order kinetics constant, k , in Eq. (5) can be expressed in a simple way, as:

$$k = KC_{S_0}^a c_z^b I_{\text{av}} \exp \left\{ -c \left(1 - d \frac{C_S}{C_{S_0}} \right) \right\} \quad (10)$$

where C_{S_0} , C_S and c_z are in g L^{-1} . The constants in Eq. (10), K , a , b , c and d , which were determined using the present experimental data obtained in the wide range of experimental conditions are 3.0×10^{-5} , -0.91 , 1.6 , 3.9 and 1.2 , respectively. It should be noted that this equation is applicable for $c_z \leq 1500 \text{ mg L}^{-1}$ in which the decolorization rate increased with increasing c_z as shown in Fig. 7 and at pH 7.7 which was the optimum solution pH as presented in Fig. 8. As mentioned above, in the first stage decolorization of Orange II was rapid, whereas in the second stage the decolorization rate was rather slow due to the intermediates accumulated in the first stage. In Eq. (10), the slow decolorization rate in the second stage is considered by introducing the last term for the ratio of Orange II concentration to its initial concentration besides that in the first stage. Therefore, Eq. (10) is applicable in the whole decolorization process.

In order to evaluate the average light intensity over the cross-sectional area of the photoreactor, I_{av} , in Eq. (10), the light intensity profiles in the photoreactor can be determined by integrating local light intensity in which the decrease of light permeation due to the light absorbance by Orange II and the light scattering and shielding by ZnO powder. The average UV light intensity over the cross-sectional area of the external irradiation photoreactor, I_{av} , can be obtained by integration of local UV light intensity with respect to r (from r_1 to $r_1 + 2R$) and θ (from $-\theta$ to θ) (Fig. 1b), and finally it is given as [25]:

$$I_{\text{av}} = \frac{1}{A} \int I ds = \frac{1}{\pi R^2} \int_{r_0}^{r_0+2R} \int_{-\theta}^{\theta} I(r, \theta) r dr d\theta \quad (11)$$

where A is the cross-sectional area of the photoreactor.

Using Lambert's law [2,25], the light intensity at point P(r , θ) shown in Fig. 1b, $I(r, \theta)$, is written as:

$$\frac{I(r, \theta)}{I_0} = T^l \quad (12)$$

where the light path length l and the light intensity at the photoreactor wall I_0 are given by:

$$l = r - r_1 \quad (13)$$

and

$$I_0 = \frac{S_L}{2\pi r} \quad (14)$$

respectively.

The distance between light source and photoreactor wall, r_1 , and the cylindrical angular coordinate shown in Fig. 1b, θ , are related with each other by the following equations:

$$r_1 = (r_0 + R) \cos \theta - \sqrt{(r_0 + R)^2 \cos^2 \theta - (2r_0 R + r_0^2)} \quad (15)$$

and

$$\theta = \cos^{-1} \frac{2Rr_0 + r_0^2 + r^2}{2r(R + r_0)}. \quad (16)$$

We adopted the linear light source model to evaluate UV light intensity profiles in the external irradiation photoreactor [25].

We considered the decrease in light permeation due to the existence of Orange II and the dispersion of ZnO powder in the solution since UV light entering the photoreactor can be absorbed by both the catalyst and the dye in the solution. From separate experiments in which a small glass cell 0.01 m was used to measure the change in the light permeation with the concentrations of Orange II and ZnO powder, we obtained the following relationship for the light permeation ratio decreasing with an increase of photocatalyst loading, T_z :

$$T_z = \exp(-0.22c_z). \quad (17)$$

If the concentration of the dye is decreased by the photocatalytic decolorization, the path length of UV light penetrating into the solution is increased. For the decrease in light permeation ratio due to the absorbance of light by Orange II, T_0 , the following equation was obtained in our previous work [21]:

$$T_0 = \exp(-1.67C_S) \quad (18)$$

As a result, the overall light permeation ratio, T , was assumed to be given as:

$$T = T_z T_0 \quad (19)$$

From the above equations, we have the following expression for local intensity at $r = r$ in the photoreactor:

$$I(r, \theta) = I_0 \exp(-(0.22c_z + 1.67C_S)l) \quad (20)$$

It should be noted that C_S and c_z in Eqs. (17), (18) and (20) are in g L^{-1} .

Fig. 10 depicts typical comparisons between measured decolorization performances by the UV light and calculated values based on the UV light intensity profile model described above,

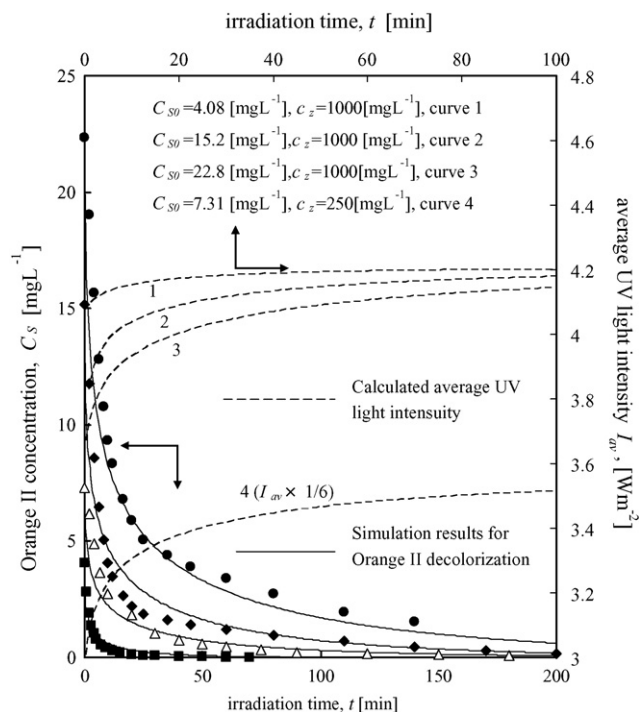


Fig. 10. Comparison between the model predictions and the experimental results.

Eq. (5) with Eqs. (10)–(20). It should be noted here that we must solve the ordinary differential equations numerically since T is a function of the Orange II concentration C_S and as a result the pseudo-first-order reaction kinetic constant, k , depends on C_S . We used the fourth-order Runge–Kutta method. On the whole, reasonable agreement was obtained for all experimental results. For reference, the changes in the average UV light intensity with decolorization of Orange II estimated by the present model are given. It can be seen that the light intensity increased with decreasing the color of Orange II solution.

4. Conclusions

We have investigated the potential of ZnO as a photocatalyst for the color removal of azo-dye Orange II in aqueous solutions. The present results lead to the following conclusions:

- (1) Experimental results of the photocatalytic decolorization of the azo-dye Orange II using ZnO as photocatalyst reveal that almost complete decolorization can be achieved in a short period of irradiation time.
- (2) At higher Orange II concentrations, the photons got intercepted before they could reach the catalyst surface, decreasing the decolorization of Orange II by ZnO photocatalyst.
- (3) It was found that the catalyst loading for the maximum decolorization of Orange II is around 1000 mg L^{-1} . When the concentration of ZnO catalyst increased above the limiting value, the decolorization rate leveled off due to the intercept of the light by the suspension. While the availability of active sites increased with the suspension of catalyst loading, the UV light penetration was reduced. The trade-off

between these two effects resulted in the ZnO loading for maximum photodecolorization of Orange II being around 1000 mg L^{-1} .

- (4) The decolorization rate in the first stage of photodecolorization increased with increase in the UV light intensity and their relationship was linear.
- (5) The optimum pH condition required for maximum decolorization rate was 7.7 (natural).
- (6) It was found that oxygen gas plays an important role as electron scavenger.
- (7) The proposed model could simulate the decolorization of Orange II with ZnO photocatalyst both in the fast decolorization stage and the subsequent slow decolorization stage reasonably well. It can be concluded, therefore, that it is very useful for practical engineering design of slurry photoreactors in the treatment of wastewater including textile dyes.

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