

Photocatalytic Removal of Rhodamine B from Aqueous Solutions Using TiO₂ Nanocatalyst

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ABSTRACT

Heterogeneous photocatalysis is an effective treatment method for the removal of toxic pollutants from industrial wastewaters. In this work slurry photoreactor using TiO₂ (Degussa P-25) as catalyst was evaluated for its effectiveness in removing Rhodamine B (RB) from aqueous solutions. The effects of operating conditions such as RB initial concentration, pH value, catalyst loading, and types of UV light irradiation on the removal efficiency were evaluated. The results of experiments indicated that the removal of Rhodamine B increased with increasing the catalyst loading and dye initial concentration. Also the wavelength of the light used for photoactivation has a significant impact on the dye degradation rate; shorter wavelengths lead to faster degradation. The order of degradation rate using different light sources was shown to be UV-C>UV-A>UV-LED. According to experimental data, the photocatalytic degradation of Rhodamine B can be simulated by using pseudo-first-order reaction rate.

Keywords: Photocatalyst; Degradation; UV light; Reaction rate; Dyes.

INTRODUCTION

Colored compounds comprising pigments and dyes are used widely in textile, plastic, food, dyeing, paper, printing, pharmaceutical and cosmetic industries. These compounds color the water and make penetration of sunlight to the lower layers impossible and hence affecting aquatic life. Many of these are toxic, carcinogenic, mutagenic, or even stable to biological degradation [1]. The conventional wastewater treatment methods are usually ineffective in removal of these compounds or just transfer the contamination from one phase to another. Moreover, some biodegradation by-products are more toxic than the degraded compound [2].

Advanced oxidation processes have gained importance in the last decade because of their application in the purification of wastewater containing toxic, recalcitrant, and/or colored compounds. Photocatalytic degradation, as an advanced oxidation process, can oxidize a wide variety of toxic and persistent organic compounds to harmless inorganics such as mineral acids, carbon dioxide and water [3]. The mechanism of the degradation consisted of promoting an electron from the valence band to the conduction band of the semiconducting oxide to give an electron/hole pair. The valence band potential is positive enough to generate hydroxyl radicals at the surface and the conduction band potential is negative enough to reduce molecular O₂. The hydroxyl radical is a powerful oxidizing agent and attacks organic pollutants present at or near the surface of the TiO₂. The simplified mechanism is shown in equations 1, 2, 3, and 4 [4,5,6].



TiO₂ semiconductor photocatalysts, is the most commonly used owing to its stable, harmless and inexpensive properties. It also activated with ultraviolet (UV) light. TiO₂ has been used for the degradation of different kinds of compounds. However, two typical defects including only exciting by high energy UV irradiation and a low quantum yield rate resulted from a low rate of electron transfer to oxygen and a high rate of recombination between excited electron/hole pairs, limit the photooxidation rate of TiO₂ nanoparticles [5].

Rhodamine B is one of the most important dyes of the xanthene group, which is a highly water soluble. It is found as a reddish violet powder and comes under the trade name of D&C Red No. 19. It is harmful if swallowed by human beings and animals, and causes irritation to the skin, eyes and respiratory tract and is widely used in many industrial processes, such as paper dyeing and the production of dye laser [3-7]. The maximum absorbance (λ_{max}) of RB is around 550 nm-555 nm [8]. The molecular structure of RB is presented in Figure 1. The color of dyes results from conjugated chains or rings which absorb light at visible wavelength [9].

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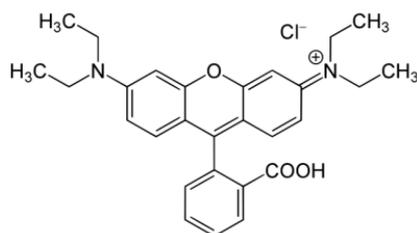


Figure1. Molecular structure of Rhodamine B

Published studies have dealt with the degradation of RB using TiO₂ films [2, 10, 11, 12], sand supported TiO₂ [13], and ZnO as catalyst [14]. Also, recent articles have shown that Rhodamine B can be destroyed in aqueous suspension using TiO₂ [15], TiO₂-coated silica [16] and TiO₂-coated silicone sealant [17].

The main goal of this study was to investigate the effect of different operation conditions such as dye and TiO₂ concentration, pH, and feasibility of applications of the UVLED as the light source instead of the traditional UV lamps.

MATERIALS AND METHODS

Chemicals

The catalyst used was P-25 titanium dioxide (TiO₂ 70:30% w/w anatase to rutile) with an average particle size of 21 nm and a BET surface area of 50±15 m² g⁻¹, supplied by Degussa. The Rhodamine B (purity, 99%) was purchased from Merck Co. Ltd. (Darmstadt, Germany) It consists on green crystals or reddish-violet powder, its molecular formula is C₂₈H₃₁ClN₂O₃ (molecular weight: 479.02). All the other reagents used in this study were analytical grade. Deionized laboratory water was used for making aqueous mixtures.

Photocatalytic reactor

Experiments were carried out using a cylindrical batch reactor, 4 cm in diameter and 25 cm in working height. The photocatalytic reactor consists of two parts: Pyrex glass reactor and a UV lamp. Various lamps were tested, including UVC, UVA, and UVLEDs which was placed inside the well of a reactor of 250 mL capacity. The UV light sources were surrounded by a Quartz glass tube to preventing direct contact with dye solution. Suspensions of the photocatalyst and aqueous contaminant solutions were kept aerated and stirred by a steady stream of air to improve contact between RB molecules and TiO₂ particles and maintain homogeneity. The reactor set-up was covered by aluminum foil, as were the sides and the bottom of the reactor in order to guarantee maximum use of the radiation and to prevent the effects of external radiation.

Apparatus

Measurements of solution pH were carried out using a digital pH meter DB 1011 fitted with a glass electrode. Spectrophotometer (Jenway 6305) was used to measure the absorbance of the liquid samples at appropriate wavelengths.

Experiments of photocatalytic degradation were conducted in a photocatalytic reactor. Irradiation was carried out using a UVC (Philips TUV 6W, low pressure Hg lamp close to monochromatic output at 254 nm), 365 nm UV lamp UVA (Black Light, Hitachi F6T5 6W, Japan / Black Light Blue, Haichao F6T5 6W, China), Day light lamp (Philips, F6T5 6W) and 48 UVLEDs (20 mW per UVLED, λ = 385 nm).

Experimental and analytical procedures

Photocatalytic experiments were conducted at different initial concentrations (5 -10- 20 mg/L) and inherent pH of about 7. Different amounts of TiO₂ (varying from 0.1 to 0.7 g/l) were added to the dye solution. Irradiation was provided by various UV lamps under continuous oxygen flow and a constant temperature of 25 °C to start the reaction.

The RB aqueous solutions were filtered by proper centrifugation and the concentrations of the dyes in the filtrate were determined from UV–visible absorbance characteristic with the calibration curve method. The maximum adsorption wavelength (λ_{max}) was 550 nm. The reaction was thought to be completed when the dye solution became completely colorless and at this stage measurements were stopped.

The photocatalytic degradation efficiency of the RB solutions was calculated using the following equation:

$$R(\%) = \frac{A_0 - A}{A_0} \times 100 \quad (5)$$

Where A_0 is the absorbance of RB dye solution before the illumination, A is the absorbance of RB solutions in suspension after time t .

RESULTS AND DISCUSSION

Effect of Catalyst Loading

TiO₂ loading in slurry processes is a significant factor that can affect the performance. The optimum TiO₂ dosage depends on the different parameters such as characterization of contaminant, exposure area, applied UV lamps, and agitation conditions [18]. Experiments were performed by varying the catalyst loading from 0.1 to 0.7 g/l. A photolysis test was conducted by injecting the same concentration of Rhodamine B into the reactor without the presence of photocatalysts but with the UV lamp turned on. The effect of photocatalyst concentration was analyzed to optimize the amount of TiO₂. The results showed that the photocatalytic degradation efficiency increased by increasing the amounts up to 0.3 g/l (Figure 2).

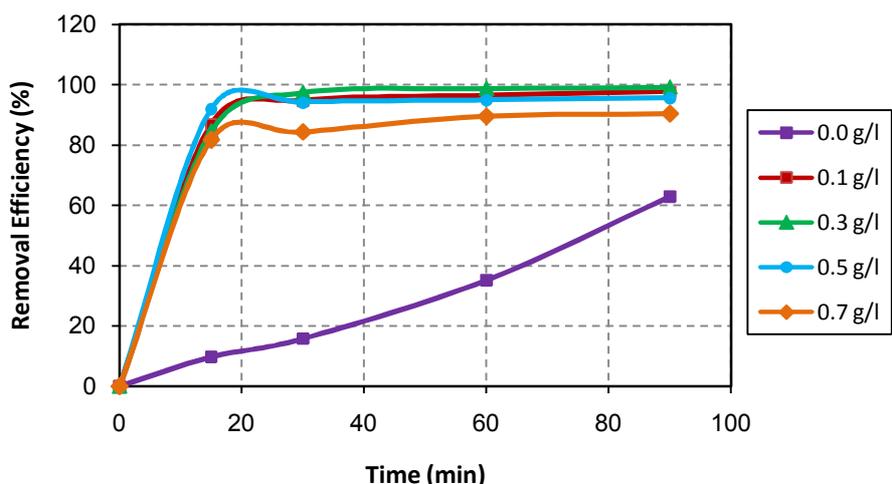


Figure 2. The Effect of TiO₂ loading on degradation of RB; T= 25°C pH₀ = 7, Under UV-C light ($\lambda=254\text{nm}$, 6W)

Generally, decomposition increases with catalyst loading due to a higher surface area of the catalyst that is available for adsorption and degradation. An optimum value is present, while above a certain concentration, the solution opacity increases (due to increased light scattering of the catalyst particles) causing a reduction of light penetration in the solution and a consequent rate decrease [19].

Reaction kinetics gives information about the reaction rates and the mechanisms by which the reactants are converted to the products. Kinetics is determined by both the catalyst and substrate concentration. The results of experiments showed that the photocatalytic degradation of RB obeys apparently pseudo-first order kinetics and the rate expression is given by Eq. (6).

$$-\frac{dC}{dt} = k_{obs} C \tag{6}$$

Where k_{obs} is the apparent rate constant and is affected by dyes stuff concentration. Integration of Eq. (6) from $C = C_0$ to $C = C$ yield the following equation:

$$-Ln\left(\frac{C}{C_0}\right) = k_{obs} t \tag{7}$$

Where C is the concentration of RB at time t , C_0 the initial concentration of RB and k_{obs} the pseudo-first-order rate constant.

The slope of the plots of $-Ln(C/C_0)$ versus t gave the values of k_{obs} , as listed in Table 1.

Table 1. The effect of TiO₂ loading on the photodegradation rate of RB solutions

TiO ₂ (g/l)	K _{obs} (min ⁻¹)	R
0	0.010	0.967
0.1	0.035	0.865
0.3	0.050	0.905
0.5	0.026	0.722
0.7	0.021	0.797

Effect of RB concentration

Successful application of photocatalytic oxidation system requires the investigation of the dependence of photocatalytic degradation rate on the substrate concentration (C_0). The effect of initial RB concentration on the degradation rate of RB during the reaction time is presented Table 2. The highest photocatalytic degradation rate of RB was occurred in initial concentration of 10 ppm.

Table 2. Effect of initial RB concentration on the photodegradation rate of RB

Initial conc. (ppm)	K_{obs} (min^{-1})	R
5	0.049	0.905
10	0.051	0.918
20	0.040	0.954

The photocatalytic degradation was also investigated at different concentrations of RB as a function of irradiation time. The results are presented in figure 3.

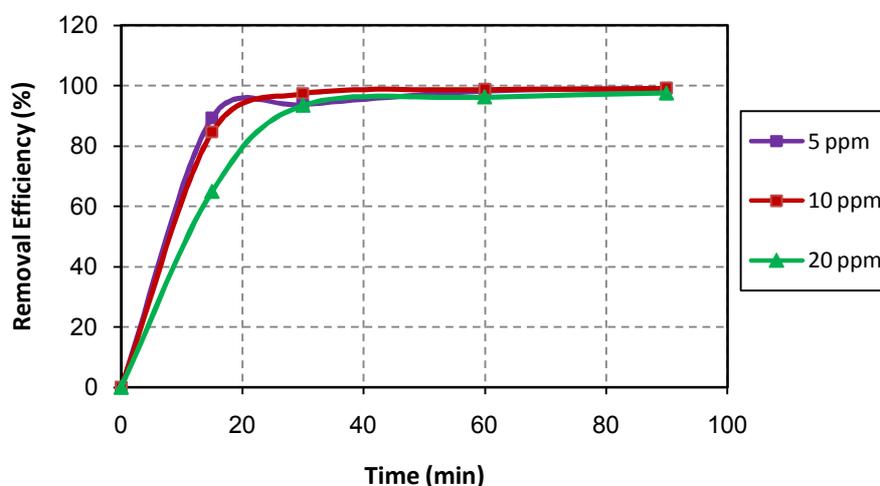


Figure 3. Effect of RB concentration on the photocatalytic degradation; $T=25^{\circ}\text{C}$ $\text{pH}_0=7$, Under UV-C light ($\lambda=254\text{nm}$, 6W)

Effect of pH

pH plays an important role in the photocatalytic degradation of RB. The pH of solution influences adsorption, catalyst surface charge, oxidation potential of valence band, and other physicochemical properties. The pH of the reaction has a significant effect on the surface properties of the TiO_2 catalyst, which include the surface charge of the particles, the extent of aggregation of the catalyst particles, and the band edge position of TiO_2 . The zero charge point (pH_{ZPC}) for Degussa P-25 TiO_2 is at $\text{pH}=6.7$. The extent of positive charges on the TiO_2 surface decreases with increasing pH and reaches zero at pH_{ZPC} . Therefore, pH significantly affects the adsorption-desorption properties of the compounds on the surface of the catalysts [20]. At $\text{pH} > \text{pH}_{ZPC}$, TiO^- is the predominant species, whereas at $\text{pH} < \text{pH}_{ZPC}$, TiOH_2^+ is the predominant species according to the following equilibrium:



The effect of pH on the photocatalytic degradation of RB was studied at the pH range of 3 to 9 using initial concentration of 10 ppm and optimum value of catalyst loading (0.3 g/l). The pH value was adjusted by adding dilute NaOH or HCl solutions. The effect of pH on the reaction rate of RB is shown in Figure 4. As can be seen from this figure, the maximum degradation of RB occurs at $\text{pH}=7$. However, after 90 min treatment at $\text{pH} 7.0$ and 9.0 , the removal rate reaches 98.71% and 88.09% respectively.

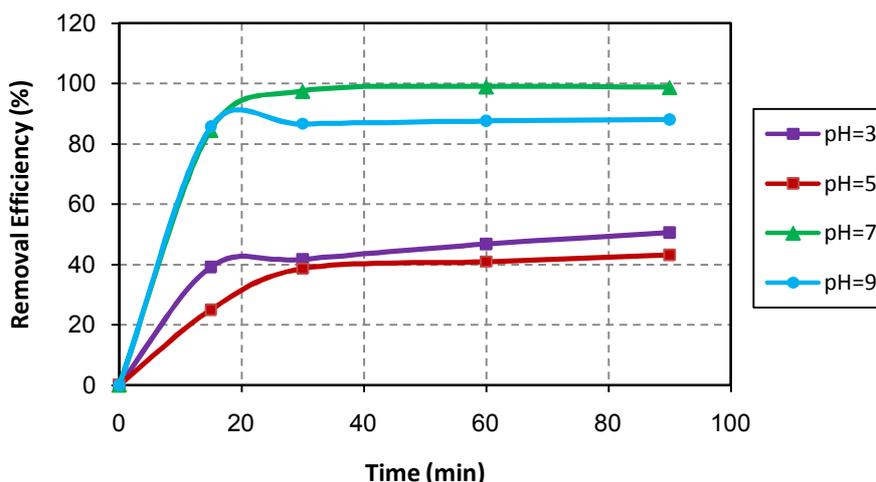


Figure 4. Effect of pH on the photocatalytic degradation of RB; T = 25°C, Under UV-C light ($\lambda=254\text{nm}$, 6W)

As a result, pH 7.0 was selected as the optimal operational pH value in the present study. The pseudo-first-order reaction rate constants obtained for the photocatalytic degradation of RB within 90 min irradiation time at different pH values are presented in Table 3.

Table 3. Effect of pH on the photodegradation rate of RB at different irradiation times

pH	$K_{obs}(\text{min}^{-1})$	R
3	0.0062	0.808
5	0.0055	0.843
7	0.050	0.905
9	0.0075	0.831

Effect of different light sources

The effect of different light sources on the photocatalytic degradation rate is shown in Table 4 and Figure 5. The results of experiments indicated that the wavelength of the light used for photoactivation has a significant impact on the dye degradation rate; shorter wavelengths lead to faster degradation. UVC lamp as a light source resulted in the highest apparent rate constant ($k_{obs}=0.051 \text{ min}^{-1}$) that may be due to the highest illumination intensity. It means that the activity of the photocatalyst depends strongly on the light-illumination (energy per unit area) or the photon flux on the surface of the photocatalyst. The order of degradation rate using different light sources was shown to be UV-C>UV-A>UV-LED.

It should be noted that, the light source of UVLEDs (960 mW) can save a lot of energy in comparison with the traditional UV lamps (6 W). Using UVLED as a light source can enhance not only the safety with less UV intensity but also the energy usage efficiency. Among the UVA lamps, Black Light Blue (BLB) has the highest removal efficiency.

Table 4. Effect of different light sources on the photodegradation efficiency of RB

Light sources	$K_{obs}(\text{min}^{-1})$	R
UV-C	0.051	0.905
Black light (UVA)	0.026	0.971
Black light blue (UVA)	0.035	0.928
Day light	0.016	0.982
UV-LED	0.005	0.967

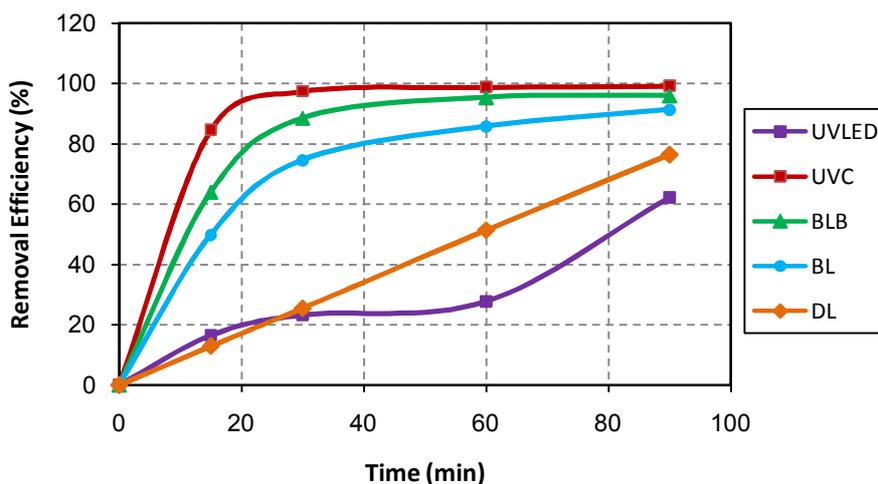


Figure 5. Effect of different light sources on the photocatalytic degradation of RB; $T = 25^{\circ}\text{C}$, $\text{pH}_0 = 7$

CONCLUSION

A detailed feasibility study has been carried out on the photocatalytic degradation of Rhodamine B using TiO_2 as a photocatalyst under UV light radiation. This process was efficient in the degradation of RB, a dye of industrial importance. It was observed that RB initial concentration, pH, and catalyst loading significantly affect the photoactivated process. Furthermore, this study also proposed the photocatalytic kinetic models. For the configuration used, the optimum ranges of RB concentration (10 mg/l), pH (7), and catalyst loading (0.3 g/l) were determined. The order of the degradation rate using different light sources was shown to be $\text{UVC} > \text{UVA} > \text{UVLED}$. UVC lamp has the highest apparent rate constant ($k_{\text{obs}} = 0.051 \text{ min}^{-1}$) that may be due to the highest illumination intensity. Finally, it can be concluded that UV/ TiO_2 process can be used successfully for the treatment of RB contaminated wastewaters.

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