Remediation of Anionic Dye Simulated Wastewater Using TiO$_2$ as a Photocatalyst under Various Light Irradiation Wavelength

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Heterogeneous photocatalytic process employing UV/TiO$_2$ batch photo-reactor system was demonstrated to be effective in the photodegradation of C.I. Reactive Black 5 anionic dye. Various artificial lamps (UV-A, UV-B, UV-C and solar irradiation) were used to activate the TiO$_2$-P25 Degussa photocatalyst. UV-C was found to be the best in degrading RB5 with 100% efficiency at the 25th min with an R^2 = 0.9786 according to the first order reaction kinetic model. The effectiveness of UV-C is due to the shorter penetration capability with higher energy photon, so there was more electron-hole pairs available for the target compound. Photodegradation with UV-B was also similarly effective while UV-A and solar irradiations were least effective.

Increasing the initial dye concentration reduced the degradation rate due to the inner photon filtering effect by the dye molecules. Since RB5 is anionic dye, by increasing the pH of the system, the degradation rate was reduced to 99.65% in 1 h at pH10. This is due to the electrostatic attraction between the dye molecules and the negatively charged TiO$_2$ particles. Photocatalytic degradation was found to be affected by the pollutant concentration and solution pH which were explored and described in detail in this article.

Key words: Dye, RB5, photocatalysis and titanium Dioxide

The textile industry is the most polluting sector among the different human industrial activities with high effluent discharge volume due to the water demanding nature of its industrial process. These effluents are then release into the water system with little or no treatment at all. The effluents normally consist of high concentrations of dyes, surfactants, suspended solids and organic matter [1]. Textile wastewater also includes aqueous discharges from fibre and fabric preparations, desizing, scouring, bleaching, dyeing, finishing and other textile processing stages. Most mills operate their own wastewater treatment or pre-treatment plants to remove contaminants from effluent prior to discharge into water bodies or publicly owned treatment facilities [2].

Over the years, numerous physicochemical treatments, including coagulation, flocculation, filtration and membrane adsorption, were used to remove colour from textile effluents. Unfortunately, it has been found that these treatments have the disadvantages of generating sludge, difficulty in regeneration of spent adsorbents and fouling of the membrane filters [3]. Advanced oxidation processes (treatment with ozone, H$_2$O$_2$, Fenton's reagent and UV radiation) are the potential alternatives for the traditional decolourisation

methods of the dye contaminated wastewater. Among the advanced oxidation processes treatment for decolourisation, the photocatalytic method was found to be effective [4].

The semiconductor TiO$_2$ has been widely utilized as a catalyst in photocatalysis method [5] and is well known for its widespread applications in paints, sunscreens, environmental treatment and purification purposes due to its high level of photoconductivity, ready availability, nontoxicity, chemical stability, superhydrophilicity and low cost as well as high photoefficiency [6]. The high photocatalytic activity of TiO$_2$ is due to its excellent chemical and optical properties such as quantum size effect and strong adsorption in ultraviolet or visible region [7]. According to Baran *et al*. [8], the mechanism of the photocatalytic reaction in the presence of TiO$_2$ involves a free radical reaction initiated by UV light. Since, the resulting hydroxyl radical ($\cdot$OH), being a very strong oxidizing agent with a standard redox potential of +2.8 V, it can oxidize most of the organic pollutant which will subsequently undergo a complete mineralization process [9].

The aim of the present work is to investigate the influence of various parameters on photocatalytic decomposition of an azo dye, called Reactive Black 5(RB5). The influence of different light irradiation wavelength, initial dye concentration and solution pH were studied and presented.

EXPERIMENTAL

The photocatalyst used was titanium dioxide (Aeroxide® TiO$_2$ P25) obtained from Evonik, Germany (formerly known as Degussa). The average primary particle size of the photocatalyst was 21 nm while having a specific surface area (BET) of 50 ± 15 m^2/g. The crystalline components of TiO$_2$ consist of 80% anatase and 20% rutile. RB5 is a water-soluble dye which was easily dissolved in distilled water. RB5 was obtained from Sigma (55%) and used without further purification. Thisdye was prepared as 1000 ppm stock solution and was used throughout the experiment in various concentrations. The prepared stock solution was covered in a black plastic bag and stored in a dark cupboard to prevent interference from ambient light. RB5 was determined to have a peak maxima of 597 nm [10].

Photocatalysis Experiment

A 25 ppm of 500 ml RB5 aqueous solution at natural pH was placed in a 1000 ml beaker. Exactly 0.05 g of TiO$_2$-P25 Degussa was weighed and added to the prepared aqueous solution of RB5. The reaction mixture was then irradiated with 9 W UV-C BLB (Sylvania) lamp in a batch photo-reactor as show in Figure 1. The lamp was placed in a quartz lamp sheath and fitted to the centre of the beaker. The experiment was carried out at room temperature with stirring done continuously using a magnetic stirrer throughout the whole experiment to ensure well mixing of the solution.

The experiment was conducted for one hour with the samples collected every two min for the first 20 min and then every five min after that using a Nilon-membraned syringe filter and collected in a sample vial. These samples were analysed with the UV-vis spectrophotometer-Lambda 25 and the data was recorded.

The experiments were repeated in triplicates with the average taken and plotted into graphs. The experiments in the presence of catalyst were carried out with 1 g/l TiO$_2$, and with an initial concentration of RB5 varying between 5 and 25 ppm. The whole experiment was then repeated by changing the UV light wavelength; UV-A, UV-B and solar lamps, to study the effect of the different irradiation wavelength on the target pollutant. The solution pH was adjusted using 0.10 M HCl for acidic pH or 0.10 M NaOH for alkaline pH.

Light Intensity Measurements

The lamps used for this study were 9 W UV-A (Sylvania), 9 W UV-B (Philips), 9 W (Pro UV) UV-C lamps and 9 W Solar lamp (Coralife). The light intensity for each lamps were taken from the manufacturer's specification that is 10 mW/cm^2 while having a total radiating surface are of 86.4 cm^2 for each lamp.
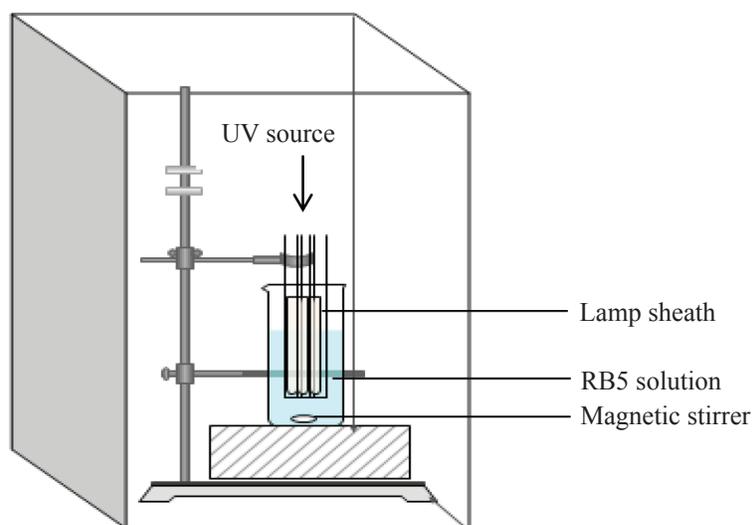
Figure 1. Set up of batch photo-reactor.

Dark Experiment

In order to prove the adsorptivity of RB5 on TiO$_2$-P25, a simple adsorption experiment was carried out. 25 ppm of 500 ml RB5 aqueous solution at natural pH was placed in a 1000 ml beaker. About 0.05 g (dry weight) of TiO$_2$-P25 Degussa was measured using an electronic balance and added to the prepared aqueous solution of RB5. The reaction mixture was placed under dark condition without any light sources and stirred continuously. The experiment was conducted for an hour with samples extracted every 5 min using a syringe filter and analyse with the UV-vis spectrophotometer.
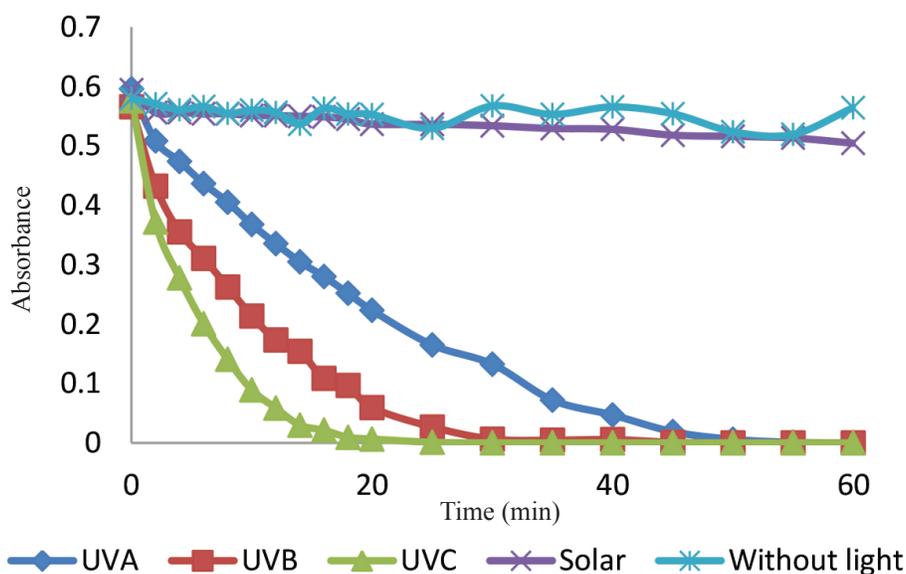

Figure 2. Degradation of 25 ppm of RB5 solution during photocatalysis with different UV radiations and without radiation using 0.1g/l TiO$_2$ catalyst loading.

RESULTS AND DISCUSSION

Photocatalysis Result

In order to prove the adsorptivity of TiO$_2$, the dark experiment was carried out under the same reacting conditions for all experiments in the absence light source. Adsorptivity of RB5 on TiO$_2$ surface can be found in Figure 2. From Figure 2, not much of a change in concentration of RB5 solution can be observed throughout the hour. After 12 min, the line appears to be fluctuating signifying that the adsorption equilibrium was reached. The highest degradation efficiency achieved was just 4.03% within 12 min. Similar findings were reported with 9% of absorbance of RB5 on TiO$_2$ and the 99% of dye is degraded after photocatalysis. This reveals that the dye can be degraded only in the presence of TiO$_2$ and light irradiation. Therefore the adsorption of about 4.03% is negligible [11].

The absorbance against time graph in Figure 2 shows the photocatalysis using UV-A, UV-B, UV-C, solar irradiationand catalysis under dark condition. Photodegradation using UV-A, UV-B, UV-C showed a significant drop in absorbance compared to solar radiation. However, all of these photocatalysis experiment showed reduction in UV absorbance throughout the whole experiment.

Figure 3 shows the temporal changes in the UV–vis absorbance spectrum of dye samples taken at different exposure times. RB5 exhibited three characteristic absorbance peaks which were progressively reduced upon coming into contact with UV-A, UV-B, UV–C light irradiation in the presence of TiO$_2$. The peak at 595 nm in visible region was typical characteristic of the chromophore containing long conjugated π system, link by two azo double bond group of RB5. The absorption peak at 310 and 254 nm in UV region are characteristic peak of naphthalene and benzene ring structure respectively which are assigned to $\pi - \pi*$ transition of electron [8, 12]. During this photocatalysis process, the complex organic structure of the pollutant broken down into smaller intermediate compounds. Hydroxyl radicals generated during TiO$_2$/UV photocatalysis process attacked the organic pollutant continuously through a series of chain reactions.

The peak at 597 nm in visible region was typical characteristic of the chromophore containing long conjugated π system, link by two azo double bond group of RB5. The peak at 597 nm decreased very rapidly for UV-C photocatalysis followed by UV-B and UV-A respectively. There was zero absorbance at the peak 597 nm for UV-A, UV-B and UV-C irradiations after 60 min, 50 min, and 25 min respectively. On the other hand, the peak at 310 nm decreased slowly, indicating the cleavage of naphthalene ring and the cleavage might have resulted in the formation of some benzene intermediates compounds by fragmentation [8, 12]. This phenomenon was clearly observed at 254 nm. The absorbance decreased slowly at 254 nm as a result of the degradation or complete breakdown of benzene intermediate compounds. Most of the RB5 photodegradation pathway proposed in the literature shows similar type of intermediates containing both naphthalene and benzene ring structures together with some ionic end-products.

In this study, it was proven that UV-C radiation was able to degrade the organic pollutant effectively compared to UV-B, UV-A or solar lamp radiation. In their comparative study between 254 nm and 350 nm excitation of TiO$_2$ in simple photocatalytic reactors the UV-C is considerably more effective compared to UV-A [13]. Similar findings was reported by Bayarri *et al*. [14] that the effectiveness of UV-C is due to the shorter penetration capability with higher energy photon, so more electron-hole pairs were available for the target compound.

Effect of Initial Dye Concentration

Figure 4 shows the effect of initial dye concentration on the photocatalytic degradation as function of exposure time. The degradation patterns were similar as discussed above. 100% of degradation degree of RB5 solution at 5 ppm, 10 ppm and 15 ppm were achieved at 8th, 25th and 25th min during the photocatalysis experiments, respectively. At concentration of 20 ppm and 25 ppm complete degradation was achieved after 30 min.

This result shows that the degradation of the less concentrated RB5 solution took shorter time
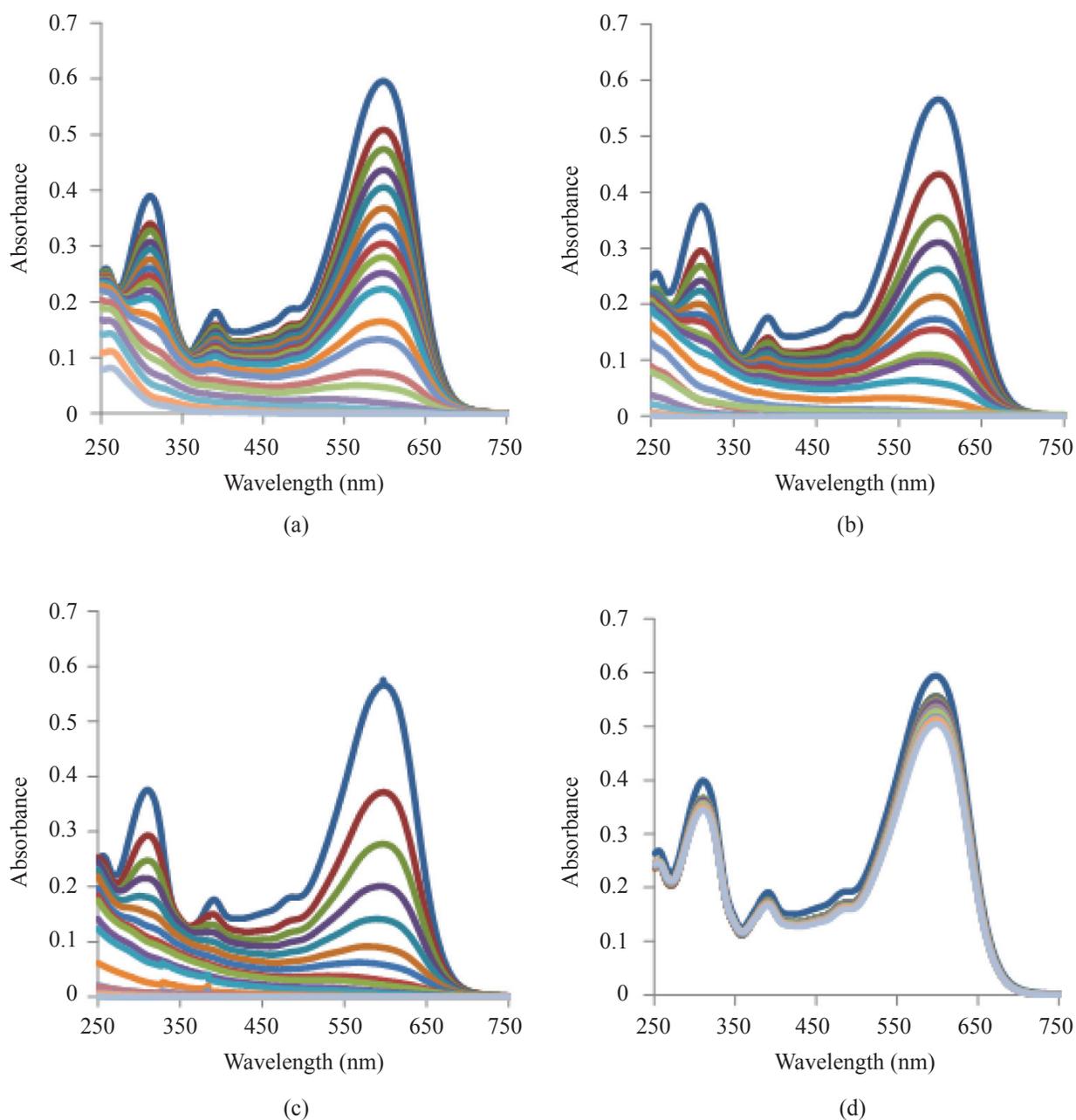
Figure 3. Degradation pattern of RB5 (a) UV-A; (b) UV-B; (c) UV-C;
(d) Solar irradiation (C$_0$= 25 ppm, Catalyst loading = 0.1g/l).

than that of the higher concentration of RB5 solution. Similar results were reported previously for the Acid Red 14 and C.I. Basic Violet 10 degradation using TiO$_2$ catalysts [15, 16] stating that the higher the concentration, the lower the degradation efficiency. This is because the increase in the initial dye concentration causes less photon to reach the photocatalyst surface, resulting in slower production of hydroxyl radicals [17]. This is also due to the UV–screening effect of the dye itself which absorbs a part of the light photon [18]. Therefore, only fewer hydroxyl radicals were available to oxidize the dye molecules in higher concentrations.
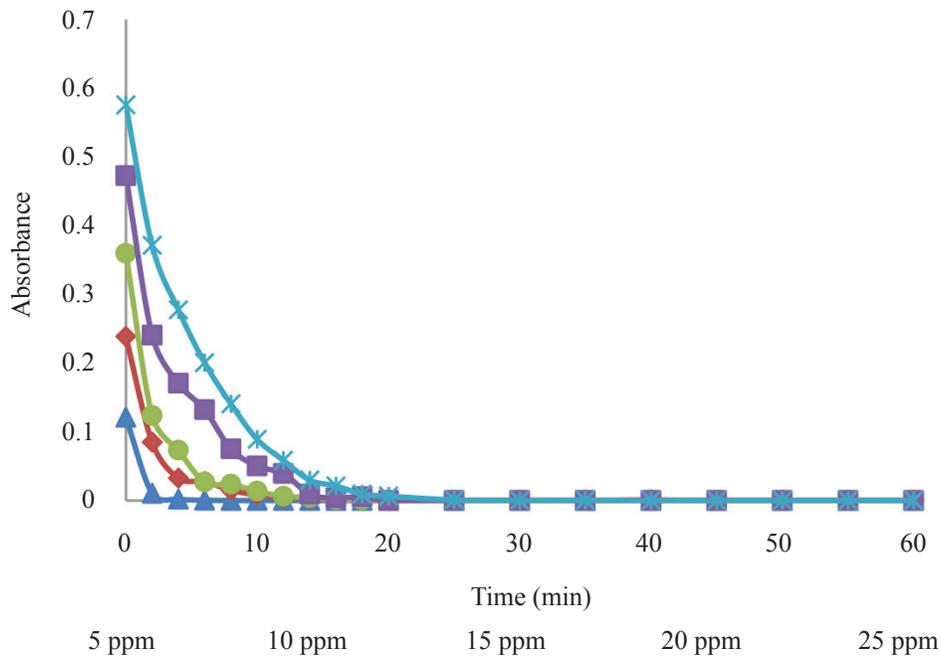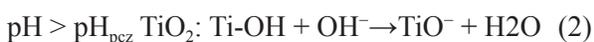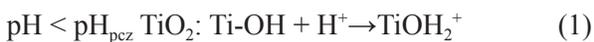
Figure 4. Degradation of 25 ppm of RB5 solution during photocatalysis with different concentrations
using different UV-C irradiation with 0.1 g/l TiO$_2$.

Effect of pH

Figure 5 shows RB5 degradation as a function of irradiation time during photocatalysis under acidic, alkaline and neutral conditions. Aqueous RB5 photocatalysis at pH 4 and pH 7 had achieved highest degradation efficiency at 50th and 60th min, respectively. For pH 10, the degradation efficiency at 60th min is 97.45%. Similar work was reported by Daneshvar *et al*. [15], whom obtained the best results for photocatalytic degradation of azo dye acid red 14 in acidic solution. These findings can readily be explained in terms of the amphoteric behaviour of TiO$_2$. Researchers have determined that the change in pH of the solution affects the surface charge property of the P25-TiO$_2$ particles [11]. The point of zero charge (pH$_{pzc}$) for TiO$_2$-P25 was 6.8. When pH was lower than pH$_{pcz}$, the TiO$_2$ surface was positively charged (Equation 1). In basic solution the surface is negatively charged (Equation 2).

$$pH < pH_{pcz} \; TiO_2: Ti\text{-}OH + H^+ \rightarrow TiOH_2^+ \qquad (1)$$

$$pH > pH_{pcz} \; TiO_2: Ti\text{-}OH + OH^- \rightarrow TiO^- + H2O \quad (2)$$

Considering the structure of RB5 molecule, it possesses sulphonic (–SO$_3^-$) and [2-(sulphoxy) ethyl] sulphonyl groups (–SO$_2$CH$_2$CH$_2$OSO$_3^-$) as water solubilizing and reactive groups, respectively which are both negatively [19]. Therefore at acidic condition, a positive charge excess in the TiO$_2$ surface favours a strong electrostatic interaction with SO$_3^-$ groups of the dye which is then consequently resulted in the dye degradation [9]. In other words the RB5 containing sulphonate group is better adsorbed on the positively charged TiOH$_2^+$ surface. At alkaline condition, catalytic activity of TiO$_2$ was diminished by the excess negative charge which promotes the repulsion of dye in TiO$_2$ surfaces [20]. The hydroxide ion and the positive holes are responsible for the formation of the hydroxyl radical. The positive holes are considered as the major oxidation species at low pH, whereas the hydroxyl radicals are considered as the predominant species at neutral or high pH levels. The pH affects not only the surface properties of TiO$_2$, but also the dissociation of dyes and formation of hydroxyl radicals [21].
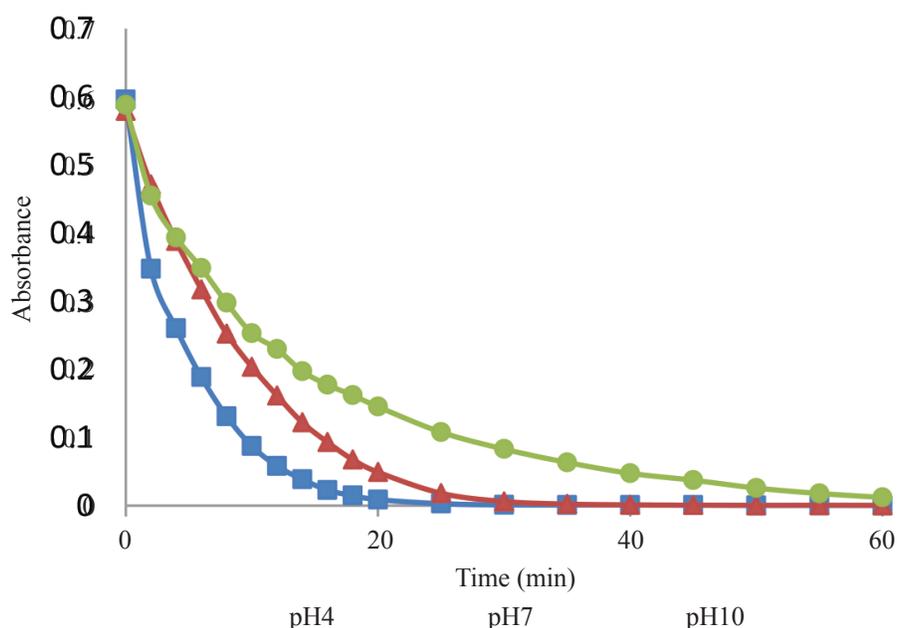
Figure 5. Degradation of 25 ppm of RB5 solution during photocatalysis at different pH using
UV-C irradiation with 0.1 g/l TiO_2.

Kinetics of Photocatalytic Degradation of RB5 in Aqueous Solution

According to Damodar *et al*. [12], usually dye degradation follows first order kinetics. The photocatalytic degradation of the majority experiments in this study followed the first order kinetic reaction as well, where the plots of ln (A_o/A_t) against time. According to [22], the regression correlation for first order reaction normally falls between 0.953 min^{-1} and 0.998 min^{-1}.

The R^2 value of UV-B and UV-C showed that both the photoctalysis followed the first order kinetics. However, UV-A and solar irradiation photocatalysis showed distortion where it did not obey neither first order nor second order kinetic reaction. The rate constant for photocatalysis using UV-B and UV-C was 0.1391 min^{-1} and 0.2450 min^{-1}, respectively which was higher than the rate constant for photocatalysis using UV-A and solar irradiation.

The regression correlation, R^2 values in Table 2 revealed that the experimental data fits the first order model well with R^2>0.90. The rate constant for photocatalysis using different concentrations decreased as the concentration increased. The

Table 1. The rate constant and regression correlation of the experiment using different light
sources with RB5 solution.

Photocatalysis	First order		Second order
	Rate constant (k) min^{-1}	Regression correlation (R^2)	Regression correlation (R^2)
UV-A	0.0955	0.8742	0.3270
UV-B	0.1391	0.9676	0.4903
UV-C	0.2450	0.9786	0.4531
Solar	0.0019	0.8732	0.8883

Table 2. The rate constant and regression correlation of the experiments using different concentrations of RB5 aqueous solution.

Photocatalysis	First order		Second order
	Rate constant (k) min^{-1}	Regression correlation (R^2)	Regression correlation (R^2)
5 ppm	0.8769	0.9772	0.8186
10 ppm	0.3298	0.9753	0.5378
15 ppm	0.3232	0.9879	0.6032
20 ppm	0.3361	0.9367	0.5187
25 ppm	0.2450	0.9786	0.4531

highest rate constant could be noticed with 5 ppm of RB5 photocatalysis which was 0.8769 min^{-1} while the lowest rate was when using 25 ppm.

Sakthivel *et al.* [23], obtained a similar idea that increasing initial dye concentration would decrease the rate constant in the photocatalytic degradation of azo dye. Hydroxyl radicals are formed from the adsorbed water and OH^-. Therefore the presence of OH^- is reduced with more RB5 molecules. This phenomenon is explained as the dye ions which are formed from the dissociation of sodium salts of dye molecules will compete with OH^- to be adsorbed on the TiO_2 surface. Thus, only fewer active sites are available for the generation of OH^- at higher dye concentration.

Table 3 shows that the effect of photodegradation at different pH condition followed the first order kinetics. The correlation regression, R^2 for all these three experiments were more than 0.91. Besides that, the rate constant, k increased as the pH decreased. At the acidic, neutral and alkaline medium the rate constant obtained were 0.1745 min^{-1}, 0.1637 min^{-1} and 0.0604 min^{-1}, respectively. Similar findings were reported

previously for the degradation of RB5 in UV/TiO_2 [24]. This is because the increase in pH will decrease the oxidation potential of available hydroxyl. This is consistent with the k value being lowest at the highest test pH of 10.

CONCLUSION

This research was conducted to study the potential degradation of anionic dyes through photocatalysis reaction. Various operational parameters were found to affect the effectiveness of TiO_2-based photocatalysts. TiO_2–P25 Degussa which is an effective photocatalyst, was able to successfully degrade most of the RB5 aqueous solution at room temperature (25–30°C). The result of this study showed that UV/TiO_2 process could effectively degrade the RB5. The results also indicated that the degree of degradation of RB5 was influenced by factors such as the initial dye concentration, irradiation wavelength, and pH. Almost all of the tests conducted yielded a 100% degradation efficiency, except for photoctalysis in solar radiation wavelength. The findings proved that the degradation of RB5 was effective in UV-C irradiation with lower concentration solution at acidic condition.

Table 3. The rate constant and regression correlation of the experiments of RB5 aqueous solution at different pH.

Photocatalysis	First order		Second order
	Rate constant (k) min^{-1}	Regression correlation, R^2	Regression correlation, R^2
pH4	0.1745	0.9595	0.8281
pH7	0.1637	0.9772	0.4445
pH10	0.0604	0.9962	0.7783

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