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Photocatalytic decolorization of rhodamine B by immobilized TiO_2 onto silicone sealant

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Abstract

The photocatalytic performance of immobilized TiO_2 supported on silicone sealant was evaluated using the photocatalytic oxidation of rhodamine B (RhB) under weak illumination conditions. Three 8 W germicidal lamps were used as the light source and the reactor volume was 1.7 l. The optimum dosage of immobilized photocatalyst was 210.7 g/l (TiO_2 weight percentage: 15%). The initial decolorization rate constants of RhB in an aqueous solution were determined in the presence or absence of immobilized TiO_2 and UV irradiation in order to study each decolorization effect due to adsorption onto the immobilized TiO_2, direct photolysis by UV irradiation and photocatalytic decolorization. The order of initial decolorization rate constant was photocatalytic oxidation > adsorption > photolysis. The initial decolorization rate constant of the RhB by the immobilized TiO_2 was higher than that of the powder TiO_2. The used immobilized photocatalyst retained a constant photocatalytic activity.
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Keywords: Photocatalytic decolorization; UV/TiO_2; Dye; Immobilization; Adsorption

1. Introduction

Around 10^6 tonnes and more than 10,000 different synthetic dyes and pigments are produced annually worldwide and used extensively in the dye and printing industries. It is estimated that about 10% are discharged in industrial effluents [1]. The discharge of wastewater that contains high concentrations of dyes is a well-known problem associated with dyestuff activities. Their highly variable and complex chemical structures also make them difficult to remove using conventional wastewater treatment systems [2].

The major difficulty in treating textile wastewater containing dyes is the ineffectiveness of biological processes [3]. Physical processes, such as coagulation and adsorption, merely transfer the pollutants from wastewater to other media and cause secondary pollution. Therefore, in recent years, due to the non-toxic, insoluble, inexpensive and highly reactive nature of TiO_2 under UV irradiation, a TiO_2 photocatalytic degradation technology has been used to oxidize wastewater-contained dyes and has attracted much attention [4].

In the past, most of the studies related to such photodegradation reactions have been carried out using a suspension of fine-powdered TiO_2 (usually Degussa P-25) in the polluted aqueous solution. However, the performance of this kind of reaction can be remarkably affected by the limited penetration of the radiation in the suspension and by the fouling of the UV source due to the deposition of solid-waste particles [5].

Furthermore, the feasibility of the photocatalytic process on a realistic scale might be limited by the fact that a separation of the fine solid particles from the liquid is required after the photocatalytic treatment. These problems could be solved by immobilizing the catalyst on an inert support. For this reason, different immobilization systems have been tested employing several supports, such as ceramic, fiber-glass, glass, quartz sand, stainless steel, activated carbon and zeolites [5–9].

The present paper is focused on the use of a new immobilized photocatalyst. In this research, the photocatalytic decolorization of a dye, rhodamine B, has been studied. The system developed consisted of a continuous stirred tank reactor (CSTR) filled with immobilized photocatalyst (TiO_2) in a silicone sealant, which operated in both batch and continuous modes.

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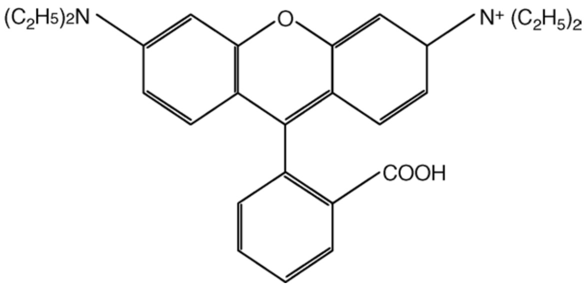

Fig. 1. The structure of rhodamine B.

2. Experimental

2.1. Rhodamine B

The dye, rhodamine B (RhB, reagent grade, 95% pure), was used as a test pollutant. Its structure is given in Fig. 1. RhB consists of green crystals or reddish-violet powder; the molecular formula is $C_{28}H_{31}CN_2O_3$ (molecular weight 479.00) and it is highly soluble in water and its color is fluorescent bluish-red. 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. However, RhB has been found to be potentially toxic and carcinogenic. This compound is now banned from use in foods and cosmetics [10]. The photocatalyst employed in this study was Degussa P-25 TiO_2 powder (particle size of 30 nm, containing 70% anatase and 30% rutile, and BET surface areas of 50 m^2/g).

2.2. Preparation of immobilized photocatalyst

Immobilized TiO_2 was formulated as follows: (1) Degussa P-25 TiO_2 powder was mixed with oxime type silicone sealant (TiO_2 weight percentages: 3.8, 7.5, 11.3 and 15.0%); (2) put the mixture of silicone sealant and TiO_2 powder on a glass and spread the mixture and make film; (3) dried for 24 h at room temperature and (4) cutting the film hexahedrons (length, 1–3 mm; width, 1–3 mm; thickness, 0.5–2 mm).

2.3. Photoreactor and analysis

A schematic diagram of the experimental reactor is shown in Fig. 2 (height, 220 mm; width and length, 100 mm; working volume, 1.7 l). In order to circulate the powder and immobilized photocatalyst, a stirrer was installed in the reactor top. The reactor was exposed to a luminous source composed of three 8 W germicidal lamps (G8T5, Sankyo Denki Co.). The dominant wavelength is 254 nm and light intensity is 3.6 mW/cm^2. For the decolorization of RhB, a solution containing known concentration of dye and immobilized TiO_2 or powder TiO_2 was prepared. After that, the lamp was switched on to initiate the reaction. During irradiation, agitation was maintained 150 rpm and the suspensions with immobilized TiO_2 or powder TiO_2 was sampled after an appropriate illumination time. To measure the light intensity pass over RhB solution filled with powder TiO_2 and immobilized TiO_2 in reactor inside, window of UV intensity measurement which has made of quartz plate (2 cm × 2 cm; thickness, 1 mm), was installed the front of the reactor. Distance between UV lamp and photoreceptor sensor of light intensity meter was 17 mm.

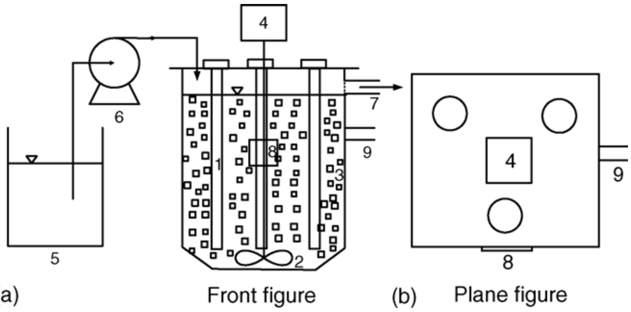

Fig. 2. Schematic diagram of photocatalytic reactor. 1, UV lamp; 2, stirrer; 3, photocatalyst; 4, motor; 5, reservoir; 6, peristaltic pump; 7, effluent; 8, window of UV intensity measurement and 9, sampling port.

The change of RhB concentration was determined by the UV–vis spectrophotometer (Genesis 5, Spectronic Co.) using the calibration curve of standard of RhB solutions.

Light intensity was measured by the light intensity meter (Cole Parmer Instrument Co., VLX-3W) and the photoreceptor sensor of 254 nm. When light intensity was measured, the photoreceptor sensor of light intensity meter of was stick to the window of UV intensity measurement of reactor, and then light intensity was measured.

3. Results and discussion

3.1. Effect of TiO_2 weight ratio on immobilization

The maximum weight ratio of the TiO_2 in the composite photocatalyst (silicone sealant-TiO_2) was 15.0%. When the weight ratio of TiO_2 was over 15.0%, the mixture consisting of TiO_2 and silicone sealant became coagulated, and so the cutting process after drying was difficult. Therefore, the maximum weight ratio of TiO_2 was fixed at 15.0%. In case of the 15.0% TiO_2 weight ratio, the specific gravity of immobilized TiO_2 was 1.18.

When the initial concentration of RhB was 4.7 mg/l, the effect of the TiO_2 weight ratio was examined. Fig. 3 shows that the decrease of the RhB concentration was accelerated with an increase of TiO_2 weight ratio. In the case of TiO_2 weight ratio of 15.0%, 94.4% of the initial RhB concentration was decreased after 20 min and 99.2% was decreased after 60 min.

This result suggested that the higher the TiO_2 weight ratio, the more TiO_2 was located on the surface of immobilized TiO_2, and the more TiO_2 participated in the photocatalytic reaction on the surface of the support media. Therefore, all of the immobilized TiO_2 used in the subsequent experiments had the 15.0% of TiO_2 weight ratio.

3.2. Effect of immobilized TiO_2 dosage and RhB concentration

Fig. 4(a) shows the decrease of RhB concentration with different dosages of immobilized photocatalyst. The decolorization

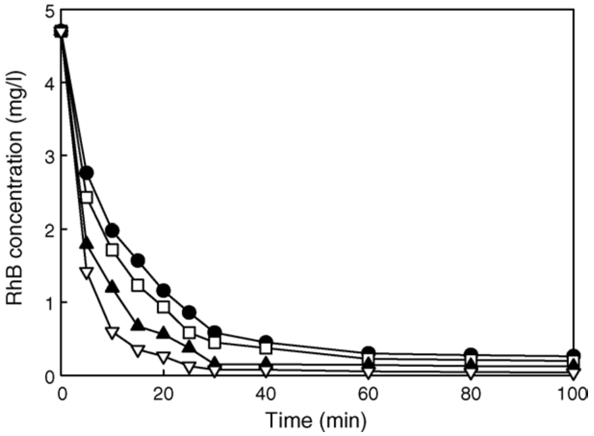

Fig. 3. Effect of TiO_2 percentage of immobilized photocatalyst on the decolorization of RhB. (Immobilized TiO_2: 210.7 g/l, RhB concentration: 4.7 mg/l.) (●) 3.8%, (□) 7.5%, (▲) 11.3% and (▽) 15.0%.

rate of RhB increased with the dosage of immobilized TiO_2. An immobilized TiO_2 dosage over 210.7 g/l was impossible, as the reactor volume was 1.7 l and the bulk volume of 210.7 g/l was about 400 ml and the higher dosage caused the overflow of RhB solution and immobilized TiO_2. The optimum dosage for this reactor system was 210.7 g/l (TiO_2 weight percentage: 15%).

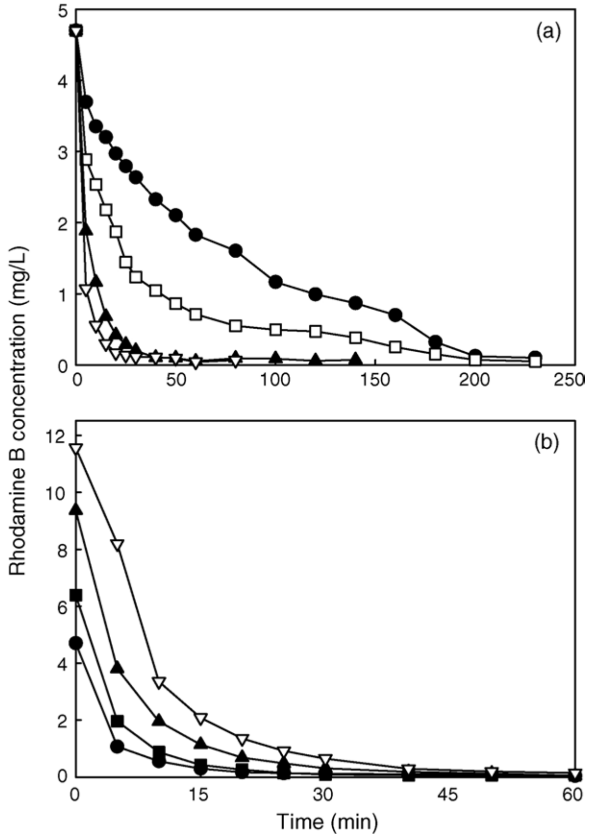

Fig. 4. Effect of immobilized photocatalyst dosage and RhB concentration on the decolorization of RhB. (a) (RhB concentration, 4.7 mg/l) Immobilized TiO_2: (●) 52.7 g/l, (□) 105.4 g/l, (▲) 158.0 g/l and (▽) 210.7 g/l; (b) (Immobilized TiO_2: 210.7 g/l) RhB concentration: (●) 4.7 mg/l, (□) 6.4 mg/l, (▲) 9.4 mg/l and (▽) 11.6 mg/l.

This result is similar to those of other researchers who reported the optimum catalyst dosages for photocatalytic reactions using immobilized photocatalyst [3,11,12].

It was believed that as the dosage of immobilized TiO_2 increased, the number of photons absorbed and the number of RhB molecules increased, owing to an increase the amount of the immobilized photocatalyst. However, above the optimum level of immobilized photocatalyst dosages, the hindrance and blocking of UV light penetration was caused by the excessive amount of immobilized photocatalyst [13].

The relative decreases of the RhB with operation time for various RhB concentrations are shown in Fig. 4(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 TiO_2 surface.

3.3. Initial decolorization rate constants of RhB

In order to examine initial decolorization rate constant, we assumed that the batch-type system used in this study had four RhB decolorization effects: (a) adsorption onto the inside of the apparatus (run 1); (b) direct photolysis by UV irradiation (run 2); (c) adsorption by immobilized TiO_2 (run 3) and (d) photocatalytic oxidation both with the immobilized TiO_2 and UV irradiation (run 4). If each decolorization effect is followed by a first-order reaction expressed as

$$\frac{-\mathrm{d}C}{\mathrm{d}t} = kC,$$

i.e., a linear relationship expressed as $\log C/C_0 = -kt$, the effects of (a), (a) + (b), (a) + (c) and (a) + (b) + (c) + (d) would be observed in runs 1–4, respectively. When the rate constants in equation in runs 1–4 are represented as k_1–k_4, the net rate constants of (a)–(d) can be represented as k_1, $k_2 - k_1$, $k_3 - k_1$ and $k_4 - (k_1 + k_2 + k_3)$, respectively [14].

Fig. 5 shows the change of RhB concentration with reaction time. We regarded this initial decolorization in the first 25 min as

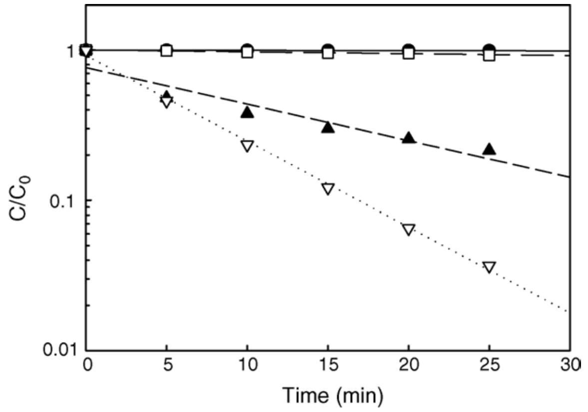

Fig. 5. Time course of the residual ratio (C/C_0) of RhB (C_0: 4.7 mg/l, immobilized TiO_2: 210.7 g/l). (●) Run 1, blank; (□) run 2, UV irradiation only, (▲) run 3, adsorption by immobilized TiO_2 and (▽) run 4, immobilized TiO_2 + UV irradiation.

Table 1
The initial decolorization rate constants of RhB (l/min)

	Rate constants
Blank (run 1)	1.46×10^{-4}
UV-irradiation only (run 2)	1.27×10^{-3}
Adsorption by immobilized TiO_2 (run 3)	2.44×10^{-2}
Immobilized TiO_2 + UV irradiation (run 4)	5.71×10^{-2}

a pseudo first-order decolorization reaction; the decolorization rate constants could be determined from the slope of the lines in Fig. 5. The initial decolorization rate constants of RhB in Fig. 5 are listed in Table 1.

To examine the singular effect of photocatalysis with the immobilized TiO_2 under UV irradiation, the initial rate constants in Table 1 were analyzed. The net-total rate constants excepting adsorption onto the inside of the apparatus ($k_4 - k_1$), was 5.71×10^{-2} (l/min). The net rate constants of photolysis ($k_2 - k_1$), adsorption ($k_3 - k_1$) and photocatalysis [$k_4 - (k_1 + k_2 + k_3)$] were 1.12×10^{-3}, 2.42×10^{-2} and 3.13×10^{-2} (l/min), respectively. It is obvious that the three initial decolorization mechanism, the order of removal is photocatalytic oxidation > adsorption > photolysis.

The results showed that fast decolorization of RhB only occurred in the presence of both a photocatalyst and UV light. The main mechanism of RhB decolorization was considered adsorption followed by photocatalytic oxidation. In addition, the adsorption of the immobilized TiO_2 may be an important factor in RhB photocatalytic decolorization. From the data and observation of the immobilized TiO_2, the sequence of RhB decolorization was estimated as follows: first, RhB can be adsorbed onto the immobilized TiO_2 by adsorption and then decolorized by photocatalysis with UV irradiation. Although the surface area of the immobilized TiO_2 was low, the high decolorization by photocatalysis was considered to result from the fact that UV light penetration was improved by the adsorption at the initial reaction time. Therefore, it can be deduced that the adsorption capacity of the immobilized TiO_2 is assisted the photocatalytic oxidation and may be an important factor in RhB photocatalytic degradation activity.

3.4. Efficiency comparison with suspended TiO_2

In order to compare immobilized $TiO_2$with powdered TiO_2, the same reactor system and UV light source, with Degussa P-25 TiO_2 were used and other conditions are fixed.

Fig. 6 shows the decrease of RhB concentration with different dosages of powder TiO_2. It can be seen that with increasing powder TiO_2 dosage, the decolorization rate of RhB increased. However, the decolorization rate was decreased as the powder TiO_2 dosage increased to 0.3 g/l. The optimum dosage of powder TiO_2 was 0.2 g/l. RhB removal by adsorption in powder TiO_2 was 0.04%, so the adsorption effect was negligible. Fig. 7 shows the initial decolorization rate constant of powder and immobilized TiO_2 for RhB. The obtained initial decolorization rate constant of powder and immobilized TiO_2 are 3.84×10^{-2} and 5.71×10^{-2} (l/min), respectively. However, the specific initial rate constant of powder and immobilized TiO_2were 1.92×10^{-1} and 1.81×10^{-3} (l/min g), respectively.

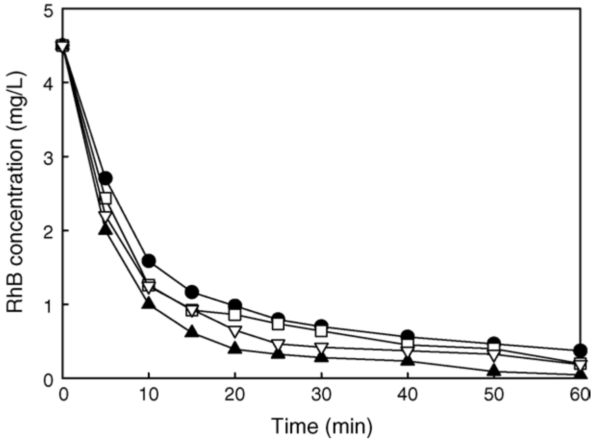

Fig. 6. Effect of powder TiO_2 dosage on the decolorization of RhB. (●) 0.05 g/l, (□) 0.1 g/l, (▲) 0.2 g/l and (▽) 0.3 g/l.

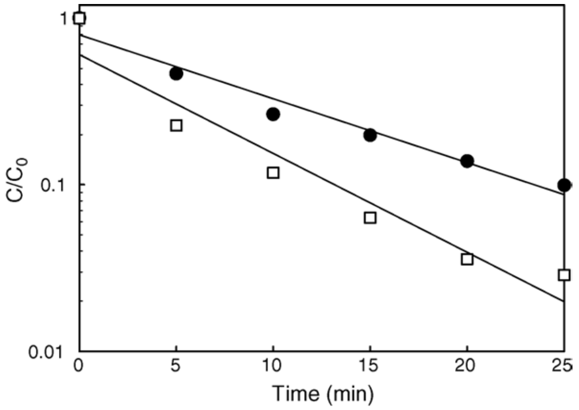

Fig. 7. Comparison of the decolorization rate constants between powder and immobilorized TiO_2. (●) Powder TiO_2 and (□) immobilized TiO_2

In order to examine the different decolorization rate constant of immobilized TiO_2 and powder TiO_2, light intensity passing over the photocatalyst from light source in reactor was measured. Table 2 shows the light intensity of reactor filled with immobilized TiO_2 and powder TiO_2. Light intensity of passing over-immobilized TiO_2 solution is higher 2.9 times than that powder TiO_2.

In spite of the fact that surface area of the immobilized TiO_2 is a much lower than that of powder, the initial decolorization rate

Table 2
Effect of reactor filling materials on the light intensity

	Light intensity of 254 nm (mW/cm^2)
Pure water	2.73
RhB solution (4.7 mg/l)	1.82
RhB solution (4.7 mg/l) + powder TiO_2 (0.2 g/l)	0.18
RhB solution (4.7 mg/l) + immobilized TiO_2 (210.7 g/l)	0.53

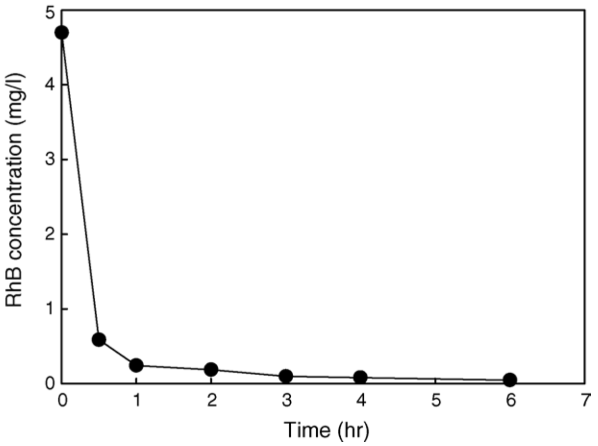

Fig. 8. Effect of HRT on the decolorization of RhB. (Immobilized TiO_2: 210.7 g/l, RhB concentration: 4.7 mg/l.)

of immobilized TiO_2 is larger than that of powder. It was considered that the adsorption capacity of immobilized TiO_2 was much larger and that light penetration was improved as Table 2; then, the light hindrance by the immobilized TiO_2 was smaller than that for the powder. Therefore, the use of the immobilized TiO_2 developed in this study increased the light penetration by adsorption, and so compensated for its small surface area. We can see that the adsorption capacity of the immobilized photocatalyst is very important in photocatalysis. However, much more immobilized TiO_2 was needed than the powder to achieve this initial decolorization rate. For this reason, a study on methods of diminishing the quantity of immobilized TiO_2 is now in progress.

3.5. Continuous operation test and duration of immobilized TiO_2

Fig. 8 shows the decolorization obtained for each hydraulic retention time (HRT: 30 min to 6 h) after operating in a steady state. It was observed that at HRT higher than 3 h the decolorization was nearly completed. Examine the durability of immobilized TiO_2 after a long period of operation, immobilized TiO_2 after continuous operation of 30 days was compared to new immobilized TiO_2. All the studies on RhB decolorization were performed using the same photoreactor and UV source. Fig. 9 shows that the photocatalytic decolorization of RhB did not decrease even after 30 days of use. It can be seen that the efficiency of immobilized TiO_2 did not change with this extensive use. This indicates that immobilized TiO_2 is not deactivated during reactions and can be re-utilized. The weight loss of immobilized TiO_2 after 30 days was about 0.1% (0.2 g).

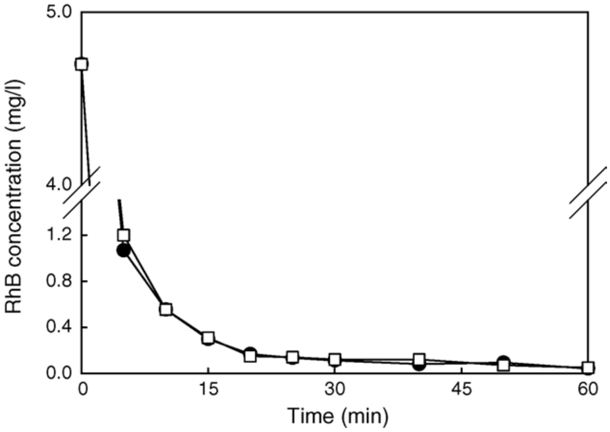

Fig. 9. Comparison of decolorization of RhB with 0 and 30 day of use. (●) Time 0 and (□) 30 days

This is an important feature for a potential use as immobilized photocatalyst working in batch and continuous photoreactor with the fundamental advantages [5].

4. Conclusions

A decolorization system using a TiO_2 photocatalyst supported on silicone sealant was applied to the decolorization of rhodamine B (RhB). The characteristics of the decolorization of RhB were investigated by determining the removal rates from the aqueous phase. The main results are summarized as follows. The optimum reaction dosage of immobilized TiO_2 was 210.7 g/l (TiO_2 weight percentage: 15%). The order of initial decolorization rate is photocatalytic oxidation > adsorption > photolysis. The use of this kind of supported photocatalyst might improve the irradiation efficiency by adsorption, avoid the need of secondary operations like liquid–solid separation and prevent the UV lamp from fouling. Activity of immobilized TiO_2 is not reduced when it is immobilized on a silicone sealant. However, the over-dosage required to achieve decolorization efficiency comparable to that of powder TiO_2 is the main disadvantage. Improvement of immobilized TiO_2 is now in progress.

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