

Photocatalytic Decolorization of Rhodamine B by Immobilized TiO₂/UV in a Fluidized-bed Reactor

Youngsoo Na, Seungkoo Song* and Youngseek Park**†

R&D Laboratory, Segye Chemical Co. Ltd., Kyungnam 626-110, Korea

*Department of Chemical Engineering, Pusan National University, Busan 609-735, Korea

**Department of Environmental Hygiene, Daegu University, Gyeongsbuk 712-830, Korea

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Abstract—The photocatalytic oxidation of Rhodamine B (RhB) was studied by using a newly developed immobilized photocatalyst (TiO₂ immobilized by support consisting of a perlite and silicone sealant) and a fluidized-bed reactor. Three 8 W germicidal lamps were used as the light source and the reactor volume was 2.8 l. When this photocatalyst was employed in a batch process, a total decolorization of the RhB in reaction times lower than 60 min was observed. The optimum dosage of photocatalyst was 33.8 g/l. The initial RhB decolorization rate of the immobilized TiO₂ was higher than that of the suspended TiO₂ and this did not agree with pseudo first-order kinetics because of the adsorption onto the surface of the immobilized TiO₂. This result indicated that the adsorption capacity of the immobilized photocatalyst is very important in photocatalysis.

Key words: Photocatalytic Degradation, UV/TiO₂, Fluidized-bed, Dye, Immobilization, Adsorption

INTRODUCTION

These days the textile industry uses about 10,000 different dyes and pigments, with a worldwide annual production of over 7×10^5 tons [Spadary et al., 1994]. The toxicity and mass production of dyes leads to the necessity of treatment. The typical methods of treating dye wastewater include biological treatment, chemical coagulation, activated carbon adsorption, and others. The major difficulty in treating textile wastewater containing dyes is the ineffectiveness of biological processes. As for physical processes, such as coagulation and adsorption, they merely transfer the pollutants from wastewater to other media and cause secondary pollution [Tang and An, 1995].

Based on the utilization of solar energy and the complete mineralization of organic compounds to carbon dioxide, water and mineral acid, the photocatalytic treatment is a more attractive alternative for the removal of soluble organic compounds in wastewater since it can avoid additional and secondary pollution [Nam and Han, 2003; Lim and Kim, 2002]. Recent development in the field of oxidative and photocatalytic degradation methods has led to a remarkable elimination of dissolved toxic organic pollutants.

For the photocatalytic degradation processes, two methods for TiO₂ are favored: (1) TiO₂ suspended in aqueous media, and (2) TiO₂ immobilized on support materials in a fixed or fluidized reactor [Chun et al., 2001; You et al., 2001; Chai et al., 2000].

In view of practical engineering, the immobilized catalyst should be preferred, to avoid downstream treatments (i.e., particle-fluid separation and/or catalyst recycling) [Pozzo et al., 2000]. This has led to a major attempt to immobilize the catalyst on supports including ceramic [Sunada and Heller, 1998], fiber glass [Shifu, 1996], glass, quartz and stainless steel [Fernandez et al., 1995], activated carbon [Takeda et al., 1998] and others. However, these efforts have

not produced materials which meet all demands of photocatalytic activity. Importantly, the photocatalytic degradation efficiency of immobilized TiO₂ is often lower than that of the suspended particles [Matthews, 1990].

The system developed in this study consisted of a fluidized bed reactor (FBR) filled with a new catalyst (TiO₂) immobilized by the support consisting of a perlite and silicone sealant, which operated in batch mode. Factors affecting the decolorization rate of RhB in an FBR are investigated, including catalyst concentration, air-flow rate and the initial concentration of RhB. In addition, decolorization efficiency was compared with the suspended TiO₂.

MATERIALS AND METHODS

1. Rhodamine B

The dye, Rhodamine B (reagent grade, 95% pure), was used as a test pollutant. Its structure is given in Fig. 1. The RhB consists of green crystals or reddish-violet powder; the molecular formula is C₂₈H₃₁ClN₂O₃ (mol wt. 479.00) is highly soluble in water and organic solvent, and its color is fluorescent bluish-red. The RhB has been used as a dye, especially for paper; as a reagent for antimony, bismuth, cobalt, niobium, gold, manganese, mercury, molybdenum, tantalum, thallium, and tungsten; and as a biological stain. How-

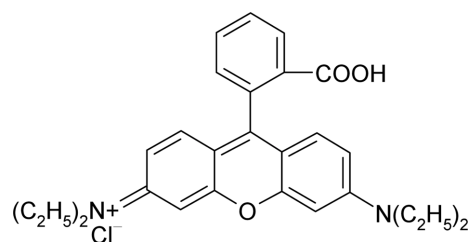


Fig. 1. The structure of Rhodamine B.

†To whom correspondence should be addressed.

E-mail: ysparkk@daegu.ac.kr

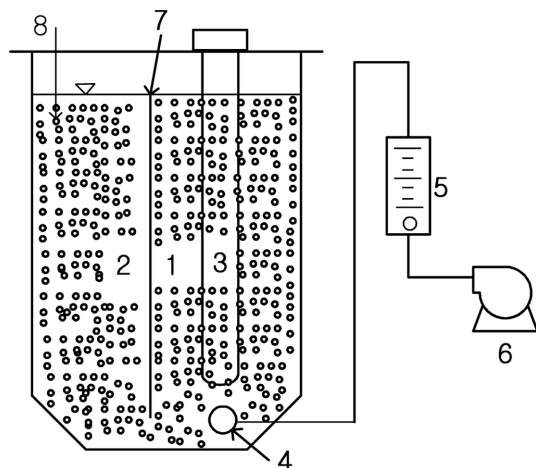


Fig. 2. The schematic diagram of photocatalytic reactor.

- | | |
|---------------|------------------|
| 1. Riser | 5. Rotameter |
| 2. Down comer | 6. Air pump |
| 3. UV lamp | 7. Draft plate |
| 4. Diffuser | 8. Photocatalyst |

ever, RhB has been found to be potentially toxic and carcinogenic. This compound is now banned from food and cosmetic usages (Ministry of Health Singapore, 2002). The photocatalyst employed in this study was Degussa P-25 TiO₂ powder (particle size: 30 nm, containing 80% Anatase and 20% Rutile, BET surface areas of 50 m²/g).

2. Preparation of Immobilized TiO₂ Photocatalyst

Immobilized TiO₂ was prepared by the following method: 1) per-lite powder (~0.1 mm) was mixed with silicone sealant (weight ratio: 1 : 1) which then formed the support; 2) The surface of the support was coated with Degussa P-25 TiO₂ (weight ratio of the TiO₂: 0.83); 3) the immobilized TiO₂ was dried for 48 hours at room temperature and then (size: 0.6-1.18 mm); and 4) the immobilized TiO₂ was washed with distilled water and dried. The shape of the immobilized TiO₂ was elliptical and the specific gravity was 1.16.

The reactor used was a rectangular acrylic vessel, 250 mm in height, 90 mm in width and 125 mm in length (working volume: 2.8 l) and is shown in Fig. 2. The reactor was divided into two areas (riser and down comer) by a baffle and the area ratio of riser to down comer was fixed at 1 : 1. In order to circulate the immobilized TiO₂, two diffusers were installed at the bottom of the reactor, the air-flow rate was adjusted by rotameter and air was supplied in a continuous way. The reactor was exposed to a luminous source composed of three 8 W germicidal lamps (G8T5, Sankyo Denki Co.).

3. Analysis

Rhodamine B was analyzed on a UV-VIS spectrophotometer (Genesis 5, Spectronic Co.). The determination wavelength was 554 nm, which is the maximum absorption wavelength. The determined absorption was converted to a concentration through the standard-curve method of dye.

RESULTS AND DISCUSSION

1. Effect of Immobilized TiO₂ Dosage and RhB Concentration

RhB decolorization at varying immobilized TiO₂ dosages in the

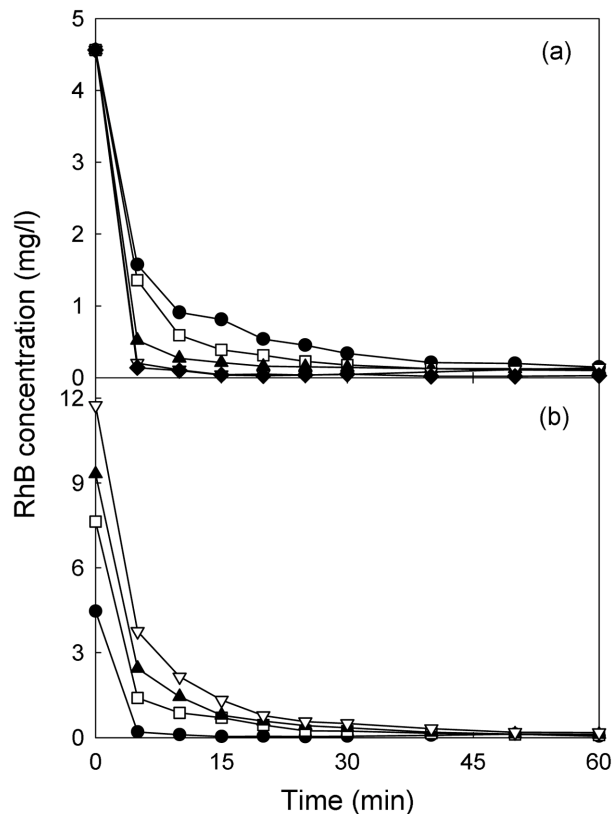


Fig. 3. Effect of immobilized TiO₂ dosage and RhB concentration on the degradation of RhB.

(a) Effect of immobilized TiO₂ dosage (RhB conc.: 4.6 mg/l, air flow rate: 7 l/min). Immobilized TiO₂ dosage ●: 8.5 g/l, □: 16.4 g/l, ▲: 25.3 g/l, ▽: 33.8 g/l, ◆: 42.3 g/l, (b) Effect of RhB concentration (Immobilized TiO₂ dosage: 33.8 g/l). RhB conc., ●: 4.5 mg/l, □: 7.6 mg/l, ▲: 9.3 mg/l, ▽: 11.7 mg/l.

8.5-42.3 g/l range is conducted in our experiment. Fig. 3(a) shows the decrease of RhB with different dosages of the immobilized photocatalyst. It can be seen that with increasing immobilized TiO₂ dosage, the decolorization increases due to the increase of surface area for adsorption and degradation. At a dosage of 33.8 g/l, the decolorization rate achieves the maximum. The decolorization rate was not enhanced anywhere as the immobilized TiO₂ dosage increased beyond 33.8 g/l. This phenomenon may be due to the hindrance and blocking of UV light penetration by an excessive amount of the immobilized photocatalyst. Therefore, 33.8 g/l was selected as the immobilized TiO₂ dosage for the photocatalytic activity study in our experiment. This result showed similar trends to those of other researchers those who reported the optimum catalyst dosage for a photocatalytic reaction using the TiO₂ powder or immobilized TiO₂ [Tang and An, 1995; Nazawa, 2001; Na, 2002].

The relative decrease of the RhB concentration with operation time for various initial concentrations of RhB is shown in Fig. 3(b). As the initial concentration of RhB increased, the reaction rate decreased. It is believed that increased RhB concentration affects light penetration into the RhB solution. Therefore, light penetration at a higher initial RhB concentration was reduced and fewer photons reached the immobilized TiO₂ surface [Nam, 2002]. It should be noted that the slope of decolorization of C/C₀ did not appear to be

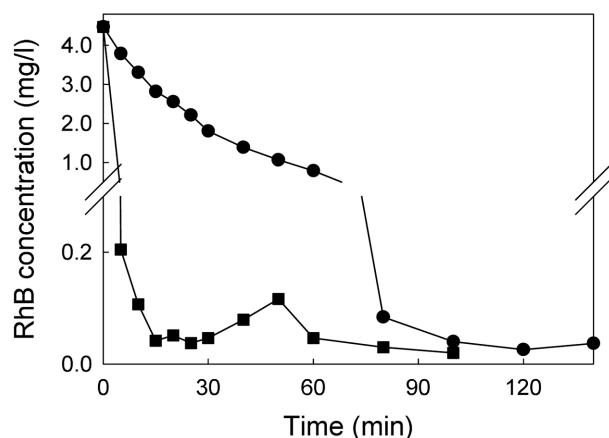


Fig. 4. Efficiency comparison between powder and immobilized TiO₂ on the degradation of RhB (RhB conc.: 4.5 mg/l, air flow rate: 7 l/min, powder TiO₂ dosage: 0.2 g/l, immobilized TiO₂ dosage: 33.8 g/l).

● : powder TiO₂, ■ : immobilized TiO₂

in agreement with pseudo first-order kinetics because of the fast adsorption of the initial state. Therefore, it could be concluded that for the photocatalytic decolorization of RhB, the Langmuir adsorption model did not describe the effect of the initial concentration.

2. Comparison of Decolorization Efficiency with Suspended TiO₂

In order to compare the decolorization efficiency of immobilized TiO₂ with suspended TiO₂, the same reactor system, UV light source and suspended TiO₂ (Degussa P-25) were used. The previous experiment showed that the optimum dosage of suspended TiO₂ was 0.2 g/l [Ahn et al., 2004]. In addition, RhB removal by adsorption was about 0.04%, so the adsorption effect was negligible. Fig. 4 shows the initial decolorization rates of suspended and immobilized TiO₂ for RhB (concerning the effect of adsorption). In the case of suspended TiO₂, the color of RhB diminished slowly, and 98.1% diminished after 80 min. However, the decolorization rate of immobilized TiO₂ was faster than that of suspended TiO₂: 95.5% was decolorized within 5 min. Adsorbed RhB was observed on the surface of immobilized TiO₂ after 5 min. The reason was considered to be the fact that RhB was primarily adsorbed on the surface of the immobilized TiO₂. Park [2003] reported that when TiO₂ was immobilized with silicone sealant, the immobilized photocatalyst showed the behavior of fast adsorption. Fast adsorption onto the surface of immobilized TiO₂ was considered that the immobilized TiO₂ consisted of silicone sealant and porous perlite, which has a high adsorption capacity.

As shown in Fig. 4, a point of inflection was observed from 30 min to 50 min. This phenomenon was considered to be due to the fact that RhB, which was adsorbed RhB on the surface of the immobilized TiO₂, was eluted from the surface of the immobilized TiO₂. However, the decolorization of the eluted RhB in the liquid phase and the RhB on the surface of the immobilized TiO₂ was almost terminated within 30 min. The reaction times that the powder and immobilized TiO₂ required for a removal efficiency of 99.1% were 100 min and 60 min, respectively. This immobilized photocatalyst showed a fast reaction rate and reaction time.

The sequence of RhB decolorization was observed by observa-

tion of the reactor and collected immobilized TiO₂ with time and estimated as follows. First, the RhB solution was adsorbed onto the surface of the immobilized TiO₂ (within 5 min). Second, the residual RhB solution of the liquid phase and adsorbed RhB on the surface of the immobilized TiO₂ was decolorized by UV light and TiO₂ (5-30 min). Third, the RhB was eluted from the surface of the immobilized TiO₂ (30-50 min). Fourth, the eluted RhB in the liquid phase and the RhB on the surface of the immobilized TiO₂ was decolorized.

Pazzo et al. [2000] said that the photocatalytic performance of the immobilized photocatalyst, as measured by its apparent quantum efficiency, was significantly poorer (about 5-6 times lower) than that obtained with the suspended photocatalyst. Several factors were targeted as potential contributors to this lower performance of the immobilized catalyst: (1) reduction of available specific surface area resulting from the binding with the supporting surface; (2) significant radiation extinction (absorption and scattering) by the support; or (3) catalyst agglomeration (surface clumping) during fixation, among others. However, in our results, in spite of the fact that the surface area of the immobilized TiO₂ was much smaller than that of the powder, initial decolorization rate of the immobilized TiO₂ was larger, and total reaction time was shorter, than those of suspended. This was considered the result from the fact that light penetration into the RhB solution was highly increased by adsorption; it was counterbalanced for the small surface area. Hung et al. [2001], who used suspended TiO₂, reported that the degradation rates of Orange G were proportional to the light intensity and the TiO₂ concentration with the power order about 0.734 and 0.726, respectively.

According to the mechanism suggested by Turchi and Ollis [1989], the attack of ·OH radicals takes place on the adsorbed substrates. Hence the species that is adsorbed in greater amount will degrade rapidly. Bhatkhande et al. [2003] reported that when the adsorption of nitrobenzene on the TiO₂ surface is greatest, the photocatalytic degradation is effectively highest and a large decrease in the concentration is observed at the beginning of the photocatalytic degradation experiments. In addition, Zhu et al. [2000] reported that the most important factor among the supports for TiO₂ is the adsorptive ability. Therefore, the use of immobilized TiO₂ developed this study increased the light penetration by fast adsorption and so compensated for the small surface area.

Judging from the above, it can be deduced that adsorption may be the important determinative factor in the RhB photocatalytic decolorization activity of catalysts.

3. Effect of Air Flow Rate

The effect of the air-flow rate on the photocatalytic decolorization rate of RhB is shown in Fig. 5. As can be seen in Fig. 5, as the air-flow rate is increased, the decolorization rate of RhB was increased. However, as the air-flow rate increased over 7.0 l/min, the decolorization rate was not in proportion to the increase of the air-flow rate. This means that some parts of the immobilized TiO₂ under the optimum air-flow rate (7.0 l/min) took part in the photocatalysis. As the air-flow rate reached the optimum air-flow rate, all of the immobilized TiO₂ took part in the photocatalysis, and the decolorization of RhB achieved a maximum. This indicates that as the air-flow rate increased, the immobilized TiO₂ taking part in the photocatalysis increased, contact between photocatalyst and RhB

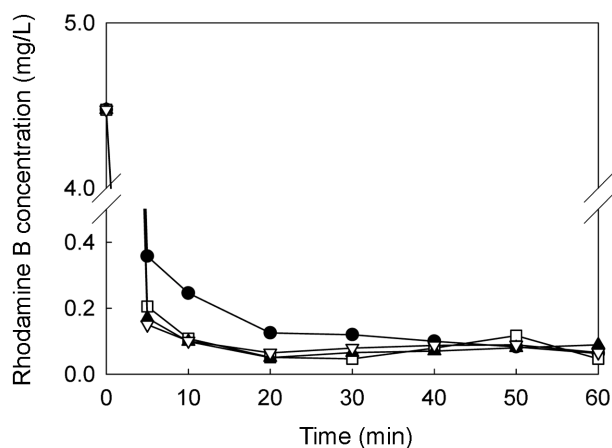


Fig. 5. Effect of air flow rate on the decolorization of RhB (Immobilized TiO₂ dosage: 33.8 g/l, RhB conc.: 4.5 mg/l).
●: 6 l/min, □: 7 l/min, ▲: 8 l/min, ▼: 9 l/min

increased and hence the higher mass transfer rates obtained. However, at a higher air-flow rate (over optimum air-flow rate), the larger number of bubbles may hinder the absorbance of UV light to the photocatalyst [Nam et al., 2002]. Therefore, it can be said that there is an optimum air-flow rate for the photocatalytic fluidized bed reactors.

4. Effect of Reused Catalyst

An experiment was performed with the used catalyst (after experiments of 20 times) to determine its reusability. The used catalyst was washed with distilled water three times and dried at room temperature during 24 h. All of the studies of RhB decolorization were performed using the same photoreactor and UV source. As can be seen from Fig. 6, the used catalyst showed no loss in activity.

CONCLUSIONS

The investigation within this study showed that a fluidized-bed reactor system with immobilized TiO₂ has higher RhB decolorization rates and a shorter decolorization time that those operating with

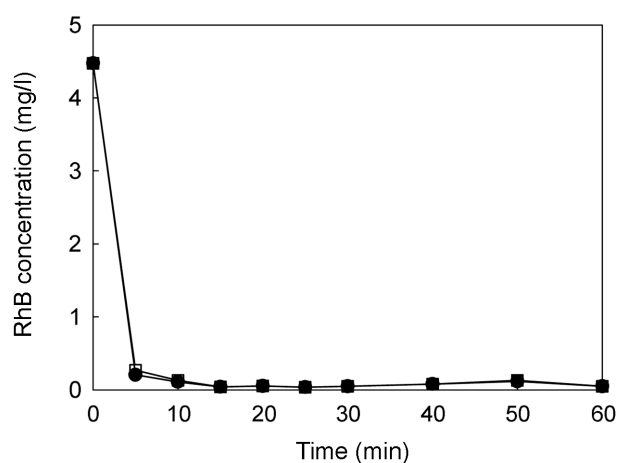


Fig. 6. Effect of reused catalyst on the on the decolorization of RhB (RhB conc.: 4.5 mg/l, immobilized TiO₂ dosage: 33.8 g/l).
●: fresh catalyst, □: used catalyst

suspended TiO₂. The use of immobilized TiO₂ developed in this study increased the light penetration by fast adsorption, and so compensated for the small surface area. It can be deduced that RhB adsorption may be the most important determinative factor in the RhB photocatalytic decolorization activity of catalysts in our study. Additionally, the used immobilized TiO₂ did not show any loss in activity.

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