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IMPACT OF TiO_2 AND H_2O_2 ON PHOTOCATALYTIC DEGRADATION OF PHODAMINE B UNDER ULTRAVIOLET C (UV-C) RADIATION FOR EFFICIENT POLLUTED WASTEWATER TREATMENT

N. HARUN[a], C. K. SHENG[a,*], M. G. M. SABRI[a], A. N. DAGANG[b],
H. SALLEH[a]
[a]*Faculty of Science and Marine Environment, Universiti Malaysia Terengganu*
21030 Kuala Nerus, Terengganu, Malaysia
[b]*Faculty of Ocean Engineering Technology and Informatics, Universiti Malaysia Terengganu 21030 Kuala Nerus, Terengganu, Malaysia*

Photocatalytic wastewater treatments applying the semiconductor photocatalysts to remove toxins or pollutants from wastewater become more important nowadays. In this study, the photocatalytic study was firstly conducted on the photodegradation of rhodamine B (RB) dye in tap water by using TiO_2 as photocatalysts under short-wavelength (high energy) UV-C light irradiation. The results show that a considerable increase in the degradation of RB can be obtained through a combination of TiO_2 and UV-C light. In addition, hydrogen peroxide (H_2O_2) was added in the RB solution containing TiO_2 to improve the degradation efficiency of RB dyes. The result shows that 98 % degradation efficiency of 20 ppm RB is achieved within 180 min irradiation time in the solution containing 0.5 g/l TiO_2 and 1 M H_2O_2 concentrations, which is higher than the reported literature value.

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1. Introduction

Recently, large amounts of colored dye pollutants were manufactured by textile industries which are toxic and non-biodegradable. These dyes created serious environmental pollution problems by releasing toxic and potential carcinogenic substances into the aqueous phases such as river and seawater [1]. There are various reported treatments to remove the dye-containing wastewater from textile matrix effluents, such as precipitation, adsorption, flocculation, coagulation, reverse osmosis and filtration. However, these techniques are non-destructive, since the non-biodegradable pollutants are transferred to the other phases, giving rise to a new type of pollution, which needs further treatments [1, 2].

Alternatively, photocatalytic degradation has been recognized as an effective tool for water treatment. This method uses a combination of light, semiconductor and suitable initiator as photocatalysts to degrade the toxic organic pollutants into harmless products [3-6]. The major observation is a change in depth of shade that apparent during the dye degradation process [7-10]. In the past decades, TiO_2 has attracted extensive interest as photocatalyst due to its capability of degrading a wide range of aqueous dye contaminant. Also, it appears to be a promising material for air and water pollution control because of its non-toxic properties [11-14].

In this study, we first investigated the effect of TiO_2 and hydrogen peroxide (H_2O_2) on the photocatalytic degradation of Rhodamine B (RB) in tap water by employing the high-energy UV-C light as irradiation source. TiO_2 with anatase phase is employed due to its high photosensitivity and stability as compared to the other catalysts and RB is chosen as contaminant because it is one of the most commonly used water soluble dyes in textile and food coloring industries [11].

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[*] Corresponding author: chankoksheng@umt.edu.my

2. Materials, preparation and characterizations

The chemicals of TiO_2, RB dye and H_2O_2 were purchased form Merck, Germany. All chemicals were analytical grade and used as received without further purification. A solution of 20 ppm RB was prepared by adding 4.0 mg of RB into 200 ml of tap water. The solution was then magnetically stirred at room temperature for 10 minutes. The optical absorption spectrum was obtained by using a Shimadzu UV-1800 UV-Vis spectrophotometer. Prior to photocatalytic activity, the structure of the TiO_2 catalyst was characterized by XRD spectrometer using a Rigaku Miniflex-TM II diffractometer, while the surface morphology of the catalyst was examined using the TM-1000 Hitachi Tabletop Microscope.

For the photocatalyst degradation study, TiO_2 was first dispersed in the RB solution under constant magnetic stirring for 30 minutes to establish an adsorption-desorption equilibrium. Then, the dispersion was irradiated with a Phillips UV-C (254 nm) fluorescent lamp at power of 15 W for 3 hours at 30 minutes recording intervals. The absorbance variation of the samples was monitored using the UV-Vis spectrophotometer. The photocatalytic degradation for each sample was then calculated using equation (1) as given below [1]:

$$\beta = \frac{C_o - C_t}{C_o} \times 100\% \tag{1}$$

where β denotes the percentage of dye degradation, C_o is the absorbance peak intensity of the sample before irradiation and C_t is the absorbance peak intensity after irradiation at time t. It is well known that the absorption intensity is directly proportional to dye concentration. The concentrations of TiO_2 used for dye degradation were varied as 0.5 g/*l* and 1.0 g/*l*. Hydrogen peroxide (H_2O_2) is commonly employed as a promoter in the photocatalytic activity [13]. Hence, in order to improve the photocatalytic effect of H_2O_2, 10 μL of 1 M H_2O_2 was added into the TiO_2 dispersion. For comparison purposes, another H_2O_2 concentration of 2 M was used for the photocatalytic degradation activity.

3. Results and discussion

Fig. 1 shows the absorption spectra for different concentrations of RB solutions in the range of 5 to 20 ppm. All the RB solutions have a well-resolved absorption peak centered at 554 nm, which corresponds to the absorption characteristics of RB [11]. As can be observed from the figure, the absorption intensity enhances with the increment of RB concentration. Thus, the 20 ppm RB concentration was chosen for photocatalytic degradation due to its highly intense absorption that can withstand longer irradiation time. The structural phase of the TiO_2 particles was characterized by XRD. Fig. 2 shows the XRD pattern of TiO_2 particles. The XRD result confirms the occurrence of anatase phase of TiO_2 with sharp crystalline peaks located at $2\theta = 25.5^o$, 38.2^o, 48.3^o, 54.5^o, 55.0^o, 63.2^o, 70.1^o, 75.7^o and 83.1^o corresponding to the (101), (103), (004), (112),) (200), (105), (211), (204) and (215) lattice planes, respectively. The anatase form of TiO_2 has been proven to possess excellent catalytic abilities that can be used for the degradation of many organic pollutants in aqueous solutions [11]. Fig. 3 shows the morphological image of as-received TiO_2 particles used in the present study. It shows that the TiO_2 particles have small spherical shape with uniform size distribution. This observation is in agreement with those reported by Jain et al. [3] and Thamaphat et al. [16].

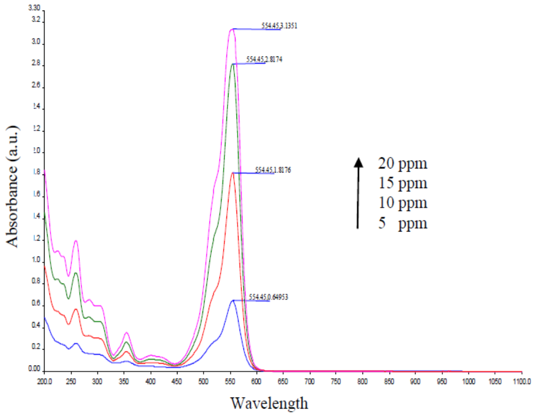

Fig. 1. Absorption spectra of RB solutions at different concentrations.

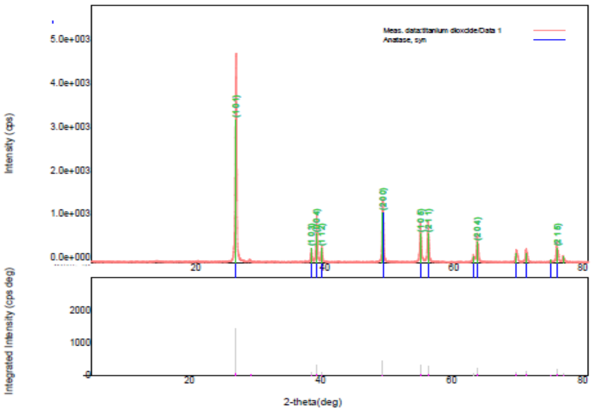

Fig. 2. XRD pattern of as-received TiO_2.

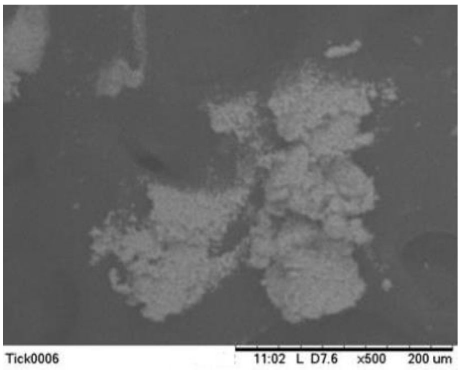

Fig. 3. Surface morphology of TiO_2 partices.

Initially, a preliminary photocatalytic degradation study was conducted in the dark and under the UV-C light illumination on the RB solution containing 0.5 g/*l* TiO_2 catalyst concentration, and the UV-irradiated solution without the presence of TiO_2 as reference. As can be monitored from the absorption spectra, a decrease in the absorbance of RB solution in the absence of either UV light or TiO_2 is slower when compared to the one loading with TiO_2 under the UV-C illumination. The calculated degradation percentage of dye solution at different conditions by applying equation (1) is depicted in Fig. 4. From the plots, the degradation percentage rises with illumination time, in which it shows a significant increase for the first 30 minutes illumination due to a rapid dye degradation and then increases gradually over the entire irradiation period. Also, the solution containing TiO_2 with UV-C irradiation has a steeper slope for the first 30 minutes, which reflects that the dye degradation takes place at a faster rate when compared to the others. After irradiation for 3 hours, it is found that only a minor loss of 63 % on absorption intensity in the absence of UV-C light, whist better degradation of 95 % is obtained when a desired amount of TiO_2 was added into the RB solution in the presence of UV-C light. Clearly, this result indicates that the presence of only TiO_2 particles does not effectively catalyze the degradation of dye. The TiO_2 must be in coupling with UV light to improve the catalysis degradation. Hashim et al. [4] reported that the TiO_2 suspension was mineralized when the suspension was illuminated under the UV light. Combination of light and semiconductor based material as photocatalysts would provide a more profound effect on dye degradation [1]. The photochemical degradation of dye without TiO_2 in the presence of only UV-C light illumination was also investigated. It is found that 62 % of dye degradation is attained without any catalyst loading, which is slightly lower than the one with only catalyst loading in the absence of UV-C light. This is due to the fact that the semiconductor based catalyst provides an active site required for the degradation process of RB. Without the presence of catalyst, the degradation of dye occurs instantaneously by direct penetration of UV light onto the dye molecule. This process is shown to be ineffective as indicated by low percentage degradation of RB dye. However, with the presence of the catalyst, the UV light would first irradiate the catalyst to produce the electron-hole pairs or active sites, and then the RB dye molecules are adsorbed on the active sites for photocatalytic degradation [15]. Hence, the combination of catalyst and UV light plays an important role in the photodegradation of RB. It is well known that the TiO_2 owns a band gap of 3.2 eV, which corresponds to a wavelength of 385 nm. Therefore, the electron-hole pairs are created when the TiO_2 is radiated with UV light at wavelength shorter than 385 nm, and the electrons from the valence band will be excited to the conduction band. As a result, the positive hole (h^+_{vb}) is created in the valence band as represented by equation (2) [17].

$$TiO_2 + \quad h\nu\ (<385\text{nm}) \rightarrow e^-_{cb} + h^+_{vb} \qquad (2)$$

In heterogeneous photocatalysis, the photocatalysts would capture the photons with energy greater than the band gap (3.2 eV) to create electron–hole pairs. Subsequently, the charged carriers would interact with water and oxygen to produce the oxidizing intermediates as hydroxyl radicals (OH•), which have the ability to oxidize the pollutants to inorganic compounds. After successive free radical attack and fragmentation, most organics are mineralized to water, carbon dioxide and mineral acids [3].

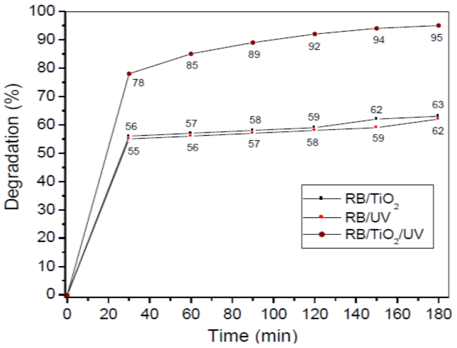

Fig. 4. Degradation efficiency of RB dye solution at different conditions.

Subsequently, in order to verify the effect of higher catalyst concentration on photodegradation, higher TiO_2 dosage at 1.0 g/*l* concentration was studied on RB degradation under the UV-C light excitation. Fig. 5 illustrates the degradation percentage versus time for 0.5 g/*l* and 1.0 g/*l* TiO_2 concentrations. Obviously, during the first 30 minutes of irradiation, the plot becomes steeper at higher TiO_2 concentration, indicating that the dye degradation takes place at a faster rate. The results indicate that higher degradation percentage and rate are obtained at higher TiO_2 concentration. After 30 minutes of irradiation, 1.0 g/*l* TiO_2 concentration has already degraded 94 % of dye color as compared to 0.5 g/*l* TiO_2 concentration that yields only 78% dye degradation. Afterwards, the percentage degradation increases slowly with time until the entire irradiation period. The final percentage degradation achieved for 1.0 g/*l* TiO_2 and 0.5 g/*l* TiO_2 concentrations are 97 % and 95 %, respectively, in which higher TiO_2 concentration improves slightly the degradation at prolonged irradiation time. It is reported that an increase in the number of TiO_2 particles will increase the number of photons absorbed by the RB molecules. Therefore, the degradation efficiency can be enhanced with the increase of TiO_2 concentration due to the increase in total surface area available for contaminant adsorption**.** However, it is not preferable to utilize a very high catalyst concentration in order to avoid aggregation of catalysts particles, which may substantially decrease the photocatalytic activity and in turn reduce the degradation efficiency [17-19].

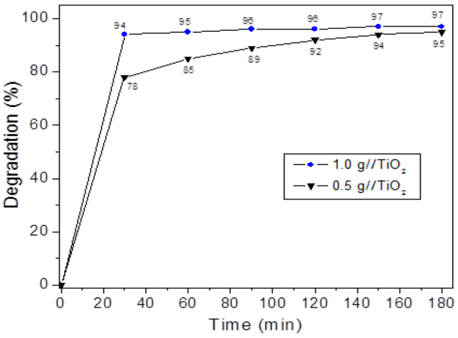

Fig. 5. Degradation efficiency of RB dye solution at different TiO_2 concentrations.

Fig. 6 depicts the percentage degradation of RB dye solution under UV-C illumination with a loading of 0.5 g/*l* of TiO_2 at different H_2O_2 concentrations of 1 M and 2 M. From the figure, it can be observed that by adding a small concentration of H_2O_2, the photodegradation efficiency of RB increases slightly from 95 % to 98 % after 3 hours irradiation time. This result implies that the content of H_2O_2 might play an important role to increase the degradation percentage of RB, since the H_2O_2 concentration is directly related to the number of OH• radicals generated in the photo-assisted catalytic reaction [3]. A similar observation has also been reported in the literature for the photocatalyst degradation of other organic pollutants using H_2O_2 [19]. However, the photodegradation efficiency shows a little decline to 97 % when the H_2O_2 concentration increases from 1 M to 2 M. At higher H_2O_2 concentration, the excess H_2O_2 molecules scavenge the valuable •OH which is generated by the direct photolysis of H_2O_2 and form a much weaker oxidant of 2•OH (Equation 3) [19]. Moreover, higher H_2O_2 concentration might absorb and attenuate the incident UV light available for the photocatalysis process [15, 20]. Therefore, the total oxidation capabilities of the system are reduced (equation 4) and the degradation rates are retarded according to the following equations:

$$H_2O_2 + {\bullet}OH \rightarrow HO_2{\bullet} + H_2O \qquad (3)$$

$$HO_2{\bullet} + {\bullet}OH \rightarrow H_2O + O_2 \qquad (4)$$

Consequently, in the present investigation, the concentration of 1 M H_2O_2 and 0.5 g/*l* TiO_2 gives the optimum photocatalytic degradation of RB under UV-C irradiation. As reported by Razali et al. [17], the production of •OH can be increased in the presence of strong peroxide agent such as hydrogen peroxide (H_2O_2) through photolysis process as stated in equation (5). H_2O_2 is not only known to generate hydroxyl radicals on the abstraction of an electron from the conduction band, but is also known to inhibit the electron–hole recombination process at higher concentration [3].

$$H_2O_2 + h\nu\ (<385\text{nm}) \rightarrow 2{\bullet}OH \quad (5)$$

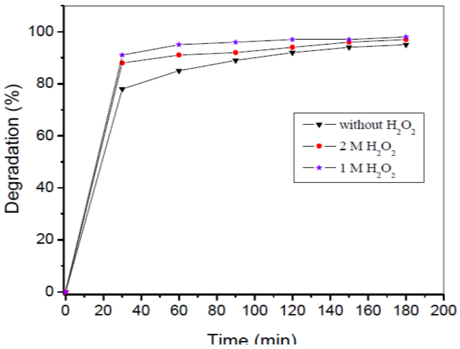

Fig. 6. Degradation efficiency of RB with the addition of different H_2O_2 concentrations.

5. Conclusion

In summary, we have successfully investigated the photocatalytic degradation of RB dye aqueous solution in the presence of TiO_2 and H_2O_2 under UV-C light irradiation. The photodegradation efficiency of RB dye in the presence of TiO_2 catalyst with UV light was found to be much higher as compared to the one without catalyst or UV light. Also, the photocatalytic degradation percentage of RB was found to be increased with the increase of catalyst concentration. Most importantly, the presence of 1 M H_2O_2 in the RB/TiO_2/ UV system enhances the degradation efficiency up to 98% within 3 hours of irradiation. The results obtained in this study indicate that the optimum degradation could been achieved by using the high-energy UV-C light as the irradiation source.

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