Photodegradation of Rhodamine B in TiO$_2$ suspension

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In recent years, rapid technological advances in the textile and dyeing industry have yielded benefits to society but have also generated new and significant environmental problems. The treatment alternatives applicable for the removal of color vary, depending upon the type of dye wastewater. Advanced oxidation processes are considered to provide more permanent merits. One of these oxidation treatments attracting much attention is photocatalytic oxidation, which uses TiO$_2$ due to its non-toxic, insoluble liquid as well as a highly reactive nature under UV irradiation. This study sets out to demonstrate the effect of photocatalyst dosage, dye concentrations, pH and light intensity on color removal efficiency under aerobic conditions. The results of this study show Rhodamine B(RhB) was not decolorized when a dye solution was exposed only to air or treated by TiO$_2$ only. In the presence of both TiO$_2$ and UV light, however, the presence of RhB decreased up to 95 % within 60minutes. The more addition TiO$_2$ and the more diluted dye solution, showed a higher removal rate.

Key words : Photocatalyst, UV light, reaction rate, oxidation

1. Introduction

The total number of industrial factories equipped with wastewater disposal plants in Korea was 37,621 in 1998, and the methods of wastewater treatment largely depended on physical process(5 %), chemical process(50.8 %), biological process (4.5 %), integrated treatment process(6.6 %), advanced treatment process(0.1 %), consigned treatment company(30.8 %) and the rest(2.2 %). But there are some serious difficulties in the case of biological treatment because most of the industrial wastewaters have highly concentrated organic compounds, which are characteristic of toxic or non-biodegradable substances.

Particularly, the textile industries require fairly large capacities of water with organic materials[1]. Most of these manufactures adopt the biological treatment method. However research to increase the efficiency of the process is being performed lately because the wastewater contains a large amount of nonbiodegradable organic material[2].

Physical and chemical methods are largely dependent on coagulation and adsorption at present, and these processes usually produce secondary pollution. Thus, lately many research groups have investigated the decomposition of organic compounds by UV/ TiO$_2$ photocatalytic systems.

The COD value was remarkably decreased during the decolourization reaction of colored sewage using the UV/ TiO$_2$ system devised by David et al.(1994)[3]. Chen et al.(1993)[4] reported that the decolorization of methyl orange was achieved completely within 40 minutes. Z. Li X. et al. (1996)[5] made an experiment of decomposition of reactive dye under various conditions using UV energy(NEC black light lamp) with TiO$_2$ powder and reported a distinct decrease of COD after about 4~6 hours through the step to form intermediates. Shu et al.(1994)[6] showed the possibility of treatment of azo dye wastewater using ozone and a low-pressure UV lamp(500W). Keiichi Tanaka et al.(2000)[7] reported that the step when a TiO$_2$ surface absorbs dye molecules is the rate-determining step for the photocatalytic

decomposition of commonly used azo dye, and the photocatalytic reaction proceeds by reacting between a positive hole and a OH radical, through the reduction reaction of electrons on the conduction band.

In this study, we investigated factors that affected the reaction efficiency of decomposing RhB by UV/TiO_2 process and produced optimum reaction conditions.

2. Material and Method

2.1. Reactor

A cylindrical reactor made of pyrex was used in this experiment. Its inside diameter is 12 cm and the height is 10 cm. The solution was convectively mixed by a magnetic stirrer to accelerate the rate of reaction. The rotation speed was kept at 200 rpm.

2.2. Materials

The chemical reagent, RhB(N-[9-(2-carboxy-phenyl)-6(diethylamino)-3H-xanthen-3ylidene]-N-ethylethan-ammoniumchloride ; tetraethyl-rhodamine) with a purity of 95 % was used as a target material for photocatalytic decomposition. RhB is a dye named Basic Violet 10 and consists of green crystals or fine reddish-violet particles. The solubility in water and organic solvents is high and the color of a RhB-solution shows bluish-red and fluorescence[8].

TiO_2 used as a photocatalyst is a special-grade reagent of Junsei Chemical Co., Ltd. and its crystalline structure was confirmed by XRD analysis as an anatase structure. UV lamp of Sankyo Danki GL 20(10W, 254 nm) was used as a light source and all experiments were carried out under a constant light intensity except for the experiment which measured the effect of UV light intensity on efficiency.

2.3. Determination of RhB concentration

After TiO_2 powder is removed from the slurry solution by centrifuging at the speed of 2500 rpm for 30 minutes, a solution free from TiO_2 powder is obtained. The concentration of RhB is measured by using the calibration curve, which is drawn at 550 nm absorbance in a UV/VIS spectro-

photometer(Lambda 20 ; PERKIN ELMER).

2.4. Experimental procedures

The test of photodegradability of TiO_2

To examine the photodegradability of TiO_2 in the RhB solution, four different experimental conditions were studied : (1) in the dark without TiO_2(control condition) ; (2) UV irradiation without TiO_2 ; (3) in the dark with of TiO_2 ; (4) UV irradiation in the presence of TiO_2. The power of the UV lamp was 10W and the illumination proceeded for 450 minutes. During the experiment, the initial concentration of RhB was kept at 22 μM, and the amount of TiO_2 was 0.1 g/L.

The effect of Photocatalyst dosage

The concentration variation of RhB was measured at constant time intervals when the amount of TiO_2 was varied as 0.1 g/L, 0.25 g/L, 0.5 g/L, 1.0 g/L, 2.0 g/L and 5.0 g/L and the initial concentration of RhB was 22 μM.

The effect of initial concentration of RhB

The concentration change of RhB was investigated under various initial concentrations of RhB, 5.74 μM, 9.58 μM, 15.2 μM, 21.1 μM, 28.2 μM and 37.9 μM when the amount of the TiO_2 catalyst was kept at 2 g/L.

The effect of pH

The change of pH and the rate of decolorization of the RhB were monitored during the course of photocatalytic reaction when the initial pH of solution was changed from 3.2 to 10.83. NaOH solution(1N) and HCl solution(1N) were used to adjust the pH of the solution. The amount of the TiO_2 catalyst was kept at 2 g/L and the concentration of RhB was 22 μM.

The effect of light intensity

The effect of light intensity change on the rate of photoreaction was investigated and the intensity of light illumination was measured by Radiometer(International light Inc.). The initial concentration of RhB was kept at 5 μM and the amount of TiO_2 was 1g/L.

3. Results and Discussions

3.1. The test of photodegradability of TiO₂

As shown in Fig. 1, a very small decrease in the concentration of RhB was observed when only TiO₂ was applied to decompose. This result shows that the photodegradability of TiO₂ dose not appear in the absence of UV light, while 18% decomposition efficiency was obtained with only UV light. However, when both TiO₂ and UV light were applied simultaneously, more than 80% decomposition efficiency was obtained. From these results, it is concluded that RhB is relatively stable to air and UV light, but when TiO₂ and UV light are present, the photocatalytic decolorization of RhB can be easily achieved.
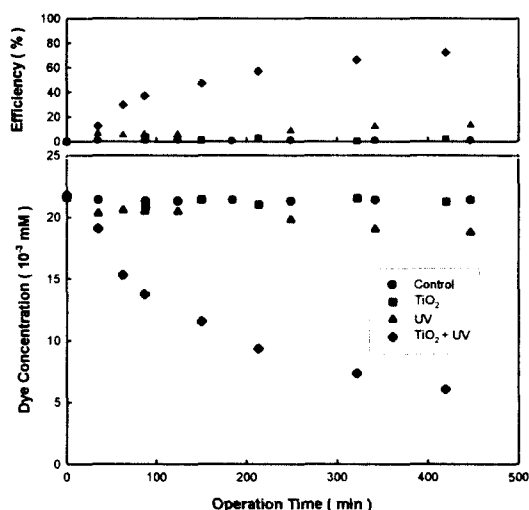
Fig. 1. Variation of Rhodamine B concentration with operation time(Lamp : Sankyo Danki GL 20, 254 nm).

3.2. The effect of photocatalyst dosage

The variation in degree of decolorization of RhB against the concentration of TiO₂ is shown in Fig. 2. More than 70 % decomposition efficiency of RhB was obtained at the concentration of more than 1g/L TiO₂ within 60 minutes. The rate of reaction increases when the amount of the phtocatalyst increases. It is considered that the contact area between the photocatalyst and the UV light broaden as the concentration of TiO₂ increases.

At a concentration of 0.1 g/L TiO₂, the efficiency was lower than 50 % even though the

reaction time was within 100 minutes. It was considered that the concentration of the photocatalyst is so low that the contact point which produced OH radicals was limited. This result was identical with the results of Turch *et al.*[9] study that the rate of reaction decreases with the low concentrations of the photocatalyst. Active site are required to form OH radicals and they sufficiently exist with excessive amount of TiO₂. However, the opposite effect appears in a photocatalytic oxidation reaction when TiO₂ presents too excessively.

In this study, the rate constant at TiO₂ concentration 2.0 g/L was higher than that at TiO₂ concentration 5.0 g/L.

This result was identical with the results of Hermann *et al.*[10] that the rate of reaction increases with the amount of photocatalyst until the photocatalyst can completely absorb the UV light, but the rate of reaction can't be expected to increase if the amount of TiO₂ is excessive.
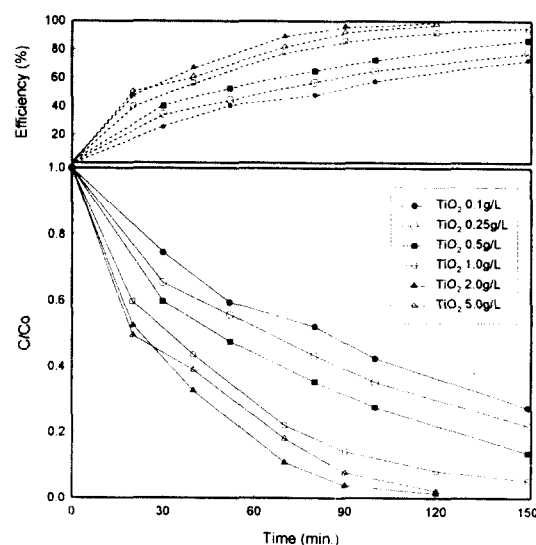

Fig. 2. Effect of TiO₂ concentration on Rhodamine B degradation(Lamp : Sankyo Danki GL 20, 254 nm).

3.3. The effect of RhB concentration change

The effect of RhB concentration on decomposition efficiency is shown in Fig. 3. The initial concentration of RhB was varied from 5.74 μM to 37.9 μM and more than 90 % removal efficiency was obtained within 100 minutes below
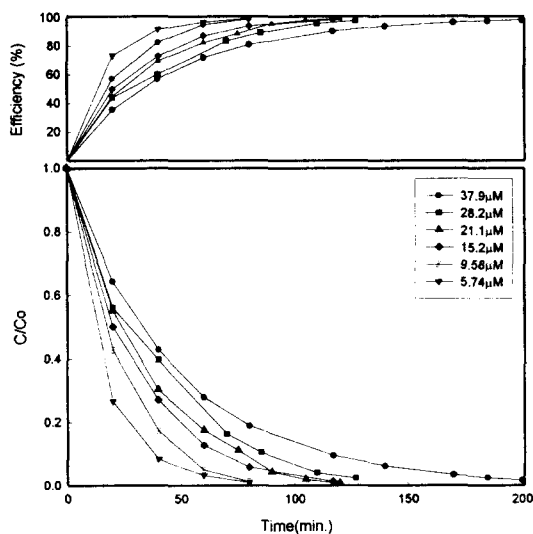
Fig. 3. Effect of dye initial concentration on photo-catalytic degradations(Lamp : Sankyo Danki GL 20, 254 nm).

the concentration of 37.9 μ M. Higher efficiency was obtained when the concentration of the target material is low in the photocatalytic oxidation reaction. Generally, it was reported that the kinetic formula of the photocatalytic oxidation reaction was represented by the Langmuir-Hinshelwood mechanism.[11~13] The formula of reaction kinetics is as follows.

$$r = - dC / dt = k_r KC / (1+KC)$$

k_r : kinetic constant

K : equilibrium adsorption constant

For low concentration of RhB, the equation becomes,

$$r = k_r KC$$

If $k_r K$ is represented as k,

$$r = -dC / dt = kC$$

Since,

$$C = C_0 \text{ at } t = 0, \ \ln(C/C_0) = -k_t$$

It is reported that the photocatalytic decomposition reaction follows pseudo-first-order rate kinetics.[14] When the change of concentration was plotted versus time, the slope became steeper as the concentration decreased, which shows the same results(Fig. 4).

If this equation and the preceeding equation are compared, the following relation can be obtained.

$$k_d = k_r K / (1+KC)$$

From this expression, it shows that the reaction rate constant k_d increases as the initial concentration of RhB decreases.
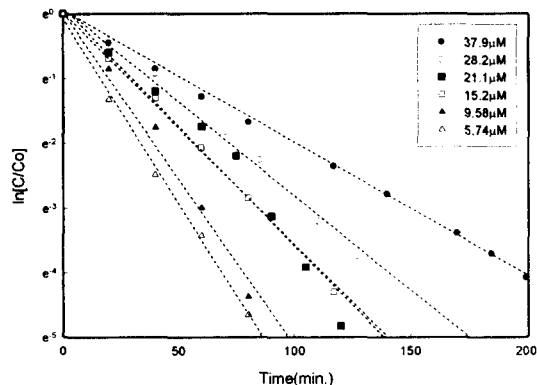

Fig. 4. First-order plot of Rhodamine B in various initial concentration(Lamp : Sankyo Danki GL 20, 254 nm).

3.4. The effect of pH change on pho-tocatalytic reaction

To examine the effect of pH change on photocatalytic reaction rate, the decomposition of RhB was investigated under various ranges of pH(Fig. 5). The pH of the slurry solution approached pH 4 ~ 5 even if the initial pH changed to 3.2 ~ 8.57 after 200 minutes of reaction time. More than a 90 % removal efficiency of RhB was obtained for all ranges of pH within 100 minutes(Fig. 6). The removal efficiency was increased slightly when the pH was decreased. The zeta potential of TiO_2 and RhB is represented in Fig. 7. When the pH was increased, the zeta-potential value became negative from a positive charge, i.e., 6.65 mV, -17.49 mV, -26.26 mV at pH 3, 7, 10 respectively at the TiO_2 powder. When the pH was increased, the repulsion between TiO_2 surface and RhB molecule was increased, so the removal efficiency was decreased because the amount of initial adsorption of RhB on the TiO_2 surface was decreased. And it was expected that the removal efficiency was high at pH 3.2 because the adsorbed amount of RhB was increased on the TiO_2 surface in an acidic condition. But the removal efficiency was slightly higher at pH 3.2 than at any other pH condition. This was a result of the isoelectric point of

solution. At a low pH the coagulation of TiO_2 particles occurs because the potential of TiO_2 surface decreases, and the coagulation occurs maximally at pH_{zpc} 3.96. Considering the coagulation only, the removal efficiency would be lower at pH 3.2 close to pH_{zpc} than at any other pH, since the mean diameter of particle becomes the largest at the vicinity of zero potential charge and the reaction surface decreases. Consequently, the effects of RhB adsorption on the TiO_2 surface was counterbalanced by the effect of coagulation on the TiO_2 particle.
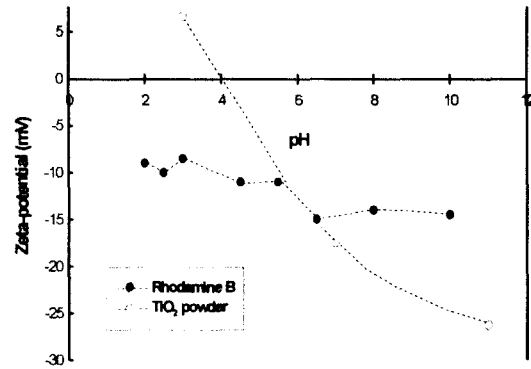
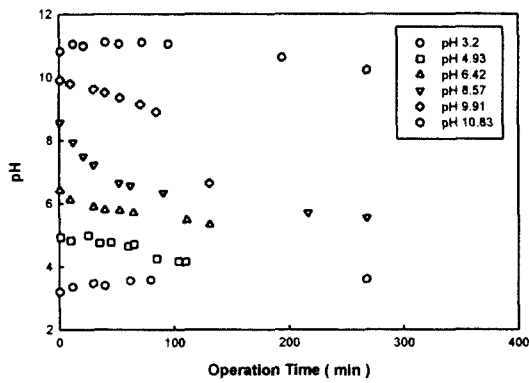Fig. 7. Zeta potential of RhB and TiO_2 as function of pH.

3.5. The effect of intensity of light illumination

A light wavelength lower than 400 nm is required to examine the characteristics of TiO_2 photocatalyst. Generally, it is known that the rate of reaction is proportional to I(light intensity) at low intensity of illumination and $I^{1/2}$ at high intensity of illumination. If the intensity of UV illumination becomes high, the efficiency of reaction can be improved owing to the elevation of quantum yield. Particularly, the temperature of the solution increases owing to the vigorous illumination of UV irradiation, and the higher temperature accelerates the reaction rate of decomposition, and increase the efficiency.[15] To adjust the illumination intensity of a 10 W UV lamp, the relation between distance and illumination intensity was studied by using a Radiometer(Fig. 8). From this result, the relation equation $Y[mW] = -0.1308 \times X[cm] + 0.9596$ was derived. The result of RhB decomposition is shown in Fig. 9 when UV light intensity was increased. More than 95 % decomposition efficiency of RhB was obtained at the UV light intensity of 1060 mW within 60 minutes. The reaction rate constant increases with increasing intensity of light, i.e., 0.026 min^{-1}, 0.029 min^{-1}, 0.038 min^{-1}, 0.051 min^{-1} at 701 mW, 750 mW, 832 mW, 1060 mW, respectively. In Fig. 10, the reaction rate constant was increased linearly with the intensity of UV light as showing high correlation(r = 0.982) within the range of UV light intensity in this study.

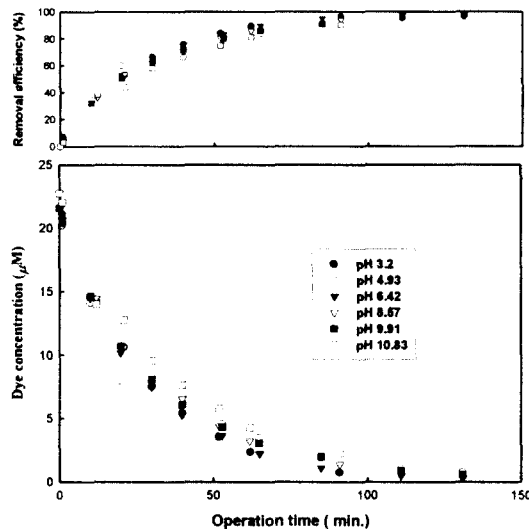Fig. 5. Variation of pH with operation time(Lamp : Sankyo Danki GL 20, 254 nm).

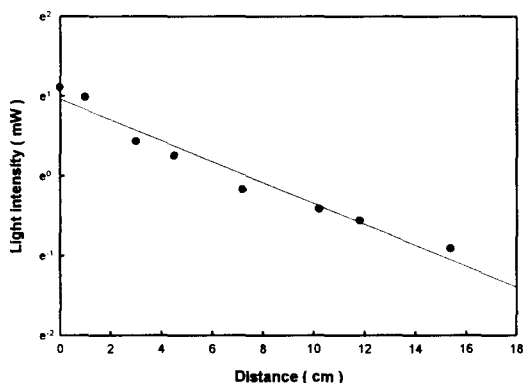Fig. 6. Variation of Rhodamine B concentration with operation time(Lamp : Sankyo Danki GL 20, 254 nm).

Fig. 8. Variation of light intesity with distance between UV lamp and suspended solid surface(Lamp : Sankyo Danki GL 20, 254 nm).
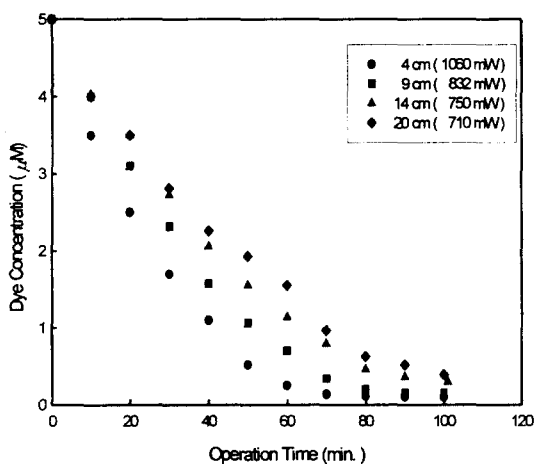

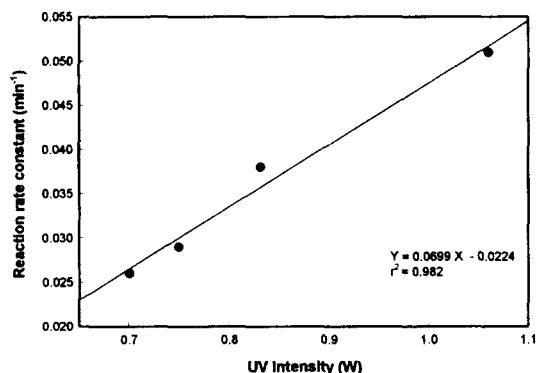Fig. 9. Variation of Rhodamine B concentration with UV light intensity.

Fig. 10. Variation of reaction rate constant with UV intensity.

4. Conclusions

We investigated factors which affect the phtocatalytic oxidation reaction of RhB. The decomposition of RhB dye by using TiO_2 did not occur when the UV light was absent. However, when both TiO_2 and UV light were present, RhB decomposed substantially by way of an OH radical which was formed on a photocatalyst surface.

More than 70 % decomposition efficiency of RhB was obtained at concentrations of more than 1g/L TiO_2 within 60 minutes. The rate of reaction increased when the phtocatalyst increased. It was considered that the contact surface area of photocatalyst and UV light became broader as the concentration of TiO_2 increased. Therefore the rate of photocatalytic reaction became faster. For the effect of initial concentrations of RhB, the efficiency of decomposition increased when the initial concentration decreased because photocatalytic oxidation reaction occurs on the surface of the catalyst, so that the surface area which produces OH radicals is large compared to the target material at low initial concentration. The pH of the slurry solution approached pH 4 ~5 at any initial pH of 3.2~8.57 after 200 minutes. It was shown a RhB removal efficiency of more than 90 % was obtained for all ranges within 100 minutes. The removal efficiency increased slightly when the pH was decreased. When the pH was increased, the zeta-potential value of TiO_2 went from positive to negative, i.e., 6.65 mV, -17.49 mV, -26.26 mV at pH 3, 7, 10 respectively and the zeta-potential value of RhB decreased slightly. When the pH increased, the repulsion between TiO_2 surface and RhB molecule was increased, so the removal efficiency decreased because the initially adsorbed amount of RhB on the TiO_2 surface decreased.

To adjust the illumination intensity of the 10W UV lamp, the relation between distance and illumination intensity was studied by using the Radiometer. From this result, the relation equation $Y[mW] = 0.9596 - 0.1308 \times X[cm]$ was derived. The efficient of RhB decomposition increased when UV light intensity increased.

Acknowledgements

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