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DECOLORIZATION OF REMAZOL BLACK B IN AQUEOUS SUSPENSION OF TIO_2

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ABSTRACT: *Commercially available titanium dioxides from two different companies, one from Fluka, Switzerland (designated as n-TiO_2) and another from Merck, Germany (designated as p-TiO_2) were used for the removal of Remazol Black B (RBB) from aqueous solution. The experimental results reveal that p-TiO_2 acts as an adsorbent as well as a photocatalyst owing to porous surface morphology, whereas n-TiO_2 does not demonstrate adsorption characteristics due to its non-porous and granular surface morphology. Adsorption of RBB on p-TiO_2 was found to occur rapidly and more than 40% dye was adsorbed within 5 minutes. Under irradiation of sunlight and UV-light, the photocatalytic activities of the p-TiO_2 and n-TiO_2 were also examined, and the results manifest the higher degradation efficiency of the p-TiO_2 than n-TiO_2. Different experimental parameters such as catalyst loading, pH, and concentration of solution have been varied to search optimum conditions. Photodegradation efficiency was also found higher under sunlight irradiation than UV-light.*

KEYWORDS: Adsorption, Photodegradation, Kinetics, Langmuir-Hinshelwood, Remazol Black

INTRODUCTION

Increased industrial, agricultural and domestic activities result in the production of large amounts of wastewater (Bhatnagair and Minocha, 2006). Wastewater contaminated with industrial effluents or household wastes are the main source of environmental pollution and are the severe setback for the environmental protection issues. In most of the third world countries, waste from various factories, industries, agricultural and domestic effluents are discharged directly to different bodies of water sources without prior treatment generating pollution and secondary effects on the environment (Toze, 2006). The textile industry utilizes about 10,000 different dyes, pigments and about 17–20% of water pollution occurs from textile and dyeing industries (Beltrán-Heredia et al., 2009, Yang et al., 2013, Liang et al., 2014).

Among the dyes, azo dyes constitute the largest and the most important class of commercial dyes and over 60-70% of all the dyes used in the industry are azo dyes (Riaz et al., 2013). Among all the synthetic dyes released in the industrial wastewater, the azo dye is one of the most detrimental classes because it is toxic, non-biodegradable and highly persistent in the aquatic environment (Camargo and Morales, 2013). Most of these dyes are resistant to microbial degradation and thus disposal of these dyes into the open sources demolish our ecosystems by changing the reproduction of animals and plants. Therefore, their removal from the waste streams is very essential and an environmental priority.

Industrial wastewater can be treated by a number of techniques such as adsorption (Yagub et al., 2014, Zhu et al., 2014, and Zeng et al., 2014), flocculation-precipitation (Beltrán-Heredia et al., 2009, Yang et al., 2013), membrane filtration (Liang et al., 2014) and electrochemical techniques (Singh et al., 2013, Steter et al., 2014) etc. Among these methods, adsorption is well-established, sophisticated and more appropriate technique because of their inexpensiveness, the easiness of device formation and availability of huge number of adsorbents (Bhattacharyya and Sharma, 2005, Ofomaia and Ho, 2008, Piccin et al., 2013). All these methods including adsorption process have secondary sludge disposal problem, as they do not degrade the pollutant completely, they just transfer dyes from one phase to another (liquid- to solid-phase) and causing secondary pollution (Padermpole and Hisanaga, 2000). Therefore, further treatments are necessary, which are relatively expensive due to repetitive procedures. In this respect, advanced oxidation or semiconductor mediated photocatalysis becomes an effective and efficient alternative treatment approach, which can be applied potentially for the destruction of dyes from industrial effluents (Nishio et al., 2006, Marugan et al., 2007). Advanced oxidation methods of wastewater treatment not only transfer the pollutants from one phase to another but also mineralize the pollutants completely into harmless products such as CO_2, water and salts. Thus, the oxidation of contaminants under irradiation of light in either water or air using photocatalyst has fascinated significant attention (Sharma et al., 1995, Gouvea et al., 2000).

Conventional oxidation processes like ozonation and chlorination are efficient in demolishing only several classes of organic pollutants. Advanced Oxidation Processes (AOPs), which produce hydroxyl radicals, have been considered as the most effective technologies for treating organic chemicals including dyes in wastewater. AOP usually engenders reactive oxidative species like •OH radicals, O_2^- and H_2O_2, which oxidize a wide range of organic contaminants hastily and non-selectively (Yang et al., 1998, Das et al., 1999). Generally, AOP comprises of a combination of either semiconductors and light, or oxidants and light e.g. H_2O_2/UV, Ozone/UV, Ozone/H_2O_2, Fenton's reagent; photo-Fenton, etc. have been widely studied for complete degradation of organic pollutants in industrial wastewaters (Kim et al., 2012, Teunissen et al., 2012, Yao et al., 2014). In the advanced oxidation process, when a semiconducting material is irradiated with light of energy equal or greater than the band gap energy of the semiconductor, the photons are absorbed and electron–hole pairs are generated. These electrons and holes, then, either recombine or drift towards the surface participating in several redox reactions. Consequently, generating reactive oxygen species (ROS) such as •OH radicals, O_2^- and H_2O_2 (Matthews, 1986, Chong et al., 2010). These ROS then induce a number of reactions, which end up in complete mineralization of the contaminants or dyes.

Titanium dioxide (TiO_2) is a superior and excellent photocatalyst and has the capability to decontaminate water from a large number of contaminants/pollutants (Khodia et al., 2001, Kusyuran et al., 2005). TiO_2 is attractive since it is stable, insoluble, non-toxic, resistant to corrosion and relatively inexpensive (Serpone and Pelizzetti, 1989, Alberici et al., 1994). In this report, we have used two different types of commercial TiO_2, one may be rutile TiO_2 (from Fluka, Switzerland, later denoted *n*-TiO_2) and another is Degussa p 25 TiO_2 (from Merck, Germany, denoted as *p*-TiO_2), are used as the adsorbent and the photocatalyst for degradation of dye (Remazol Black B, denoted as RBB) from aqueous solution. Experiments were also carried out in the presence of different types of light sources such as sunlight and artificial UV-visible light and compared the results to find the maximum efficiency.

EXPERIMENTAL METHODS

Commercial titanium dioxides *n*-TiO_2 and *p*-TiO_2 (Degussa p 25) were purchased from Fluka, Switzerland and Merck, Germany, respectively. RBB was obtained from Dystar, Germany and all the samples were used without further purification. Adsorption and photocatalytic degradation of RBB were carried out in the presence of TiO_2 under different experimental conditions. In a standard experiment, a fixed amount of the TiO_2 was taken in a 100 mL standard flask at room temperature. 20.0 mL deionized water was added and kept overnight for soaking and smoothening of the catalytic surface. 80.0 mL of the specified concentrated dye solution was added to the suspension to obtain a desired concentration of the dye solution and stirred for a defined amount of time for adsorption of RBB onto TiO_2. Similar fashion, after the addition of RBB solution to the suspension of TiO_2, the UV- lamp was turned on and this was taken as ‘‘time zero’’ for the degradation reactions. After a definite interval of adsorption or photodegradation, 5 mL of the solution was withdrawn from the solution of experimental system and the aqueous samples were centrifuged at 4000 rpm to remove suspended solid TiO_2. The absorbance of the clear solution was measured at the λ_{max} = 595 nm (corresponds to the absorption maxima of the dye) using UV-visible spectrophotometer (UV-1650 PC, Shimadzu, Japan). In the presence of sunlight, the photodegradation of RBB solutions was executed in the same conditions. The shape and surface morphology of the TiO_2 was investigated by field emission scanning electron microscope (JEOL, JSM-6490LA, Japan) under an acceleration voltage of 15 kV.

RESULTS AND DISCUSSION

Adsorption of RBB on TiO_2

Effect of contact time

Scanning electron microscopic (SEM) images of the *p*-TiO_2 and *n*-TiO_2 are presented in Figure 1. The micrograph of *n*-TiO_2 shows granular shape agglomerated into big particles, but that of *p*-TiO_2 presents porous texture. Figure 2 displays the adsorption of RBB on *p*-TiO_2 and *n*-TiO_2, where it is found that RBB does not undergo adsorption on *n*-TiO_2 at the normal pH~6.8 of the aqueous solution, but undergoes adsorption on *p*-TiO_2. This result of adsorption could be explained with the help of surface morphology of the TiO_2. Because of the porous morphology of *p*-TiO_2, it demonstrated a consideration extent of adsorption of RBB from aqueous solution.

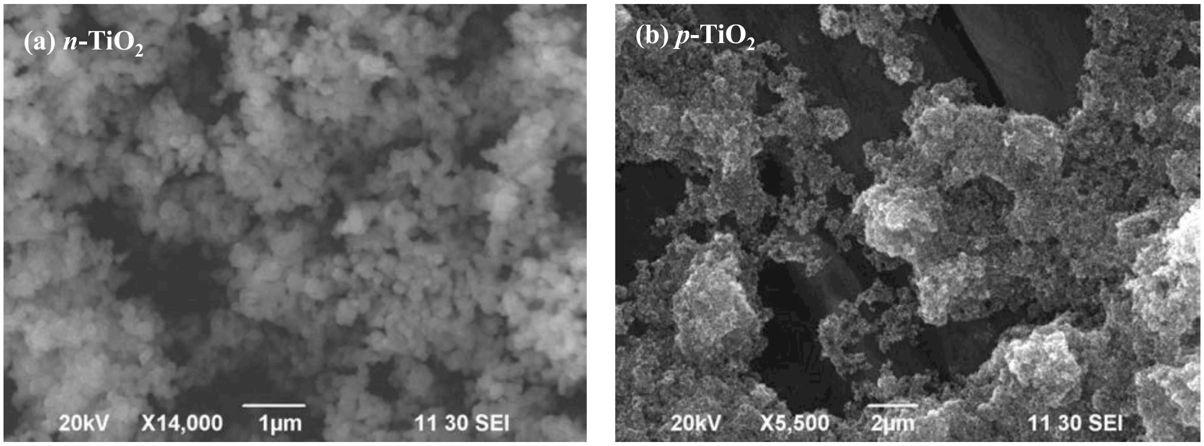

Figure 1 SEM micrograph of TiO_2. (a) *n*-TiO_2 and (b) *p*-TiO_2.

The extent of dye removal increased with the increase of contact time. The adsorption of RBB on *p*-TiO_2 from aqueous solution reached equilibrium within 40 minutes and about 45% of dye was removed by adsorption process. Initial adsorption was rapid due to the adsorption of dye onto the exterior surface, after that dye molecules might enter into the pores (interior surface), relatively slow process.

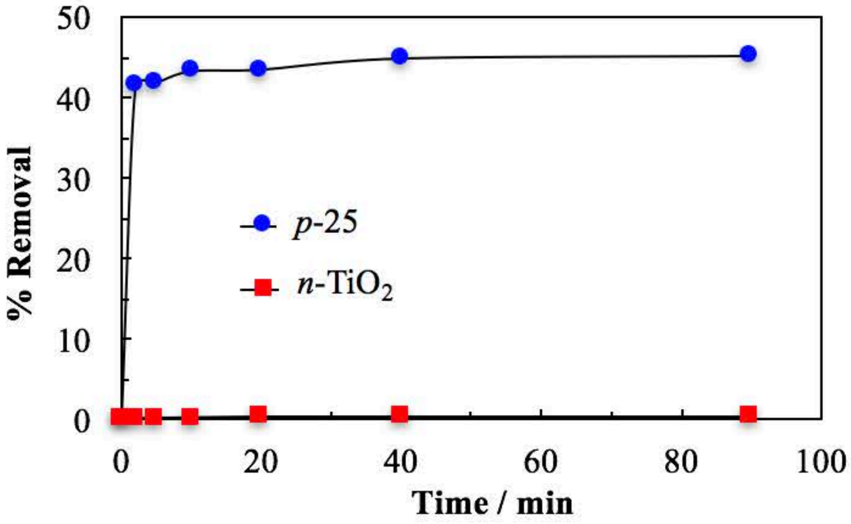

Figure 2 Removal of RBB by adsorption on TiO_2, TiO_2 loading 0.2 g/100 mL, $[RBB]_o = 3 \times 10^{-5}$ M, and pH = 6.86.

Effect of pH on adsorption

Adsorption isotherms were measured at two different pH such as 6.86 and 3.03. It is clear from the figure 3 that the adsorption of RBB is considerably higher at a lower pH = 3.0. RBB (a sodium salt) is an anionic azo dye and dissociated completely in aqueous media. Due to TiO_2's

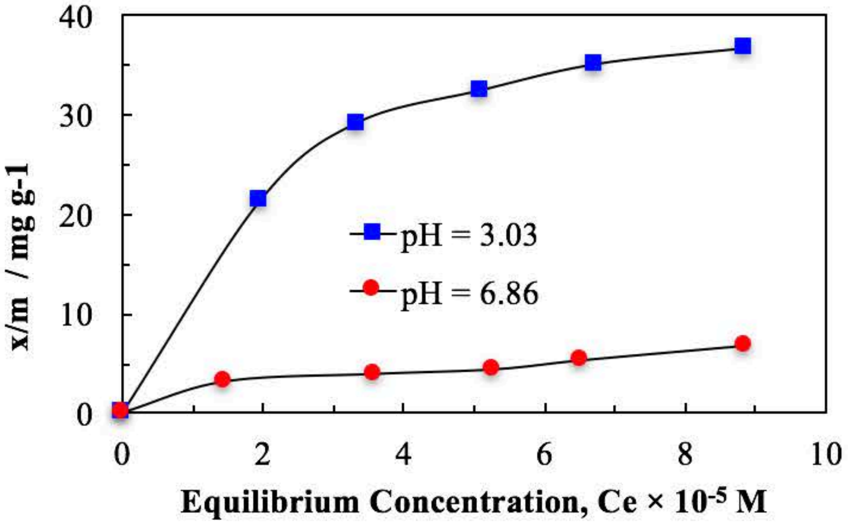

Figure 3 Effect of pH on the adsorption of RBB on *p*-TiO_2, TiO_2 loading 0.2 g/100 mL, $[RBB]_o = 3 \times 10^{-5}$ M.

amphoteric character, either a positive or a negative charge can develop on its surface (Gupta, 1994). In acid media pH < 7, surface of TiO_2 becomes positively charged. Thus a very strong electrostatic attraction of anionic dye molecules together with the capturing of the molecules into the pores of *p*-TiO_2 is expected to occur. This produces a large extent of adsorption at lower pH.

Adsorption isotherms

To gain an insight about the adsorption behavior of the RBB onto TiO_2, the equilibrium adsorption data were analyzed using two adsorption isotherm models; the Freundlich (Namasivayam and Kanchana, 1992) and the Langmuir (McKay et al., 1989) expressed by equations 1 and 2, respectively.

$$log q_t = log K_F + 1/n \, log C_e \dots\dots\dots\dots\dots\dots (1)$$
$$1/q_t = 1/q_0 + (1/K_L \, . \, q_0). {}^{1}/_{C_e} \dots\dots\dots\dots\dots (2)$$

Where, K_F parameter is related to the adsorption capacity and n is a measure of adsorption intensity.

The Langmuir constant K_L, is related to the energy of adsorption and q_o is the maximum values of adsorption capacity (corresponding to complete monolayer coverage). The plots of Freundlich and Langmuir isotherms are shown in Figure 4. Binding parameters for the adsorption of RBB on TiO_2 calculated from the gradient and intercepts of the adsorption isotherms are listed in Table 1, along with the correlation coefficients (R^2). The values of correlation coefficients (R^2) for the two models (Table 1) stipulated that experimental data fitted the Freundlich model than to the Langmuir models more satisfactorily.

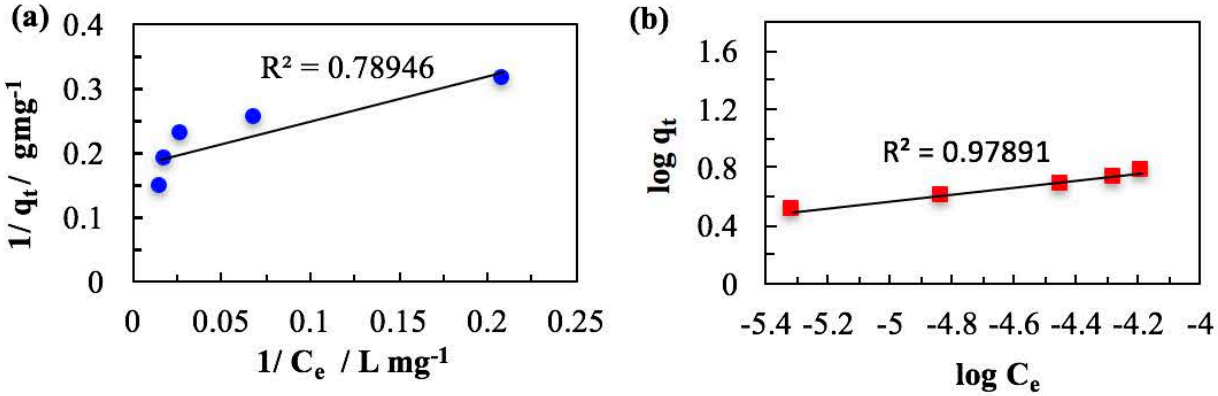

Figure 4 (a) Langmuir and (b) Freundlich isotherm of the adsorption of RBB on *p*-TiO_2 at pH = 3.0 and TiO_2 loading 0.2 g/100 mL, $[RBB]_o = 3 \times 10^{-5}$ M.

Table 1 Characteristic parameters of adsorption of RBB on to the *p*-TiO_2.

Freundlich isotherm			Langmuir isotherm		
K_F x 10^{-3} (mg/g).(L/M)$^{1/n}$	n	R_1^2	q_o (mg/g)	K_L x 10^{-6} (L/M)	R_2^2
287.73	4.531	0.97891	4.7619	1.7	0.78946

Photodegradation of RBB by TiO_2

Effect of time course

The absorbance of the supernatant solution taken from the reaction suspension after a various time of degradation were recorded and percent degradation were calculated. Figure 5 displays the photodegradation of RBB (6×10^{-5} M) under UV-light irradiation in the presence of TiO_2. The figure shows after 90 minutes of degradation about 98% of the dye degrades under illumination of UV-light for *p*-TiO_2, whereas 95% of the RBB is degraded after 210 minutes of illumination for *n*-TiO_2. The higher effectiveness of the *p*-TiO_2 might be attributed from the higher number of active sites provides by the both surfaces and pores of the *p*-TiO_2.

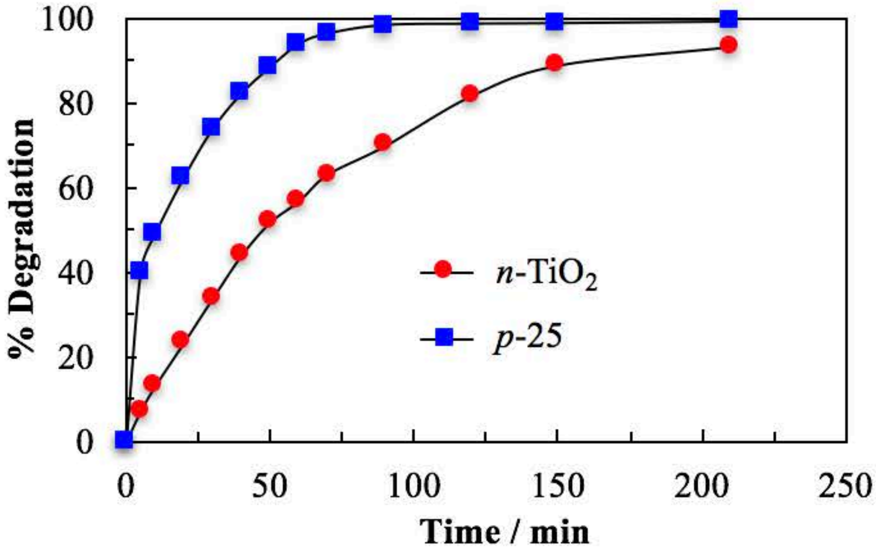

Figure 5 Degradation of RBB with time under UV irradiation in the presence of TiO_2 suspension. $[RBB]_0 = 6.0 \times 10^{-5}$ M, pH=3.0, TiO_2=0.6 g/100 mL.

Effect of catalyst dosages

To investigate the effect of catalyst dosage on the degradation rate of RBB in presence of TiO_2 and find out the optimum removal parameters, photodegradation experiments were carried out using different concentration of TiO_2 (0.2 to 1.2 g/100 mL) with other parameters remaining constant (concentration of RBB 6.0 x 10^{-5} M and pH ~ 6.8). The degradation of RBB as a function of time with the various amounts of TiO_2 was shown in supporting Figure S1 and S2. It is observed that with an increase of TiO_2 loading the percent of the RBB degradation increase from 63 to 98 % and 34 to 65 % after 90 minutes' irradiation of UV-light for *p*-TiO_2 and *n*-TiO_2, respectively. It is noteworthy that the initial rate of photodegradation is found higher for *p*-TiO_2 than *n*-TiO_2. This result is expected because *p*-TiO_2 demonstrates rapid adsorption (more than 40 % dye removes within 5 minutes of adsorption as shown in Figure 2) of RBB from aqueous solution. Whereas, the rate of degradation of RBB is initially (from 0 to 5 minutes) very slow for *n*-TiO_2 (Figure S2). The rate becomes sufficiently higher at the latter stage of photodegradation (after 5 minutes). Such behavior is usually observed for autocatalytic reaction (Rubnov et al., 1999, Carlos et al., 2009). It seems that one or more intermediates would be formed from RBB by the exposure of UV-light. This intermediate would then catalyze the reaction, which increases the rate of reaction after several minutes of irradiation. Another possibility is that light-induced adsorption of the dye molecules occurs on the surface of the TiO_2 according to the equations (3) and (4). The step (4) might be responsible for enhancing the rate of reaction.

$$RBB + h\vartheta \rightarrow {}^{*}RBB \ldots\ldots\ldots\ldots(3)$$

$$^{*}RBB + TiO_2 \rightarrow TiO_2(e) + RBB^{+}_{ads} \ldots\ldots\ldots(4)$$

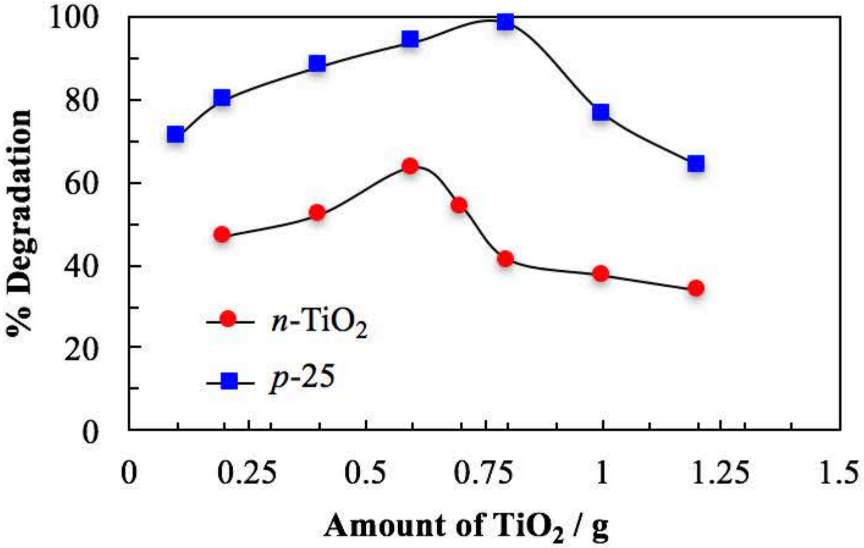

Figure 6 Effect of catalyst dosage on the degradation of RBB by TiO_2, [RBB] = 6 × 10^{-5} M, pH = 6.86.

Figure 6 shows a plot of percent degradation after 90 minutes of photolysis against the amount of TiO_2. It is found that the rate of degradation of RBB increases steadily with the increase of TiO_2 loading, reaches an optimum at 0.8 g/100 mL and 0.6 g/100 mL for *p*-TiO_2 and *n*-TiO_2, respectively, and then decrease again. This observation could be explained in terms of availability of active sites on the catalyst surface (Velusamy et al., 2015), photon absorption capacity and the penetration of UV light into the suspension (Shibin et al., 2015**.** Formation of reactive $^{\bullet}OH$ radicals and other reactive oxidative species (ROS) enhanced by the amount of TiO_2 due to the availability of a higher number of active surface sites and more photon absorption. Therefore, more frequent and efficient interaction occurs between the RBB and ROS, which augment degradation. When the optimum amount of TiO_2 is attained, further increase of an amount of TiO_2 might lead scattering of the photon and miniaturized the transmission of light in the solution. Furthermore, there is a chance to form aggregates by TiO_2 particles at higher concentration, resulting in reduced number of active surface sites for interaction between RBB and catalyst (Shibin et al., 2015)**.** Moreover, at higher concentration of catalyst, a part of the excited TiO_2 might collide with non-activated catalyst and deactivated, which also abridged the photocatalytic degradation (Rabindranathan et al., 2003).

Effect of pH

The pH of the aqueous solution is one of the important environmental parameters, which significantly influence the physicochemical properties of semiconductors, including the surface charge of the TiO_2 particle, the aggregation number of particles and the position of the conduction and valence bands. The electrical character of the TiO_2 surface varies with the pH of the dispersion (Piscopo et al., 2001). Experiments were carried out at various pH values, ranging from 2 to 10 for constant dye concentration (6.0×10^{-5} M) and catalyst loading (0.6 g/100 mL for TiO_2) and the percent degradation time profiles are given in supporting information Figure S3 and S4, respectively. Figure 7 reveals that the percent degradation is much higher at acidic pH values and minimum at pH 6-7, which is consistent with the literature results (Kaur et al., 2007, Lu et al., 2008, Kansal et al., 2009). The pH not only affects the properties of TiO_2 but also the dissociation of RBB and formation of hydroxyl radicals (Gupta, 1994).

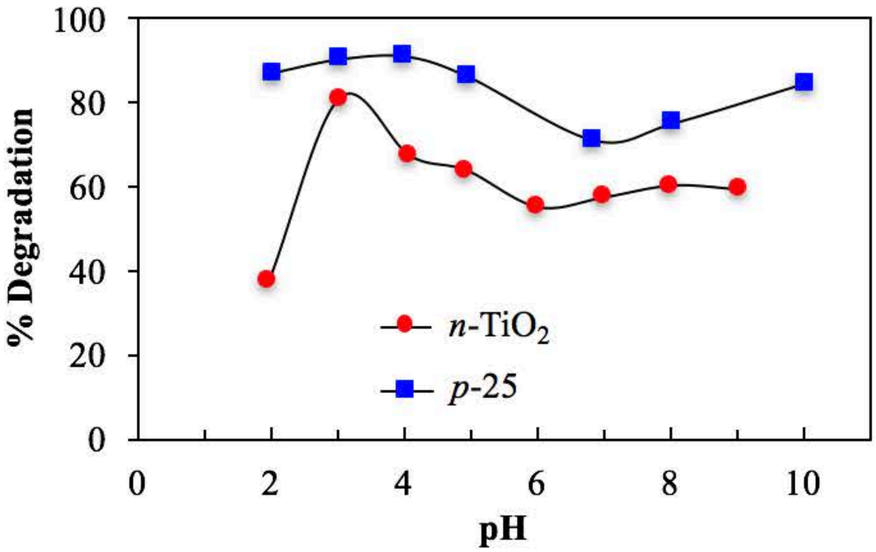

Figure 7 Percent degradation of RBB by TiO_2 at different pH of the solution. Amount of TiO_2 = 0.6 g/100 mL and $[RBB]_0 = 6.0 \times 10^{-5}$ M.

RBB is an anionic azo dye and dissociated in aqueous media. In acid media pH < 7.0, surface of TiO_2 becomes positively charged. The positively charged surface of TiO_2 adsorbs anionic species readily. Hence adsorption of RBB^- is favored on TiO_2 surface and degradation becomes faster. Figure 7 shows that the maximum photodegradation occurs at pH 3.0-4.0. With a further decrease in the pH, the percent degradation decreases might be due to coagulation of the TiO_2 particles (Cao et al., 2010), which are settled down at the bottom of the beaker and are less effective in producing electrons or holes.

With the increase of pH from 3.0, the percent degradation decreases and goes to a lower value at pH 6.0-7.0. This is because in this pH the surface of TiO_2 remains uncharged and the RBB are not adsorbed strongly on the TiO_2 surface. But above pH 7 the percent photodegradation is found to increase slightly. In alkaline condition, the surface becomes negatively charged. Hence, it is difficult for an anionic dye to adsorb onto the negatively charged TiO_2 surface, but enhancement of the degradation rate under alkaline condition would be accredited to the presence of large number of hydroxyl ions, which induces more hydroxyl radical formation (Gupta, 1994).

Effect of initial concentration of RBB

After optimizing the variables, i.e. concentration and pH of TiO_2 suspension, the photo catalytic degradation of RBB was investigated by changing the initial concentration of RBB in order to obtain the suitable concentration for maximum degradation. Figure 8 (supporting information Figure S5 and S6) displays the effect of RBB concentration on photodegradation by using 0.6 g/100 mL of TiO_2 at pH 3.0. It is observed that percent of degradation decreases with the increase of the concentration of RBB. This is because in the reaction system the RBB collide with the ROS or other reactive species, thereby, as the concentration of RBB becomes adequate to collide with the optimum amount of available ROS and other reactive species, any further increase of concentration, then, does not boost up the reactions and thereby rate of degradation becomes independent of the concentration of RBB.

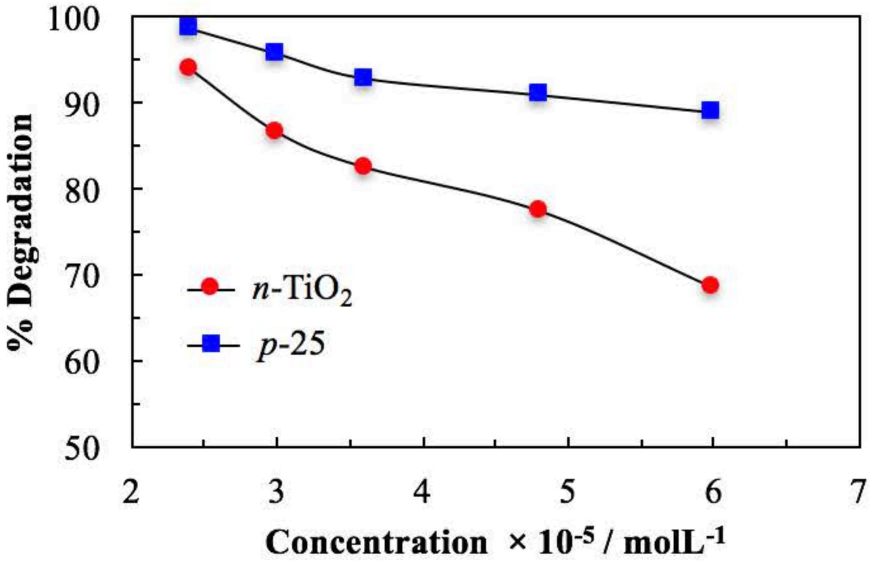

Figure 8 Effect of initial concentration on the degradation of RBB under UV irradiation by TiO_2 with amount of 0.6 g/100 mL at pH 3.0.

Moreover, at a higher concentration, a number of intermediates might be formed and some of the intermediates might remain in the medium and/or loosely attached into the vicinity of the catalyst surface for a relatively long period, which might halt collisions between fresh RBB and ROS (Shibin et al., 2015). Furthermore, the more number of RBB molecules adsorbed on the catalyst increases the light absorption rather than catalyst surface or the intermediates that have loosely stayed in the vicinity of the catalyst surface might absorb more photons at higher concentration, thereby reduces the photons availability for TiO_2 activation. Additionally, the path length of light entering to the solution is contracted and fewer number of photons are going on the catalyst surface due to the overriding interaction between reactant/intermediate/product, which results in a decrease of engenderment of ROS species and hence the removal efficiency diminished (Daneshvar et al., 2003, Gupta, et al., 2012).

Kinetic analysis

Under optimized conditions, photodegradation of RBB was carried out in order to analyze the kinetic. Figure 9 shows the kinetics of disappearance of RBB under optimized conditions. The experimental data show that the photocatalytic degradation of the RBB in the TiO_2 suspension can be explained by the pseudo first order kinetic model (Langmuir-Hinshelwood) as given in equation (5), where it is assumed that there is no interaction between the dye and the reaction intermediates for the surface sites (Konstantinou and Albanis, 2003, Herrmann, 2005).

$$\ln\left(\frac{C_0}{C_t}\right) = kt \ldots\ldots\ldots\ldots\ldots\ldots\ldots. (5)$$

Where, C_o is the initial concentration of the contaminant (mg/L), C_t is the concentration (mg/L) at time t, t is the irradiation time and k is the limiting reaction rate at maximum coverage for the experimental conditions (min^{-1}). According to the equation (5) plot of ln (C_o/C_t) against t will give a straight line for first order reactions and slope of this line will be the pseudo first-order rate constant.

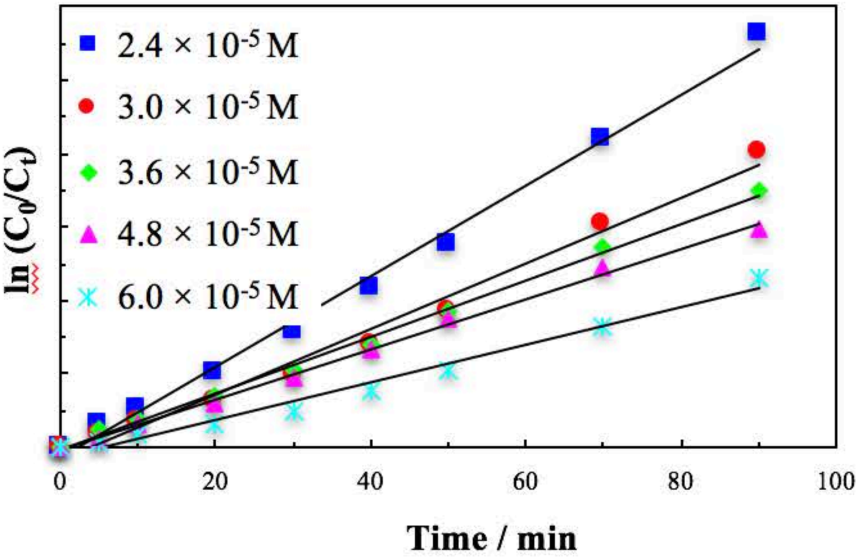

Figure 9 Kinetics of photocatalytic degradation of RBB by using TiO_2 with an amount of 0.9 g/100 mL.

The linearity of the plot of ln(C_o/C_t) vs t for the photodegradation of RBB in the presence of TiO_2 demonstrates that photocatalytic degradation follows pseudo first-order kinetics (Figure 9). From the gradient of the straight lines, the rate constants were calculated and are presented in Table 2. It is found that the rate constants for the photocatalytic degradation of RBB decrease with the increase of the concentration of dye. For a certain amount of catalyst and intensity of irradiated photon, the number of surface-generated actives species available for interaction are finite. But the number of RBB molecules is excessive at higher concentrations, which lowers a fraction of dye molecules to interact fruitfully with the ROS and subsequently decrease the rate constant (Shibin et al., 2015).

Table 2 Pseudo first order rate constants for the photodegradation of RBB by TiO_2, at 25^0C and pH = 3.0.

Concentration of RBB	Amount of TiO_2	k (n-TiO_2) / min^{-1}	k (p-TiO_2) / min^{-1}
2.4×10^{-5} M	0.6 g	0.03082	0.03170
3.0×10^{-5} M	0.6 g	0.02231	0.02902
3.6×10^{-5} M	0.6 g	0.01929	0.02527
4.8×10^{-5} M	0.6 g	0.01722	0.02311
6.0×10^{-5} M	0.6 g	0.01271	0.02199

Effect of light sources

Photodegradation of RBB was also performed by using TiO_2 as photocatalyst under solar light irradiation. Figure 10 illustrates the results of photodecolorization of the dye as a function of irradiation time under solar and UV-light. The results show, the rate of degradation of dye RBB in solar light is higher than in UV light for both the TiO_2 samples. The intensity of the solar light is much higher than the UV source used in this study (Jalil Miah et al., 2016, Kayes et al. 2016). Thus the higher effectiveness of the sunlight compared to the UV light should be related to the higher intensity of the former light sources.

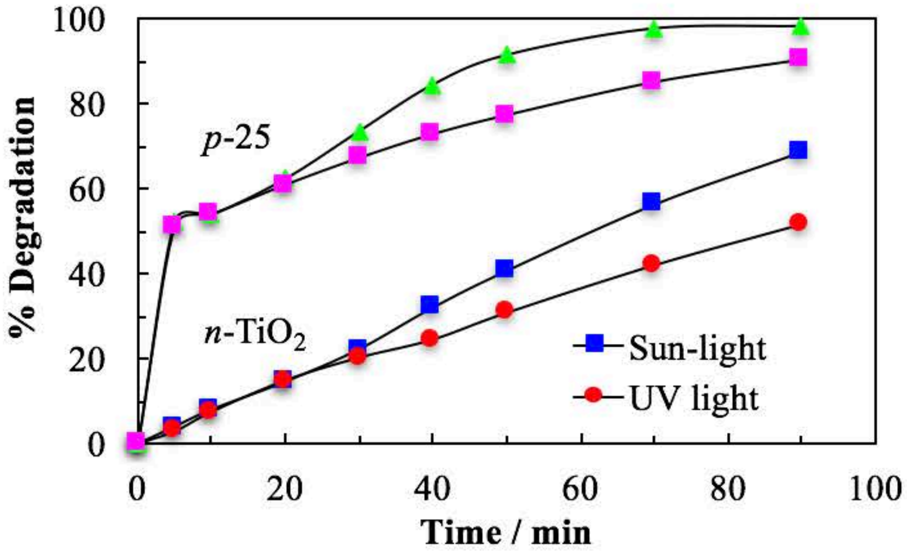

Figure. 10 Effect of different light sources on the rate of photodegradation of RBB using 0.1 g/100 mL of TiO_2, pH = 3.0.

CONCLUSIONS

Two different types of TiO_2 were employed for the removal of dye (RBB) from aqueous solution. The experimental results suggest that owing to porous surface morphology *p*-TiO_2 demonstrates a substantial amount of adsorption of RBB from aqueous solution, whereas *n*-TiO_2 does not adsorb

RBB due to granular surface morphology. Adsorption isotherm is found to follow the Freundlich model. The photocatalytic activities of the two TiO_2 were also investigated under illumination of sunlight and UV-light, and removal efficiency of the p-TiO_2 is found to higher than n-TiO_2. The optimum parameters for the photodegradation were studied. Under optimum condition, 98% and 70% of the dye was found to degrade after 90 minutes of UV-light irradiation by p-TiO_2 and n-TiO_2, respectively. Photodegradation efficiency under illumination of sunlight is found higher than UV-light illumination, due to higher intensity of the former light source.

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Supporting information

Decolorization of Remazol Black B in Aqueous Suspension of TiO_2

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Effect of catalyst (TiO_2) dosage, pH of TiO_2 suspension, and initial concentration of dye on the photodegradation of RBB under UV light irradiation in presence of two types of TiO_2 are shown graphically in this section.

Effect of catalyst (TiO_2) dosage on the photodegradation of RBB

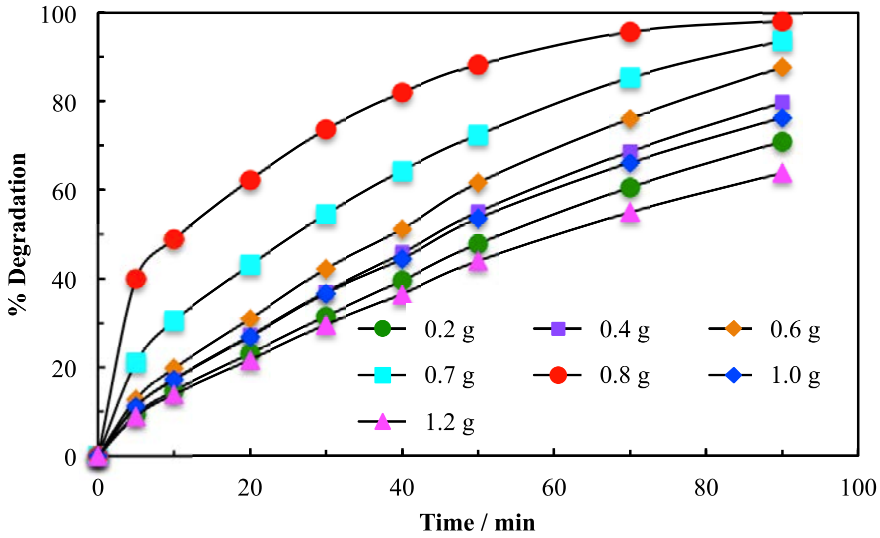

Figure S1 Effect of catalyst dosage on the degradation of RBB by *p*-TiO_2, [RBB] = 6×10^{-5} M, pH = 6.86.

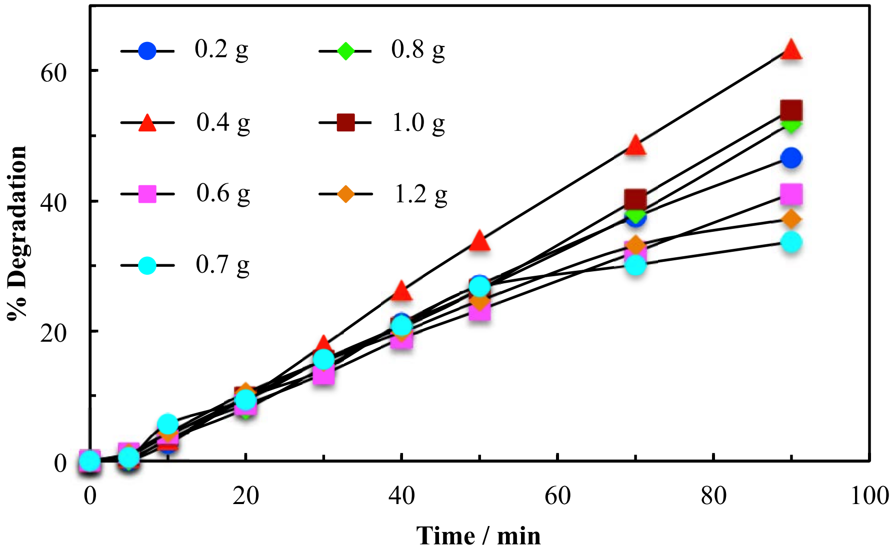

Figure S2 Effect of catalyst dosage on the degradation of RBB by *n*- TiO_2, [RBB] = 6×10^{-5} M, pH = 6.86.

Effect of pH of TiO_2 suspension on the photodegradation of RBB

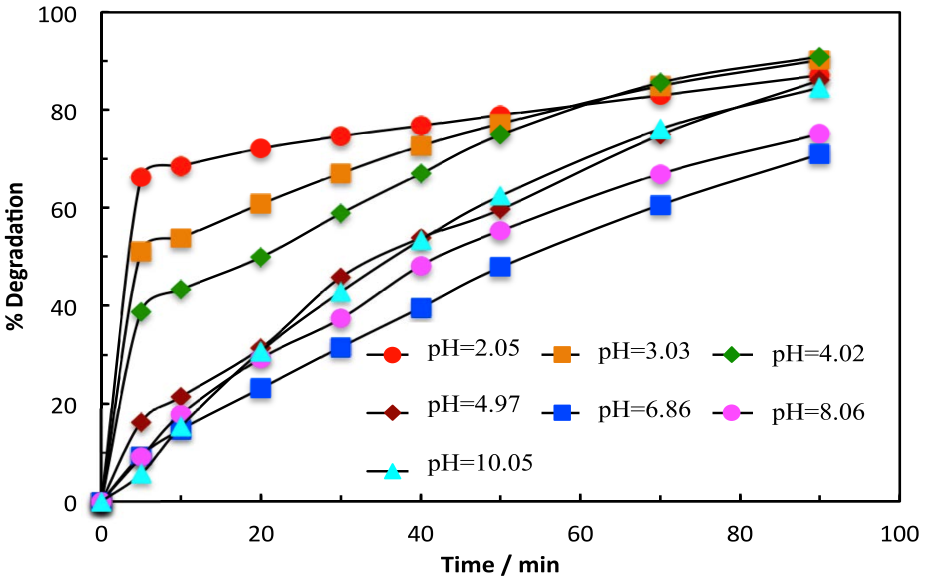

Figure S3 Percent degradation of RBB by *p*-TiO_2 at different pH of the solution. Amount of TiO_2 = 0.6 g/100 mL and $[RBB]_0$ = (6.0 x 10^{-5} M.

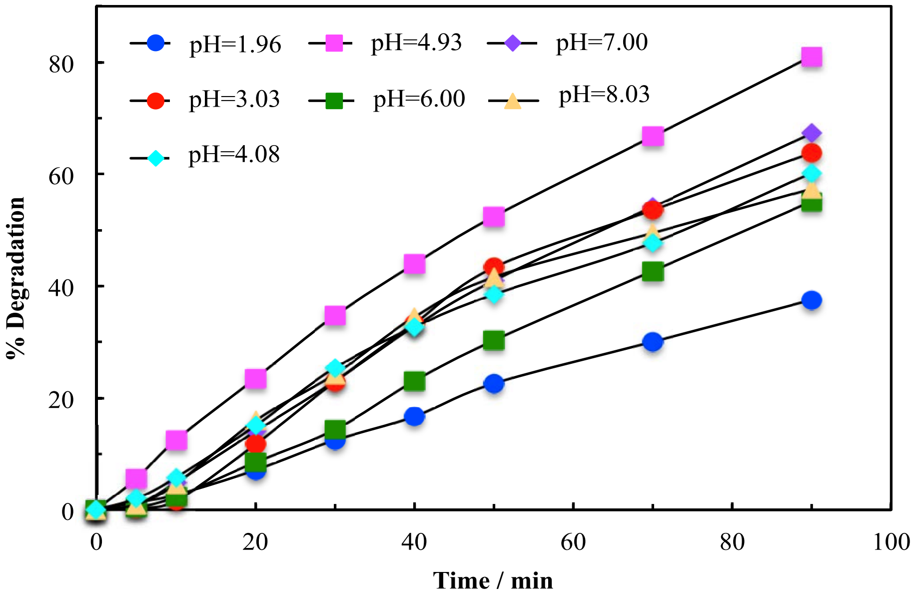

Figure S4 Percent degradation of RBB by *n*- TiO_2, at different pH of the solution. Amount of TiO_2 = 0.6 g/100 mL and $[RBB]_0 = (6.0 \times 10^{-5}$ M.

Effect of initial concentration of RBB on the photodegradation

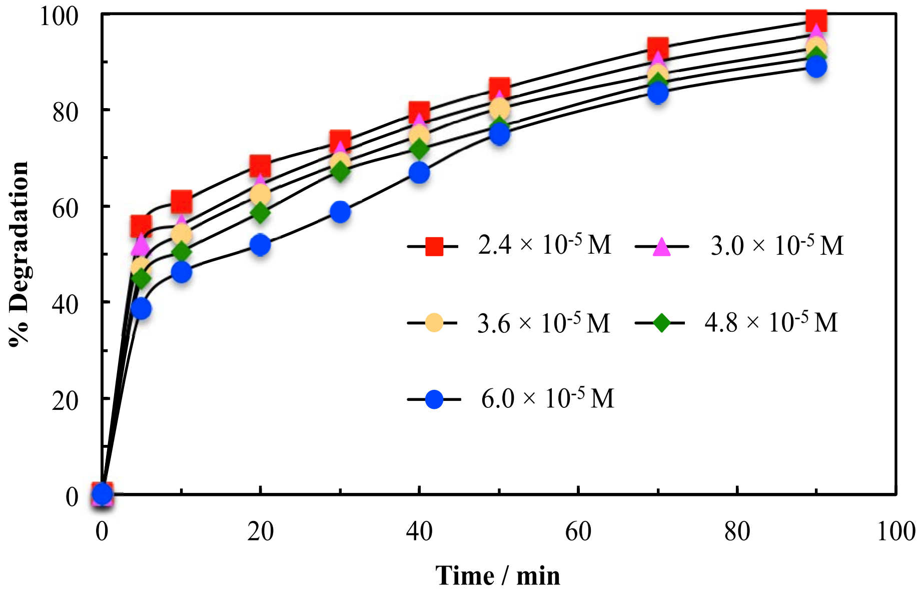

Figure S5 Effect of initial concentration on the degradation of RBB under UV irradiation by *p*-TiO_2, with amount of 0.6 g/100 mL at pH 3.0.

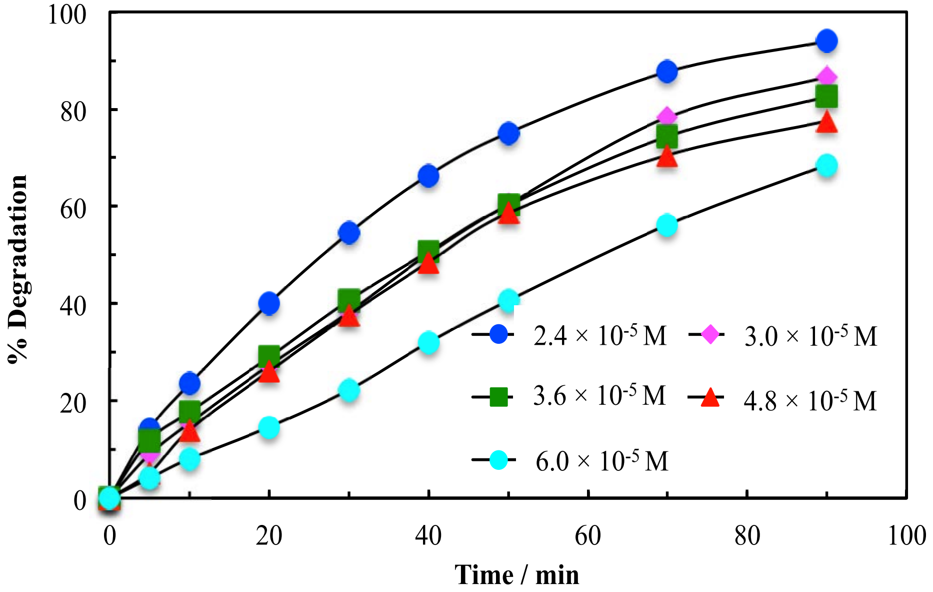

Figure S6 Effect of initial concentration on the degradation of RBB under UV irradiation by *n*-TiO_2 with amount of 0.6 g/100 mL at pH 3.0.