

Photocatalytic Decolorization of Rhodamine B by Fluidized Bed Reactor with Hollow Ceramic Ball Photocatalyst

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Abstract—Photocatalytic degradation of organic contaminants in wastewater by TiO₂ has been introduced in both bench and pilot-scale applications in suspended state or immobilized state on supporting material. TiO₂ in suspended state gave less activity due to its coagency between particles. Recent advances in environmental photocatalysis have focused on enhancing the catalytic activity and improving the performance of photocatalytic reactors. This paper reports a preliminary design of a new immobilized TiO₂ photocatalyst and its photocatalytic fluidized bed reactor (PFBR) to apply photochemical degradation of a dye, Rhodamine B (RhB). But it was not easy to make a cost-effective and well activated immobilized TiO₂ particles. A kind of photocatalyst (named Photomedium), consisting of hollow ceramic balls coated with TiO₂-sol, which was capable of effective photodegradation of the dye, has been presented in this study. The photocatalytic oxidation of RhB was investigated by changing Photomedia concentrations, initial RhB concentrations, and UV intensity in PFBR.

Key words: Photocatalyst, Fluidized Bed, Immobilization, TiO₂, Toxicity

INTRODUCTION

Industrial development is pervasively connected with the disposal of number of toxic pollutants that are harmful to the environment and the human and are also not easily degraded in nature. In particular, the wastewater from a textile dyeing process contains numerous concentrated organic compounds that are toxic and colorful, which causes ineffectiveness of biological treatment [Nigam et al., 1996]. Photocatalytic treatment is an attractive alternative, since it does not need oxidants and does not produce secondary pollutants [Ollis et al., 1991]. The mechanism of the photocatalytic oxidation of organic contaminants by TiO₂ has been studied and explained by the band gap energy model [Turchi et al., 1990]. When Ultraviolet (UV) illumination irradiates energy ($\lambda < 380$ nm) higher than the band gap energy of TiO₂ ($E_g \approx 3.2$ eV, for anatase phase), electrons in TiO₂ shift to the conduction band which creates a hole in the valence band. With the presence of water trapped by interfacial electron transfers, hydroxyl radicals (OH \cdot) are formed on the semiconductor surface, which leads to a degradation of the organic contaminants [Huang et al., 1993].

The photocatalytic degradation of organic compounds by dispersed semiconductor powder has been conducted for many years [Kim, 2001].

Two specific types of the catalyst are currently favored for photocatalytic processes: (a) finely divided and slurried powder for aqueous reactions, or (b) immobilized coating on supporting materials in fixed or fluidized bed configuration [Pozzo et al., 2000].

Since the slurry type reactor needs filtration and resuspension process, it is practically impossible to use catalytic suspension in any wastewater treatment process.

Although a fixed bed catalytic system has an advantage that no separation step is necessary, the efficiency of the fixed bed reactor is comparably low since the utilization of UV light is not effective due to absorption and scattering of the light within the reactor and the limited active surface area of photocatalyst [Wang and Ku, 2003].

A fluidized bed reactor is known as a good chemical reactor for its excellent mass and heat transfer properties. It is believed that the fluidized bed reactor has advantages in better use of light, easy temperature control, and good contacting between target compound and photocatalysts, compared to the slurry reactor or the fixed bed reactor [Nam et al., 2002].

In this study, the photocatalytic degradation of RhB was discussed. The suggested photocatalytic fluidized bed reactor (PFBR) was filled with hollow ceramic balls coated with TiO₂ powders.

MATERIALS AND METHODS

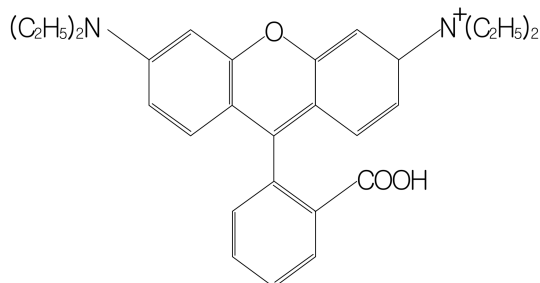


Fig. 1. The structure of RhB.

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[‡]This paper is dedicated to Professor Hyun-Ku Rhee on the occasion of his retirement from Seoul National University.

1. Materials

1-1. Rhodamine B (RhB)

The dye, RhB (reagent grade, 95% pure) is used as a test pollutant. Its structure is given in Fig. 1. The RhB is sold as a green crystal or a reddish-violet powder. It is highly soluble in water and organic solvent and its molecular formula is $C_{28}H_{31}CN_2O_3$ (mol wt 479.00). Its color is fluorescent bluish-red. The RhB has been used as a dye especially for paper and as a biological stain. But, the RhB has been found to be a potentially toxic and carcinogenic substance. This compound is now banned for food and cosmetic usages [Merck index, 1996].

1-2. Photomedia

The Photomedia were prepared by following procedures. Zeolite, glass and TiO_2 powder were mixed with silicone sealant. The mixture was coated onto the surface of the EPS (Expandable Polystyrene) with mean diameter of 1.4 mm and was dried at room temperature in a dust-free environment for 24 hours. Then, the EPS ball was calcinated at 800-1,100 °C in furnace for 4-8 hours to form a hollow ceramic ball. The hollow ceramic ball was dipped into a colloidal suspension (TiO_2 sol: TiO_2 content 1%, Deiha-international, Korea) for 1 minute and dried at room temperature in a dust-free environment for 24 hours, then calcinated at 500 °C in air for 2 hours. The average diameter of the Photomedia was about 1.5 mm and the thickness, approximately 65 μm (Fig. 4).

1-3. Photoreactors

The specific design of PFBR (Fig. 2) was as follows. Four 20 W UV lamps (Sankyo Denki) were installed inside the reactor (Volume; 24 L). The vertical plate inside the reactor and the air stream blowing from the bottom of the reactor at the rate of 1 L/min helped make it possible for Photomedia and reactants to be well fluidized and mixed perfectly.

1-4. Analysis of Data

The spectrophotometer (Lambda 20: PERKIN ELMER) was used for analyzing optical absorption spectra of degraded RhB solution. The maximum adsorption wavelength was found to be 550 nm. The RhB concentration was calculated by the calibration curve of RhB concentration at wavelength of 550 nm.

The hardness of the Photomedium was measured by DMA (Dynamic Mechanical Analyzer). Oxygen, silicon and titanium elements of the surfaces of the Photomedia were measured by the SEM/

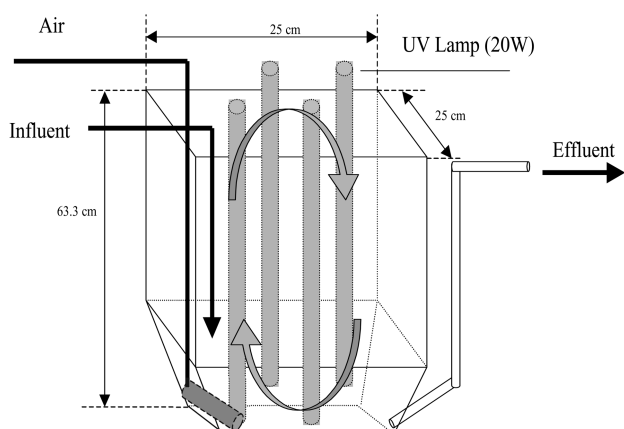


Fig. 2. The schematic diagram of PFBR.

EDX analyzer (HITACHI S-4200, Japan).

EC_{50} is the effluent concentration that causes a measurable negative effect on 50 percent of the test population. EC_{50} was investigated to evaluate the toxicity of RhB and its reaction intermediates. This was determined by Microtox Toxicity Screening Test System (Microtox M500) using *Vibrio fischeri* as a test microorganism.

RESULTS AND DISCUSSION

1. Hardness of Photomedium

Sintering time and temperature were varied to find an optimum condition for durable Photomedia. Fig. 3(a) and (b) show the hardness of the Photomedia. The Photomedia incinerated at 800 °C were so fragile that their hardness was unmeasurable. When incinerated at 1,100 °C, the particles melted. The Photomedia prepared both with/without TiO_2 powder had a maximum value in hardness when incinerated at 900-1,000 °C. At the temperatures of 900 °C and 1,000 °C (except 5 hours), the hardness of the Photomedia premixed with TiO_2 powder were approximately twice higher than those without TiO_2 powder.

Calcination temperature of 900 °C for 6 hours with TiO_2 powder showed the highest value of hardness.

2. Effect of the Number of Coating with TiO_2 -sol

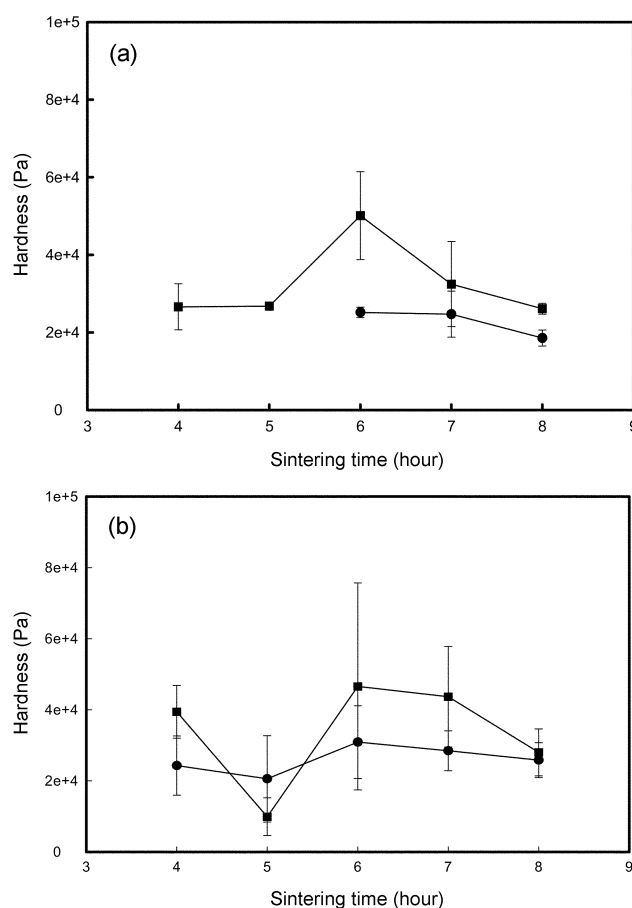


Fig. 3. The effect of sintering time on the hardness of the Photomedium.

(a) 900 °C, ● without TiO_2 ; ■ with TiO_2
 (b) 1,000 °C, ● without TiO_2 ; ■ with TiO_2

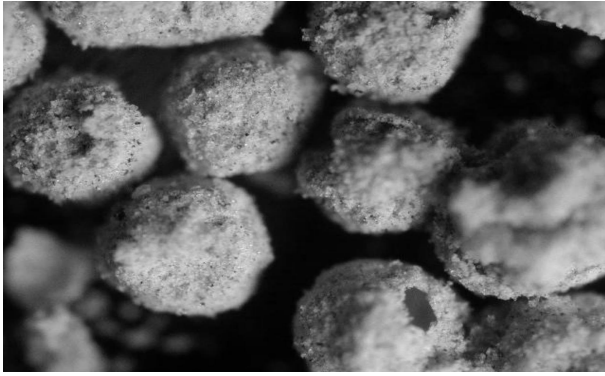


Fig. 4. The SEM photograph of Photomedia ($\times 40$).

Table 1. Atomic composition (%) of the surface of the Photomedium

No. of coating	0	1	2	3	4	5	6
O	67.83	67.83	63.41	65.03	67.10	68.78	58.32
Si	24.04	21.82	20.00	13.97	9.31	7.18	11.61
Ti	0	10.35	16.60	21.01	23.59	24.04	30.07

The preparation process of the TiO_2 coated hollow ceramic ball was previously explained in detail [Na et al., 2001]. The analysis of the EDX showed that the Photomedium has oxygen and silicon on its surface along with a small amount of potassium and calcium (Table 1).

The effect of the numbers of coating with TiO_2 -sol on dye decomposition was investigated with the initial concentration of the RhB, $6.8 \mu\text{M}$. Fig. 5 showed that the decrease of RhB concentration was steepened according to the number of coatings up to three times. But, from the quadruple coating, there was no remarkable decrease of the RhB concentration and showed similar decreasing trend of the triple coating. Although the surface coverage of TiO_2 on the Photomedia increased with the number of coatings, the increase was significant up to triple coating and no remarkable increase was shown with further coatings.

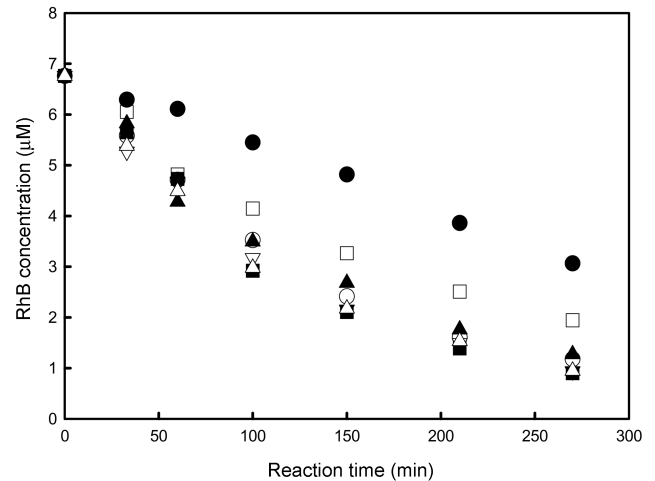


Fig. 5. The effects of reaction time on the decolorization of RhB (number of TiO_2 -sol coating; ● one, □ two, ▲ three, ▽ four, ○ five, ■ six, △ seven).

Fig. 6 showed SEM photographs of the Photomedia with the number of coatings. The Photomedium without coating by TiO_2 -sol [Fig. 6(a)] showed flat surface, whereas titania particles in the coated samples were well distributed on the surface of the supporting material with nanometer size. When the surface coverage of TiO_2 was compared in Fig. 6(b) and Fig. 6(c), the content of titania on surface of the sixfold coated Photomedium was a little higher than that of the triple coated one, but titania layer of the sixfold coated Photomedium was thicker than that of the triple-coated one due to the overlap of TiO_2 particles.

From the analysis of the Photomedia by EDX and SEM, it was found that the titanium atom showed rapid spread until triple coating, but there was no significant increase after quadruple coating. It was considered that formation of multiple layers especially more than 4 times did not alter the density of TiO_2 active site on its surface.

This result suggested that the optimum number of coating was 3 for the decomposition of RhB. Therefore, all of the Photomedia used in next experiments were fixed at triple coating.

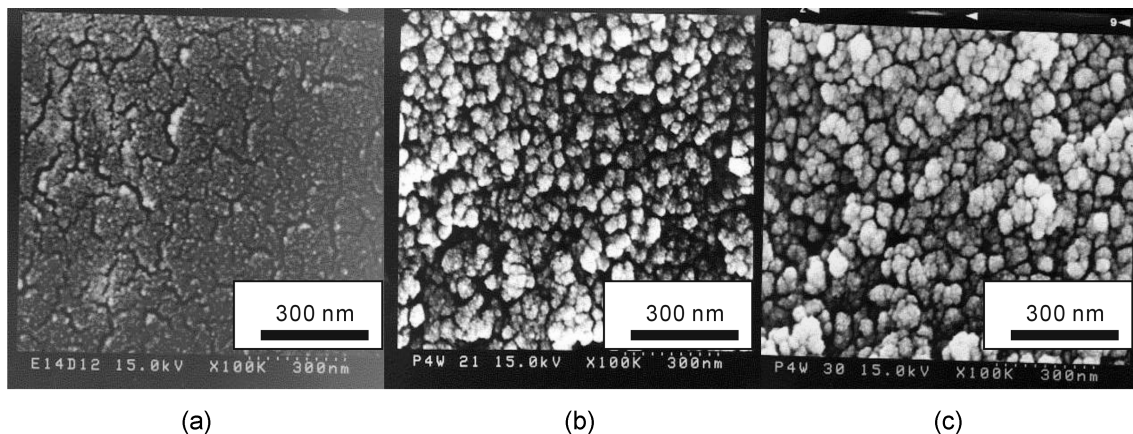


Fig. 6. The SEM photography of Photomedium ($\times 100,000$).

(a) no coating, (b) triple coating, (c) six-time coating

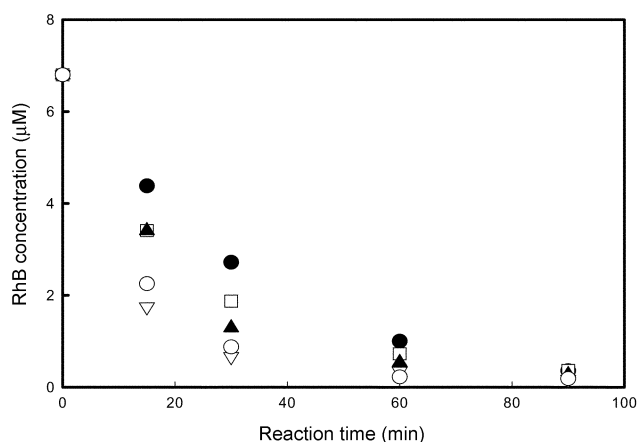


Fig. 7. The decolorization of RhB with reaction time (loading of Photomeedia; ● 5 g/L, ▲ 10 g/L, ▲ 15 g/L, ▽ 25 g/L, ○ 50 g/L).

3. Effect of Photomeedia Dosages

Since the photocatalytic reaction is governed by photon efficiency and mass transfer limitation, the reaction mechanism is believed quite different from those of conventional heterogeneous catalytic reactions. Fig. 7 showed the degradation of RhB with different dosages of Photomeedia. The degradation rate of RhB increased with the dosage of the Photomeedia. However, the degradation rate was not significantly enhanced as the Photomeedia dosage increased beyond 25 g/L. Thus, there might be an optimum dosage for this photocatalytic reaction. This result was similar to what other researchers reported the optimum catalyst dosage for the photocatalytic reaction using the TiO₂ powder [Tang and An, 1995].

It could be explained as follows. As the dosage of the Photomeedia increased, the number of photon absorption increased, but above certain level of the Photomeedia dosage, the hindrance and blocking of UV light penetration occurred in the reactor medium by excessive amount of the Photomeedia.

4. Effect of Initial Concentration of RhB

Fig. 8 shows that the relative decrease of the RhB concentration depending on the operation time for various initial concentrations.

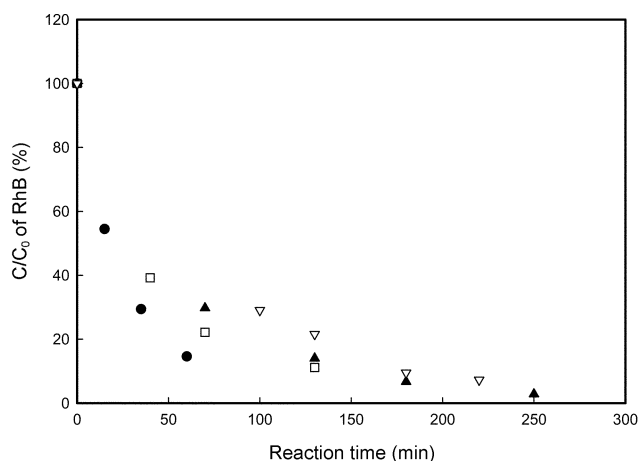


Fig. 8. The decolorization of RhB with reaction time (concentration of RhB; ● 5 μM, ▲ 13 μM, ▲ 22 μM, ▽ 29 μM).

As the initial concentration of RhB increases, the reaction rate decreases. It is believed that the increased RhB concentration bans light penetration into the RhB solution and fewer photons can reach on the TiO₂ surface.

In a previous experiment, the data from the slurry reactor (with initial concentration of 6.8 μM RhB and optimum TiO₂ dosage of 2 g/L) showed the degradation constant of RhB, $50.3 \times 10^{-3} \text{ min}^{-1}$, whereas that of the photocatalytic fluidized bed reactor (PFBR) of this study (with the same initial concentration and optimum photomeedia dosage of 25 g/L) was $41.1 \times 10^{-3} \text{ min}^{-1}$. In spite of the fact that the degradation constant obtained by PFBR with the Photomeedia was slightly lower than that by the slurry TiO₂ system, the result demonstrated that the immobilized TiO₂ in PFBR presented an active degradation of the dye. Moreover, as mentioned before, the advantage of an immobilized system was that no separation stage of photocatalysts is required.

Generally, for the photocatalysis using TiO₂ powder, Langmuir-Hinshelwood model is used to represent the adsorption of reactants on the catalyst surface. The kinetic rate of RhB was expressed as follows:

$$R = \frac{kKC}{1+KC} \quad (1)$$

Where C is the concentration of the RhB, k is the rate constant of the RhB and K is the equilibrium constant of adsorption. If this equation represents the photocatalytic reaction, a plot of initial data of 1/R vs. 1/C should be linear, because Eq. (1) can be transformed to the following equation.

$$1/R = \frac{1}{kKC} + \frac{1}{k} \quad (2)$$

The result data of the RhB decomposition reaction based on the Eq. (2) were fitted with satisfaction as a straight line (Fig. 9). Constant values corresponding to k and K were $0.106 \text{ (mg/L/min)}^{-1}$, $0.173 \text{ (mg/L)}^{-1}$, respectively. Chen and Chou [1993] and Nam et al. [2002] also investigated the reaction model for the photocatalytic oxidation of dye in a slurry and a fluidized bed reactor (TiO₂ of powder type) and obtained linear relation of reciprocal of the initial rate

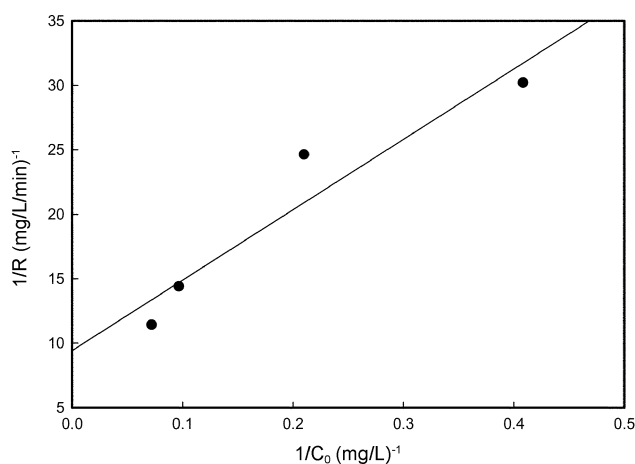


Fig. 9. The relationship between the reciprocal initial decolorization rate and the reciprocal initial concentration of RhB (Photomeedia loading of 25 g/L).

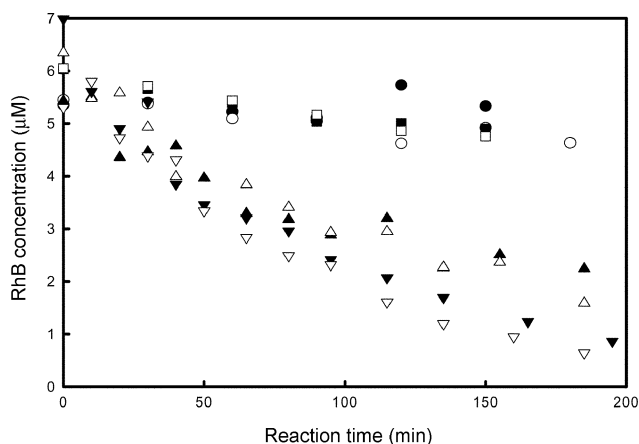


Fig. 10. The concentration variation of RhB with reaction time at various lamp condition (Photomedia of 25 g/L).

● 1 lamp without Photomedia, ○ 2 lamps without Photomedia, ■ 3 lamps without Photomedia, □ 4 lamps without Photomedia, ▲ 1 lamp with Photomedia, △ 2 lamps with Photomedia, ▼ 3 lamps with Photomedia, ▽ 4 lamps with Photomedia

with the reciprocal of initial concentration.

Therefore, it could be concluded that the Langmuir adsorption model well described the effect of the initial concentration of RhB on the photocatalytic oxidation of RhB with immobilized TiO_2 particles on the surfaces of the Photomedia in a fluidized bed reactor.

5. Effect of UV Intensity

Lee et al. [2003] reported the rate of photon generation increased linearly as the number of the lamps increased. Fig. 10 showed the effect of the irradiated light intensity and the presence of photocatalyst on the photocatalytic degradation of RhB with reaction time. When the number of UV lamps increased without Photomedia, the rate of RhB degradation increased, but the change was negligible. The result showed that fast degradation rate of RhB was possible only in the presence of both photocatalyst and suitable UV light.

The higher the light intensity, the greater photocatalytic reaction rate was observed. Both optimum Photomedia concentration and higher irradiated light intensity could enhance the degradation rate of RhB. More than 87% of conversion yield of RhB in 180 minutes of reaction time was observed in this experimental condition of 25 g Photomedia/L in the solution and four UV lamps (20 W).

6. The Test of EC_{50} of the Effluent

Total mineralization of organics to CO_2 and H_2O cannot be obtained sometimes on actual photocatalysis reactor. In this case, some of these reaction intermediates could be more toxic than the primary compounds. Jardim et al. [1997] monitored the toxicity of pentachlorophenol (PCP) and 2,3,5-trichloro phenol (2,3,5-TCP) solution irradiated in the presence of TiO_2 powder and found that the intermediates of PCP and 2,3,5-TCP were more toxic than the parent compounds.

In order to determine the toxicity of the intermediates of RhB, *Vibrio Fischeri* was used as a test microorganism for both the raw RhB and the solution after the reaction (Initial RhB concentration, 6.8 μM ; Photomedia dosage, 25 g/L; Reaction time, 270 min). EC_{50} was 1.1 μM in raw RhB but no toxicity was detected in the effluent of RhB solution (Table 2). This implied that the photodegraded efflu-

Table 2. The value of EC_{50} of the influent and the effluent on RhB treatment in PFBR

Sample	EC_{50} , %	Confidence range
Raw RhB	$\text{EC}_{50}@30 \text{ min}$ 18.37 (1.1 μM)	16.98-19.87
Effluent	$\text{EC}_{50}@30 \text{ min}$ ND*	ND

* ND: Not Detected.

ent did not influence the bioenvironmental system. Hence, it was possible to combine the photocatalytic treatment with a biological treatment of recalcitrant dyes.

CONCLUSION

It has been shown that the photocatalytic fluidized bed reactor with the hollow ceramic ball coated with TiO_2 , effectively photocatalyzed the degradation of RhB. The optimum coating of the Photomedia with TiO_2 powder was triple layer. It was also observed that the optimum catalyst loading for a slurry reactor was 25 g/L. The increase of initial concentration of RhB resulted in the decrease of photocatalytic reaction rate because of the decrease of light penetration. Initial degradation rate of RhB with the Photomedia has been successfully described by using the Langmuir-Hinshelwood rate expression. When both TiO_2 and UV light were present, the color of RhB dye was almost completely decomposed in a short time. The EC_{50} of treated RhB solution did not show any toxicity. The main advantage for the use of PFBR with the Photomedia was its potential application in flow reactors eliminating the catalyst recovering stage.

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