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Solar photocatalytic decolorization of dyes in solution with TiO_2 film

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Abstract

Application of TiO_2 film to solar photocatalysis of organic dyes, including Methylene Blue (MB) (λ_{max}, 660 nm), RR195 (λ_{max}, 540 nm) and RY145 (λ_{max}, 420 nm), was investigated. It was found that after 6-h solar irradiation, the extent of color degradation of dyes using solar photocatalytic system without TiO_2 film was quite limited. The color removal percentage for MB, RR195, and RY145 was found to be 23.3, −9.3, and −20.7%, respectively, resulting from competitions between the photosensitizing reaction and formation of colored intermediates during solar irradiation. However, as TiO_2 film was applied, the color degradation capability of solar photocatalytic system was significantly improved, in spite of the fact that only approximately 7% of solar irradiation belongs to the UV region. The color removal percentage for MB, RR195, and RY145 was up to 93.6%, 85.3%, and 71.1%, respectively, after 6-h irradiation. We believed that in such a solar photocatalytic system immobilized with TiO_2 film, both the maximum absorbance wavelength of the dye and the adsorbability of the dye on TiO_2 film played significant roles on the rate and efficiency of color removal of the dye solutions. Moreover, the possible reaction mechanism was proposed. The solar photocatalytic process with immobilized TiO_2 film was found to follow the pseudo-first order reaction kinetics. Color removal rate of MB was almost twice of that of RY145. Accordingly, the photocatalytic degradation process using solar light as an irradiation source, and immobilized TiO_2 as a photocatalyst, showed potential application for the decolorization of wastewater.

Keywords: Methylene Blue; RR195; RY145; Solar photocatalysis; TiO_2 film

1. Introduction

Color in textile effluents has become a possible serious environmental problem. Due to the nature of synthetic dyes, conventional biological treatments are ineffective for decolorization of such wastewater [1]. Therefore, in conventional industrial wastewater treatment practices, organic dyes were usually removed by using adsorbents or by coagulation. However, new environmental laws may consider the spent adsorbents or sludge as hazardous wastes that require further treatment. Consequently, intensive researches on novel technologies with more efficiency and less energy consumption have been stimulated.

Photocatalysis using a semiconductor, such as TiO_2 as a photocatalyst is an alternative to conventional methods. As TiO_2 is illuminated by light rays of wavelength below 380 nm, the photons excite valence band electrons across the bandgap into the conduction band, leaving behind holes in the valence band. The holes in TiO_2 will react with water molecules or hydroxide ions (OH^-) and then produce hydroxyl radicals ($^{\bullet}OH$) [2]. Oxygen is usually supplied as an electron acceptor to prolong the recombination of electron-hole pairs during photocatalytic oxidation. Several investigations [3–8] have reported that TiO_2

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photocatalysis was an effective method for decolorization and oxidization of organic dyes in wastewater. However, using the powder form of the photocatalyst – TiO_2 in solution usually required the separation of TiO_2 particles from the purified water after the decoloring reaction. In addition, the process was generally equipped with an artificial UV light source that lead to a considerable increase in operating cost. These drawbacks may be an obstacle for the practical application of TiO_2 photocatalysis. It has been suggested that the photocatalytic degradation of organic dye on semiconductor surfaces can extend the photoresponse of large bandgap semiconductor such as TiO_2 into the visible region [9]. In addition, solar light can be used as an alternative irradiation source for photocatalytic systems. However, the reported data related to decoloring efficiency of dye on TiO_2 film especially with solar irradiation are quite limited.

In this study, a photocatalytic degradation system, which used solar light as an irradiation source and Degussa P-25 TiO_2 as a stationary phase immobilized on the SS304 blades of the agitator and the inner surface of the SS304 reactor vessel, was employed to investigate the decolorization efficiency of organic dyes, including Methylene Blue, RR195, and RY145. The reaction kinetics and possible reaction mechanisms of color degradation of these dyes were also studied.

2. Materials and methods

2.1. Materials

Methylene Blue (MB) ($C_{16}H_{18}ClN_3S$) (λ_{max} (the maximum absorption wavelength of dye), 660 nm) was provided by Koch-Light Lab. Ltd., England. Reactive Red 195 (RR195) (λ_{max}, 540 nm) and Reactive Yellow 145 (RY145) (λ_{max}, 420 nm) with two chromospheres (vinyl sulfone and monochlorotriazine) were supplied by Sumitomo Chemical Co., Ltd. in Japan. Dyes were used without further purification. The TiO_2 powder P-25 (mainly anatase form with a mean particle size of 30 nm, and a BET surface area of $50 \pm 15\ m^2/g$) from Degussa Co. (Frankfurt, Germany) was immobilized on the surface of agitator's blades and inner surface of reactor by using the PTFE (TEFLON) resin-bonded technique [10].

2.2. Apparatus

Fig. 1 showed the experimental setup for this study. In such a photocatalytic system, separation of photocatalyst from the purified water after decolorization reaction was not necessary, and no other aeration equipment was required for oxygen supply. The effective volume of the photoreactor (36 cm L × 27.5 cm W × 8 cm H) was approximately 8.0 L. Solar light was used as the irradiation source, and the light intensity of solar light was measured by a UVP radiometer (UVP Inc., USA) at 254 nm and 365 nm. The rotating speed of the pump was kept at 70 rpm during the experiment. The size of the SS304 blades was 3 cm W × 15 cm L with a thickness of 1 mm. The total area of TiO_2 films within the solar photocatalytic reactor was approximately 2500 cm^2.

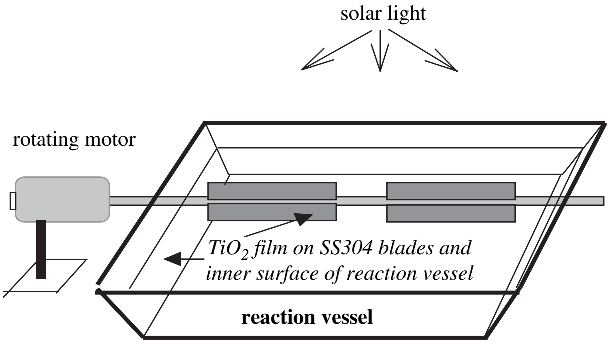

Fig. 1. Schematic diagram of the solar photocatalytic reactor used in this study.

2.3. Adsorption equilibrium studies

Bottle-point technique with a constant shaking speed of 100 rpm was used to determine the adsorption isotherms on TiO_2 films for each dye. A series of 1-L PE bottles were used as the reactors for adsorption equilibrium studies. Each PE bottle was supplied with dye solutions with different initial concentrations (1, 2, 3, 4, 5, 6, 7, 8, 9, or 10 mg/L) as well as one SS304 blade (3 cm W × 15 cm L) coated with TiO_2 on both sides. All the adsorption experiments were performed under a constant temperature of 30 °C.

For the adsorption experiments, two adsorption isotherm models were commonly used to simulate the experimental data. One is called the linear model,

$$q_e = KC_e \tag{1}$$

another one is called the Freundlich model,

$$q_e = K_F C_e^n \tag{2}$$

in which C_e and q_e represent the equilibrium solution-phase and solid-phase concentrations of adsorbate, respectively. K and K_F represent the adsorption coefficients relating to sorption capacity, and n is a characteristic coefficient relating to sorption energy or intensity.

2.4. Solar light/TiO_2 film photocatalysis degradation experiments

Solar light was used as an irradiation source. Dye solutions with a concentration of 10 mg/L were prepared for each dye studied. The prepared dye solutions were then placed into the photoreactor and irradiated by sunshine. Sampling was carried out for 6 h at preset intervals. A similar photoreactor without TiO_2 film was also performed in parallel under the same conditions as a control.

2.5. Analysis

A spectrophotometer (UV-160, Shimadsu Co., Japan) was used for absorbance measurement of dye in water and a DR/4000 spectrophotometer (Hach Co., USA) was used for ADMI (American Dye Manufacturers Institute) measurement. The decolorization efficiency was calculated on the basis of ADMI reduction of solution.

3. Results and discussion

3.1. Adsorption of dyes on TiO_2 film

It was found that the dye distribution between the aqueous phase and stationary TiO_2 film reached equilibrium within 24 h for each dye studied. Accordingly, the adsorption of dyes on TiO_2 films was believed to be due to the van der Waals forces or hydrophobic bonding. Two common adsorption equilibrium isotherm models (the linear model and the Freundlich model) were used to simulate the adsorption data. It was found that both the models could well describe the adsorption behavior of dye on TiO_2 film ($r^2 > 0.95$). Table 1 summarized the best-fit parameters for each selected dye.

As shown in Table 1, no matter which isotherm was applied, the adsorbabilities of the dyes as well as the K values decreased in the following order: MB > RY145 > RR195. This phenomenon may be due to a consequence of more hydrophobic character of MB than RY145 and RR195. The n parameter in the Freundlich model, that was believed to relate to the value of adsorption energy or intensity, increased in the following order: MB < RY145 < RR195. Furthermore, adsorption of MB on TiO_2 film showed an n value less than 1, while adsorption of RY145 and RR195 showed an n value greater than 1. It was generally accepted that under a constant temperature, the n values decreased with increasing adsorption energy, which implied that the smaller the n value, the stronger the adsorption intensity [11]. In addition, in general, $n < 1$ illustrated that adsorbate was favorably adsorbed on an adsorbent; while $n > 1$ indicated that adsorbate was unfavorably adsorbed on an adsorbent [12]. Accordingly, in this study, the adsorption intensity of dyes on TiO_2 films could be said to be in the order of MB > RY145 > RR195. Furthermore, due to the lowest n value, the adsorption of MB was believed to be more favorable than RY145 and RR195, leading to the highest decolorization efficiency of MB among the selected dyes during the adsorption experiments.

Table 1
Adsorption isotherm parameters

Dye	Linear isotherm	Freundlich isotherm		Concentration range (mg/L)
	K^a	K_F^b	n	
MB	0.00141	0.00150	0.948	0–10
RR195	0.00039	0.00025	1.267	0–10
RY145	0.00104	0.00112	1.049	0–10

[a] Linear adsorption coefficient (mg dye adsorbed/cm^2 TiO_2 film)/(mg dye/L solution).

[b] Freundlich adsorption coefficient (mg dye adsorbed/cm^2 TiO_2 film)/(mg dye/L solution).

3.2. Photocatalytic degradation of dyes

Fig. 2 showed the color removal efficiency of dye solutions as a function of irradiation time. It was found that after 6-h solar irradiation, the extent of color degradation of dyes using solar photocatalytic system without TiO_2 film was quite limited. The color removal percentage for MB, RR195, and RY145 was found to be 23.3, −9.3, and −20.7%, respectively, resulting from competitions between the photosensitizing reaction and formation of colored intermediates during solar

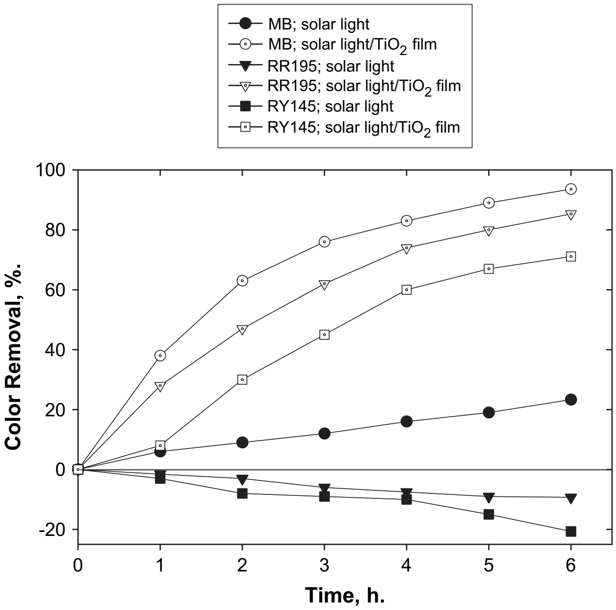

Fig. 2. Color removal efficiency of dyes by solar photocatalytic degradation (the initial concentration of dye, 10 mg/L).

irradiation. In other words, for RY145 and RR195 solutions, more colored intermediates seemed to be produced during direct solar photolysis, leading to negative color removal efficiency. Though the chemical structures of the colored intermediates were not identified yet in this study, it should not be difficult to be resolved through GC/MS techniques. As TiO_2 film was applied, the color degradation capability of solar photocatalytic system was significantly improved, in spite of the fact that only approximately 7% of solar irradiation belongs to the UV region. The color removal percentage for MB, RR195, and RY145 was up to 93.6%, 85.3%, and 71.1%, respectively, after 6-h irradiation. To understand the reaction kinetics of the color degradation of the selected dyes, the pseudo-first order model as expressed by Eq. (3), which was generally used for photocatalytic degradation process if the initial concentration of pollutant was low [13], was applied.

$$\ln\left(\frac{C_0}{C}\right) = kt \tag{3}$$

in which C_0 and C are the concentrations of dye in solution at time 0 and t, respectively, and k is the pseudo-first order rate constant. Fig. 3 shows the reaction kinetics of dye decolorization in solution. As it can be seen, a good correlation to the pseudo-first order reaction kinetics ($r^2 > 0.95$) was found. The rate constants obtained from regression lines in Fig. 3 are summarized in Table 2. It was shown that the color removal rate of dyes decreased in the order of MB > RR195 > RY145. The color removal rate of MB was almost twice of that of RY145, in spite of the fact that the MB solution was illuminated by a lower dosage of solar irradiation.

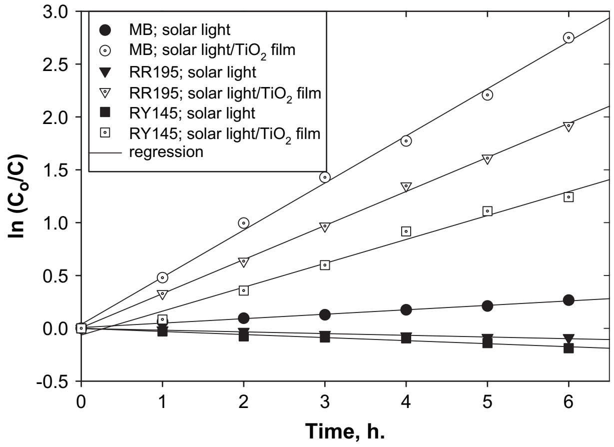

Fig. 3. Kinetics of the solar photocatalytic decolorization of dyes in solution.

Table 2
The pseudo-first order rate constant of dyes with solar light irradiation

Dye	I_1[a] (mW/cm^2)	I_2[b] (mW/cm^2)	C_o[c] (mg/L)	k_1[d] (h^{-1})	k_2[e] (h^{-1})
MB	0.121	1.65	10	0.0421	0.442
RR195	0.146	1.93	10	−0.0163	0.323
RY145	0.145	2.02	10	−0.0268	0.226

[a] Average solar light intensity at 254 nm (mW/cm^2).
[b] Average solar light intensity at 365 nm (mW/cm^2).
[c] Initial concentration of dye in solution (mg/L).
[d] The pseudo-first order rate constant under solar light irradiation (h^{-1}).
[e] The pseudo-first order rate constant with solar light/TiO_2 film system (h^{-1}).

Three possible reaction mechanisms for color degradation of selected dyes were proposed as follows. For solar photocatalytic degradation with TiO_2 as catalyst, the initiation of this process could be described by Scheme I (Eqs. (4)–(6)), in which the generated hydroxyl radicals could further oxidize the pollutants.

3.2.1. Scheme I

$$TiO_2 \xrightarrow{\text{solar light}} h^+ + e^- \tag{4}$$

$$e^- + O_2 \rightarrow \bullet O_2^- \tag{5}$$

$$h^+ + OH^- \rightarrow \bullet OH \tag{6}$$

For a photosensitization process with dye as a sensitizer, the initiation of this process could be described by Scheme II (Eqs. (7)–(9)), in which the dye adsorbed on TiO_2 was excited by solar irradiation and then an electron injected from the excited dye to the conduction band of TiO_2 where it was scavenged by molecular oxygen [14].

3.2.2. Scheme II

$$\mathrm{Dye_{(ads)}} \xrightarrow{\text{solar light}} \mathrm{Dye^*_{(ads)}} \tag{7}$$

$$\mathrm{Dye^*_{(ads)}} + TiO_2 \rightarrow TiO_2(e) + \mathrm{Dye^+_{(ads)}} \tag{8}$$

$$TiO_2(e) + O_2 \rightarrow TiO_2 + \bullet O_2^- \tag{9}$$

Particularly, the third possible initiation mechanism of photocatalytic decolorization (Scheme III, Eqs. (10)–(12)) was proposed in this study, in which the energy could be transferred from the excited dye to TiO_2 or O_2 and then produce the pair of electron-hole (Eq. (11)) or the singlet oxygen atom ($(O(^1D))$) (Eq. (12)) to promote decolorization efficiency.

3.2.3. Scheme III

$$Dye_{(ads)} \xrightarrow{\text{solar light}} Dye^*_{(ads)} \tag{10}$$

$$Dye^*_{(ads)} + TiO_2 \rightarrow Dye_{(ads)} + h^+ + e^- \tag{11}$$

$$Dye^*_{(ads)} + O_2 \rightarrow Dye_{(ads)} + 2O(^1D) \tag{12}$$

The decolorization of dye through Scheme I was related to the basic characteristics of dye such as the structure of chromosphere in the dye molecule and the energy required for decomposing dye molecular structure, i.e., the λ_{max} of dye. On the other hand, the decolorization of dye through Scheme II or III was related to the adsorbability of dye on TiO_2 and the absorbance of dye under solar irradiation. Accordingly, the higher decoloring efficiency of MB solution was believed to be due to a better adsorbability of MB molecules on TiO_2 film, a higher λ_{max} (660 nm) and a much higher absorbance in the region of visible light, as shown in Fig. 4. As compared with the decoloring efficiency of RR195 and RY145, it was found that although the adsorbability of RY145 on TiO_2 film was better than that of RR195, the λ_{max} (420 nm) of RY145 was shorter and the absorbance in the visible region for RY145 was less (Fig. 4), leading to a lower decolorization efficiency for RY145 solution. Therefore, the decoloring efficiency and rate of dyes were in the order MB > RR195 > RY145. Moreover, though there was only approximately 7% of solar irradiation that belonged to the UV region, solar irradiation alone was already able to excite TiO_2 through Scheme I mechanism. On the other hand, the visible region of solar irradiation (at least 44% of solar irradiation) [15] was useful for the excitation of dye through Schemes II and III mechanisms. Hence, it was suggested that the initiation of decoloring MB was most probably through mechanisms of Schemes II and III, while the initiation of decoloring RR195 and RY145 was most probably through Scheme I mechanism.

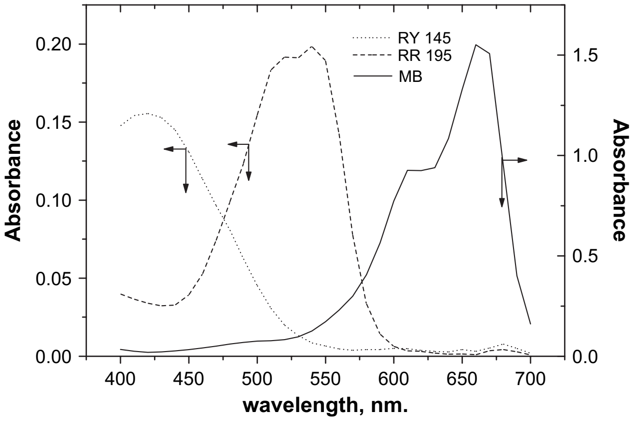

Fig. 4. Absorbance of each dye in the region of visible light (the concentration of dye, 10 mg/L).

4. Conclusions

As compared to solar photocatalytic systems without TiO_2 film, application of TiO_2 film to solar photocatalytic system has successfully improved the color degradation capability of the solutions of organic dyes. It was believed that the improved color degradation capability was due to the fact that the visible region of solar light could excite the dye molecules adsorbed on TiO_2 film, followed by a series of photosensitizing reaction. Furthermore, the UV region of solar irradiation could excite TiO_2 molecules to initiate the photocatalytic degradation by generation of hydroxyl radicals, which further promoted the decolorization efficiency pronouncedly. The decolorizing efficiency was in relation to both the maximum absorbance wavelength of dye and the adsorbability of dye on TiO_2 film. Within the conditions studied, best decolorizing efficiency was achieved for the solution of Methylene Blue. Accordingly, instead of using artificial UV light source, the solar photocatalytic process assisted by TiO_2 films showed potential application for the decolorization of wastewater

Acknowledgements

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