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Evaluation on the Photocatalytic Degradation Activity of Reactive Blue 4 using Pure Anatase Nano-TiO_2

(Penilaian pada Aktiviti Degradasi Fotopemangkinan daripada Reaktif Blue 4 menggunakan Anatase Nano-TiO_2 Tulen)

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ABSTRACT

Disposal of dye wastewater into water streams without treatment endangers human and marine lives. This work focused on the second largest class of textile dyes after azo dyes due to its high resistivity to biodegradation and high toxicity. The photocatalytic degradation of Reactive Blue 4 (RB4), an anthraquinone dye, has been investigated using pure anatase nano titanium (IV) oxide (TiO_2). The dye molecules were fully degraded and the addition of hydrogen peroxide (H_2O_2) enhanced the photodegradation efficiency. It is found that the degradation as the hydroxyl radicals in the bulk solution is sufficient for complete mineralisation. The disappearance of the dye follows pseudo-first-order kinetics. The effect of pH, amount of photocatalyst, UV-light intensity, light source and concentration of hydrogen peroxide was ascertained.

Keywords: Anthraquinone dye; hydrogen peroxide; photocatalysis; textile wastewater; TiO_2

ABSTRAK

Pembuangan air sisa pewarna ke dalam air sungai tanpa rawatan membahayakan kehidupan manusia dan marin. Penyelidikan ini memberi tumpuan kepada pewarna tekstil kelas kedua terbesar selepas pewarna azo kerana kerintangan yang tinggi untuk biodegradasi dan ketoksikan yang tinggi. Degradasi fotopemangkinan daripada Reaktif Blue 4 (RB4), satu pewarna antrakuinon, telah dikaji menggunakan anatase nano-TiO_2 tulen. Molekul pewarna diuraikan sepenuhnya dan penambahan hidrogen peroksida (H_2O_2) meningkatkan kecekapan fotopemerosotan. Didapati bahawa degradasi sebagai radikal hidroksil dalam penyelesaian pukal adalah mencukupi untuk mineral lengkap. Kehilangan pewarna adalah mengikut kinetik tertib pertama pseudo. Kesan pH, jumlah fotomangkin, keamatan cahaya UV, sumber cahaya dan kepekatan hidrogen peroksida telah ditentukan dalam kajian ini.

Kata kunci: Foto pemangkinan; hidrogen peroksida; pewarna antrakuinon; sisa air kumbahan tekstil; TiO_2

INTRODUCTION

Colored organic compounds that are fully or partially soluble when suspended in a medium are known as dyes (Aspland 1997). There are over 100,000 types of dyes available commercially, with annual production exceeding one million tons (Christie 2007). It is estimated that about 20% of dyes are lost throughout the dyeing process and are discharged directly into the environment (Houas et al. 2001; Hussein 2013). It is important to remove dye as compared to colorless compounds as even at a low concentration (below 1 ppm), it can change the color and transparency of the water stream (Regulska et al. 2013). Disposal of dyes without pre-treatment into the water stream causes intense ecological disturbance, eutrophication and pollution to marine life (Vautier et al. 2001). In addition, improperly discharged reactive dyes pose a hazard to human health.

To overcome these problems, a wide range of biological and chemical treatments have been used to treat dye wastewater. Biological treatment is well established because of its cost effectiveness. However, the adsorption of dyes only occurs on the surface of the biosorbent, without undergoing degradation (Muruganandham et al. 2006). Degradation is defined as the gradual decomposition of a substance into other substances and dye degradation is detected easily by the disappearance of the dye color. Thus, disposal of the sludge from the biosorbent is necessary to remove the dye from the wastewater. Some biological treatments involving aerobic and anaerobic processes have been used, but they are not effective for certain dyes, especially azo and anthraquinone dyes due to the present of complex aromatic compounds (Han et al. 2009; Li et al. 2004). Physical methods, such as ion exchange, adsorption and filtration do not solve the problem because they simply transfer the dyes to another phase rather than degrading them (Barka et al. 2009; Gozmen et al. 2009). As most dyes are not readily degradable due to their synthetic nature and complicated structure, full degradation and reusability are not achievable with current treatments (Robinson et al. 2001).

The introduction of photocatalysts in advanced oxidation processes (AOP) offers a great solution to those

limitations. AOP is a chemical oxidation process that is highly dependent on hydroxyl radicals to remove organic compounds found in water. According to Chatterjee and Dasgusta (2005) and Liu et al. (2005), photocatalytic reactions are triggered when a photocatalyst such as TiO_2 absorbs a photon that has a higher energy than its band gap (Figure 1). Next, an electron-hole pair is formed when an electron in the valence band is excited to the conduction band. The electron-hole pair and excited conduction-band electrons are capable of migrating to the TiO_2 surface to induce oxidation and reduction processes. Electrons from the conduction band of TiO_2 are then scavenged by oxygen molecules to form superoxide ions (O_2^-). Hydroxyl radicals (×OH) are formed when the superoxide ions react with protons or when water molecules react with an electron-hole pair (Shon et al. 2008). Repeated attacks by hydroxyl radicals and superoxide ions eventually lead to the degradation of organic compounds, including dyes.

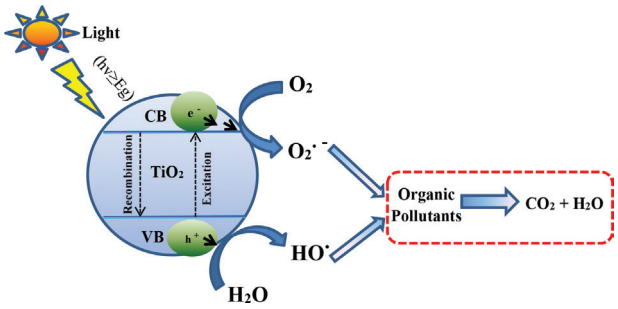

FIGURE 1. Mechanism of photocatalysis

Reactive anthraquinone dye had been proven to be responsible for chronic neurotoxic effects, including vision disturbances and can also cause skin irritation and sensitization (O'Donoghue 1985; The Merck Index 1976). Reactive Blue 4 (RB4) dye is the second largest class of textile dyes after azo dyes and is commonly used in the textile industry for coloring. Because anthraquinone reactive dyes such as RB4 are highly resistant to biodegradation and highly toxic (LD_{50} = 8.98 mg/kg) (Sigma Aldrich 2008), greater importance has been given to degrading or destroying such dye through chemical methods (Neti & Misra 2012; Walker & Weatherley 2000). Although some researchers have used carbon electrodes to oxidize the RB4 dye, full degradation was not successfully achieved (Carneiro et al. 2005). In addition, AOP using the Fenton reagent was also not efficient due to formation of unwanted intermediates, such as iron sludge (Duran et al. 2008; Uygur 1997).

Several photocatalysts have been tested and TiO_2 was shown to be an excellent catalyst for the photocatalytic degradation of organic pollutants that include reactive dyes. Furthermore, TiO_2 is less toxic, has strong oxidizing ability and offers long-term photostability (Ohtani et al. 1997). TiO_2 occurs naturally as rutile, anatase and brookite. Among these phases, anatase has been proven to be superior for photocatalytic activity (Byrne et al. 2011; Yu et al. 2002). Photocatalytic degradation of RB4 dye using Degussa P-25 nano-TiO_2 (Degussa P-25), which consists of rutile and anatase phases, has been reported (Neppolian et al. 2002a). The authors managed to degrade 250 ppm of RB4 within 8 h in the presence of UV-light irradiation. Although anatase was proven to be the best for photocatalytic activity, the use of pure anatase for the photocatalytic degradation of RB4 has not yet been reported.

In this study, we examine the photocatalytic degradation of RB4 dye using pure anatase TiO_2. The effects of pH and the photocatalytic kinetics were also studied to determine whether the degradation occurs on the TiO_2 surface or in the solution.

MATERIALS AND METHODS

PREPARATION OF CHEMICALS

Reactive Blue 4 (RB4) was obtained from Sigma Aldrich and used without further purification. The maximum absorption (λ_{max}) for RB4 is 595 nm. Solutions were prepared by dissolving the requisite quantity of the dye in deionized water. The pure anatase form of titanium oxide (TiO_2) used in the experiment was also purchased from Sigma Aldrich. The pure anatase nano-TiO_2 with a particle size < 25 nm and a surface area of 200-220 $m^2\ g^{-1}$ was used for all photocatalytic experiments except where otherwise stated. Normal-grade pure anatase TiO_2 with a particle size of 100 nm and a surface area of 11 $m^2\ g^{-1}$ was also used without further treatment. Hydrogen peroxide (30% w/w) was obtained from Merck. All reagents were of analytical grade and were used without further purification.

PHOTOCATALYTIC REACTOR

The photocatalytic reaction was performed in a 750 mL borosilicate-glass cylindrical photochemical reactor. The RB4 solution (100 mL) containing the appropriate quantity of TiO_2 was continuously stirred and irradiated by a mercury lamp (25, 70, 125 or 400 W), visible lamp (400 W) or natural sunlight (~100 000 lx) under ambient temperature. The pH of the solution was adjusted using 1 N hydrochloric acid (HCl) and sodium hydroxide (NaOH). HCl was used to adjust the pH because it does not significantly affect the adsorption-surface properties of TiO_2 (Chen et al. 1997). The suspension of the TiO_2 and RB4 solution was allowed to sit for 15 min prior to the photodegradation. Adsorption measurements to determine the dye concentration of RB4 were carried out on a UV-Vis spectrophotometer (Shimadzu UV-160 A) at 595 nm. Dye degradation is defined as the gradual decomposition of a dye into another substance and can be measured from the disappearance of the dye colour, the percentage degradation was calculated as follows:

$$\text{Degradation } (\%) = \frac{C_0 - C_1}{C_0} \times 100,$$

where C_o is the initial dye concentration and C_1 is the dye concentration after photodegradation.

Results and Discussion

Effect of Initial Dye Concentration

Since dye is an important substrate in the photocatalytic activity, the initial dye concentration was investigated. As shown in Figure 2, the percentage degradation increases with radiation time and all RB4 dye molecules undergo full degradation in the presence of pure anatase nano-TiO_2 catalyst within 60 min. Based on these results, 20 ppm dye was fully degraded after 20 min, while 100 ppm dye took the longest time to achieve full degradation. Full degradation was achieved for up to 100 ppm within 60 min. This result shows that the initial concentration has a significant effect on the degradation rate. Therefore, the higher the initial concentrations of RB4 dye, the lower the photodegradation efficiency. This result is in agreement with the findings reported in the literature using a different type of TiO_2 (Chakrabarti & Dutta 2004; Kaur & Singh 2008; Neppolian et al. 2002a). The increase in dye concentration reduces the number of photons penetrating the solution because they are absorbed before reaching the catalyst. This leads to a decreased in the absorption of photons by the TiO_2 catalyst and therefore fewer electron-hole pairs generation, creating fewer superoxide ions and hydroxyl radicals. Thus, larger amount of TiO_2 catalyst is required to provide greater surface area to degrade a more concentrated dye. With the increasing number of dye molecules, the amount of free radicals generated on the surface of TiO_2 will not be sufficient to attack and degrade the dye molecules. In addition, a longer irradiation time is needed to generate a sufficient amount of free radicals to degrade highly concentrated RB4 dye. Zhao et al. (1995) also confirm that larger amount of catalyst or longer irradiation time is needed to degrade highly concentrated dyes.

The formation of ×OH and the adsorption of dye reactants onto the TiO_2 surfaces are crucial factors affecting the degradation rate. The overall rate constant (k_1) can be represented by (1) (Neppolian et al. 2002a),

$$k_1 = k_0 P_{OH} P_{dye}, \quad (1)$$

where k_o is the reaction rate constant, P_{dye} is the probability of ×OH reacting with dye molecules and P_{OH} is the probability of ×OH forming on the catalyst surface. Previous research (Matthews 1984; Okamoto et al. 1985) have shown the importance of ×OH in degrading aromatic compounds via the hydroxylation of the ×OH reaction of electron-hole pairs with water and absorbed OH^- leads to the formation of ×OH (3). The dissociated dye ions can also occupy the electron-hole-pair active sites (Neppolian et al. 2002a). Thus, increasing the dye concentration will cause more dye ions to compete with OH^- and water for the active sites on the catalyst surface. As a result, fewer active sites will be freely available for OH^- and water to generate ×OH. Therefore, P_{OH} is actually negatively associated with the number of catalyst sites due to the coverage of the dye molecules.

To study other conditions, a suitable dye concentration was chosen based on the suitable reaction irradiation time. Because 60 ppm took 40 min to achieve full degradation, the following parameters were used under this condition.

Effect of Catalyst Loading

The amount of pure anatase TiO_2 was optimized to avoid waste while ensuring full dye degradation. The dye degradation is expected to decrease when less catalyst is used because fewer active sites will be available on the photocatalyst surface, slowing the degradation due to the insufficient number of hydroxyl radicals and superoxide ions. Importantly, UV irradiation is able to degrade RB4 in the absence of TiO_2 catalyst (Figure 3). When no TiO_2 catalyst was added to the mixture, 20% of the RB4 was degraded. Previous research has also reported dye degradation under UV-light illumination in the absence of a catalyst (Poulios & Tsachpinis 1999). This finding indicates that exposure to strong UV light may also generate free radicals that are capable of degrading RB4 dye. The degradation percentage increased with the amount of TiO_2. Full degradation was successfully achieved when 1 g/L of TiO_2 was applied. This result is in good agreement with others (Kaur & Singh 2008; Neppolian et al. 2002a), where

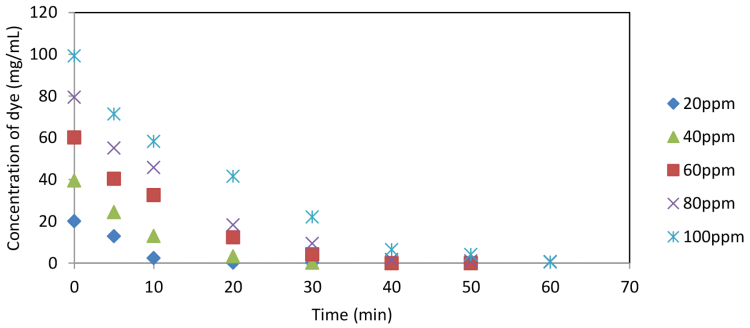

FIGURE 2. Photodegradation of RB4 dye at different initial concentrations. Reaction conditions: TiO_2= 1 g/L; 125 W UV light; stirring speed = 500 rpm; pH = 6

a higher amount of catalyst increased the percentage of degradation. When more TiO_2 is loaded, the surface area available for absorption and degradation increases. Above the optimum amount (1 g/L) of TiO_2, all dye molecules have already been fully degraded within 40 min. Therefore, there are no more dye molecules available in the solution to react with the active sites of the photocatalyst, thus a plateau is observed when the amount of TiO_2 exceeds 1 g/L. According to Carp et al. (2004), light scattering will increase the opacity of the solution, reducing the light penetration and the degradation efficiency when too much catalyst is added. However, this phenomenon was not detected in this experiment.

In photocatalytic activity, photons are absorbed by a photocatalyst, which then excites electrons from valence to conduction bands to generate electron-hole pairs. The electron-hole pairs will react with surface-bound water to form hydroxyl radicals or react directly with dye molecules. These reactions can be represented by the following equations (Gozmen et al. 2009):

$$TiO_2 + hv \rightarrow e_{CB}^- + hv_B^+. \quad (2)$$

$$hv_B^+ + H_2O\ (ads) \rightarrow \times OH\ (ads) + H^+. \quad (3)$$

$$Dye + \times OH \rightarrow \text{degradation product.} \quad (4)$$

$$Dye + TiO_2(hv_B^+) \rightarrow \text{oxidation product.} \quad (5)$$

$$Dye + TiO_2(e_{CB}^-) \rightarrow \text{reduction product.} \quad (6)$$

Based on the equations, both water and dye molecules were bind to the same active sites. As more TiO_2 is added, there are more electron-hole pairs (hv_B^+) available to bind with water and produce more hydroxyl radicals. Therefore, the typical mechanisms available to degrade RB4 are hydroxyl-radical attack (4), oxidation (5) and reduction (6).

EFFECT OF PH

In general, pH is a crucial characteristic of wastewater because it determines degradation efficiency. Therefore, the influence of pH on dye degradation at pH value from 3 to 13 was examined. As photo-oxidation is followed by the release of protons, reversible protonation on the TiO_2 surface caused by a change in pH will affect the degradation efficiency. As shown in Figure 4, full degradation was achieved in the pH range of 3 to 7. In basic solution (pH>7), the photodegradation of the dye is slower but reaches 95% at pH13. Three mechanisms have been proposed to account for dye degradation: hydroxyl-radical attack; direct oxidation by positive holes (hv_B^+); and direct reduction by conduction-band electrons (e_{CB}^-). All of these mechanisms are highly dependent on substrate nature and pH (Tang et al. 1997).

Acidic and neutral pH values were found to be more effective for degradation of RB4 dye than was basic pH using pure anatase nano-TiO_2. This finding could be related to the point of zero net charge (PZC) of TiO_2, which is pH6.8. In an acidic solution (pH<6.8), TiO_2 is positively charged, while RB4 is negatively charged due to the presence of a sulfonic group. This situation favors the adsorption of the anionic dye onto the TiO_2 catalyst surface. As more dye molecules are absorbed on the active sites of TiO_2, the degradation efficiency is enhanced. Previous literature has also related the photocatalytic activity with the absorption of dye onto the TiO_2 surface (Aguedach et al. 2005; Daneshvar et al. 2003). Based on (2) and (3), the newly generated hydroxyl radicals from the electron-hole pairs will instantly react with the RB4 dye molecules adsorbed on the TiO_2 surface due to the shorter diffusion distance between the adsorbed dye molecules and hydroxyl radicals. Nevertheless, hydroxyl radicals are also present in the solution and readily attack the dye molecules. The adsorbed dye molecules simultaneously favor direct oxidation by the electron-hole pair and reduction by the conduction-band electrons generated on the surface of the TiO_2, as shown by (5) and (6), respectively.

As all three mechanisms are possible, it is difficult to distinguish the true mechanism responsible for degrading the dye molecules, especially in acidic conditions. However, at pH7, the photodegradation is mainly governed by the hydroxyl radical in the solution because the dye molecules no longer effectively adsorb to the nearly neutral TiO_2. As shown in Figure 4, full degradation was still achievable at pH7, even when the adsorption mechanism

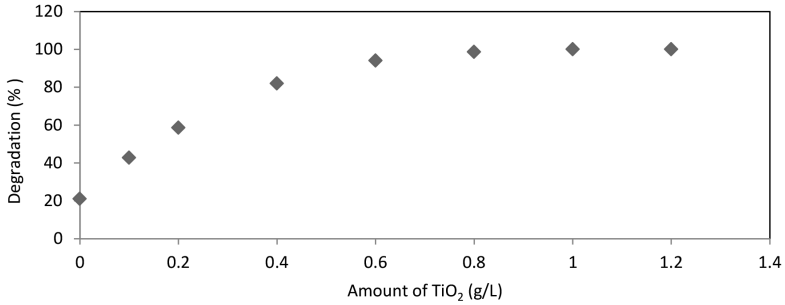

FIGURE 3. Influence of catalyst loading on the degradation of RB4 dye. Reaction conditions: initial dye concentration = 60 ppm; irradiation time = 40 min; light source =125 W UV lamp; stirring speed = 500 rpm; pH = 6

was interrupted. In other words, the hydroxyl radical in the bulk solution is adequate to degrade the dye. This result indicates that photodegradation by TiO_2 is primarily dominated by a hydroxyl-radical mechanism in the bulk solution.

At higher pH, TiO_2 is negatively charged because the pH is higher than the PZC. The electrostatic repulsion of the negatively charged TiO_2 and negatively charged dye molecules hinders the adhesion of the dye molecules onto the catalyst surface. Thus, the photodegradation becomes more difficult because degradation by electron-hole pairs (hv_B^+) and conduction-band electrons (e_{CB}^-) is obstructed. The hydroxyl radicals generated by TiO_2 degrade the dye molecules. Furthermore, OH^- interrupts the photodegradation process by causing electron donating groups such as $-NH_2$, which is located in the α-position of the carbonyl group of RB4, to form intramolecular hydrogen bonds, increasing the chemical stability of the dye (Rys & Zollinger 1972) and making it more difficult for hydroxyl radicals to attack the dye molecules. As a result, a lower photocatalytic activity was observed in alkaline solution.

Due to the unfavorable absorption of dye molecules into the catalyst surface, the hydroxyl radicals generated from the electron-hole pairs must travel farther to attack the dye molecules, resulting in slower dye degradation. In addition, the generated hydroxyl radicals might be scavenged by other ions before they can attack the dye molecules. Neppolian et al. (2002b) also agree with this explanation. The hydroxyl radicals are quickly scavenged by superoxide ions, as shown below:

$$O_2^- + OH \rightarrow O_2 + HO_2^-. \quad (7)$$

$$HO_2^- + H^+ \rightarrow H_2O_2. \quad (8)$$

Therefore, not all hydroxyl radicals directly attack the dye, which contributes to the sudden drop in degradation efficiency.

The sudden decrease at pH11 can also be explained by salt formation that results in dye aggregation in the form of a cloudy suspension. It has been reported by Epolito et al. (2005) that RB4 can form a cloudy suspension. This cloudy suspension was also observed in other types of dyes, such as Reactive Red 180, Reactive Red 2 and Reactive Blue 19 (Hamlin et al. 1999; Lee & Pavlostathis 2004). The cloudy suspension increases light scattering and greatly reduces the number of photons absorbed. As a consequence, fewer hydroxyl radicals are generated from TiO_2 to attack the dye molecules.

Interestingly, the photodegradation efficiency suddenly increases at pH13. This finding may be explained by the hydroxyl radicals generated from the excess hydroxide ions, will react with free electron-hole pairs near the TiO_2 surface to produce hydroxyl radicals. As mentioned previously, these hydroxyl radicals can directly attack the dye molecules. The conversion of hydroxide ions to hydroxyl radicals has also been proposed by others (Aguedach et al. 2005; Poulious & Aetopoulou 1999). From observation the sudden increase in photocatalytic activity favors the direct hydroxyl-radical attack mechanism because, at high pH, both the TiO_2 and the anionic RB4 dye are negatively charged. Therefore, RB4 dye molecules are repulsed and rarely adsorbed on the TiO_2 surface. There will be limited dye adsorption on the TiO_2, and thus direct oxidation by electron-hole pairs and reduction by conduction-band electrons are not likely to occur. As a result, the most suitable mechanism to account for the photocatalytic degradation of RB4 is the direct hydroxyl-radical attack mechanism. Once again, this result proves that hydroxyl-radical mechanism is mainly responsible for the photodegradation of RB4 by TiO_2.

EFFECT OF LIGHT INTENSITY

Because photocatalytic activity is highly dependent on light intensity (Ollis et al. 1991), the effect of UV light at 25, 70, 125 or 400 W was investigated. An adsorption test was carried out in the dark to evaluate the efficiency of the dye adsorption on TiO_2 at pH6. It was observed that 13% of RB4 was removed in the presence of TiO_2 without the light source (Figure 5), indicating that 13% of the dye was actually adsorbed on the surface of TiO_2 instead of undergoing degradation.

As shown in Figure 5, the percentage of degradation increased with light intensity and then plateaued. Based

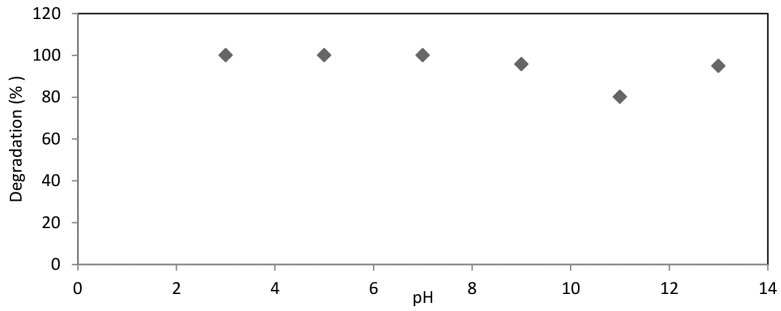

FIGURE 4. Effect of pH on the degradation of RB4 dye. Reaction conditions: amount of TiO_2 = 1.0 g/L; initial dye concentration = 60 ppm; irradiation time = 40 min; light source =125 W UV lamp; stirring speed = 500 rpm

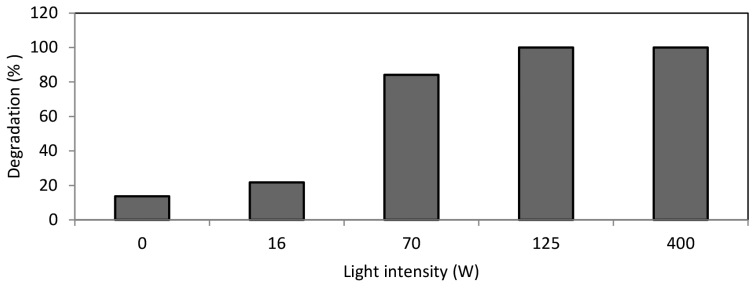

FIGURE 5. Influence of light intensity on RB4 dye degradation. Reaction conditions: amount of TiO_2= 1 g/L; initial dye concentration = 60 ppm; irradiation time = 40 min; stirring speed = 500 rpm; pH = 6

on the results, 125 W is the optimum light intensity for full degradation. Higher light intensities generate more photons, which are then absorbed by the photocatalyst to excite more electrons and produce more electron-hole pairs. This effect generates more hydroxyl radicals, which break down the dye. Based on (2) – (6), more electron-hole pairs and hydroxyl radicals are generated at high light intensity. The greater number of electron-hole pairs either react with water to produce hydroxyl radicals or directly oxidize the dye molecules. Increasing possibility facilitates dye degradation with increasing light intensity.

EFFECT OF H_2O_2

It is well known that the addition of a powerful oxidizing agent such as hydrogen peroxide (H_2O_2) leads to an increase in photodegradation efficiency (Hachem et al. 2001; Poulious & Tsachpinis 1999). As observed, full degradation was possible in the presence of H_2O_2 and not in the absence of H_2O_2 (Figure 6). The full degradation of RB4 dye in sunlight, visible light, and low-intensity UV light (16 W) was successfully achieved using 0.5 g/L H_2O_2. To verify that the degradation of RB4 was not solely due to H_2O_2, we examined the effect of H_2O_2 in the dark. In the absence of light, the photodegradation does not occur, even in the presence of TiO_2. It was clearly shown that the degradation of RB4 is only 30% in the presence of 0.5 g/L H_2O_2, which is solely caused by H_2O_2. This finding indicates the remaining 70% is due to synergic effects between photocatalytic activity from TiO_2 and H_2O_2. It has been widely reported by Neppolian et al. (2002a) and Zhao et al. (1995) that the presence of H_2O_2 enhances the photocatalytic degradation. Due to the relatively large band gap of anatase TiO_2 (3.20 eV) (Peng et al. 2008), only UV light with wavelengths shorter than 390 nm can effectively activate the TiO_2 catalyst. Because sunlight consists of only 3-5% UV light, degradation occurs very slowly (Davis & Huang 1990). For the same reason, visible light from a tungsten filament may produce a small amount of UV light (Tennakone & Bandara 2001) that slowly degrades the dye. It is interesting to note that full degradation was successfully achieved using 0.5 g/L H_2O_2 under sunlight and visible light.

We believe that H_2O_2 possesses two functions in the process of photocatalytic degradation. The addition of H_2O_2 inhibits the electron-hole recombination and promotes the formation of ×OH and hydroperoxy ($\cdot OH_2$) radicals. Gozmen et al. (2009) and Han et al. (2009) imply that TiO_2 donates an electron to H_2O_2 or O_2. As a result, the electron-hole recombination is hampered; thus, more hydroxyl radicals are induced directly (9) and indirectly (11). As for the second function, H_2O_2 can dissociate to give two hydroxyl radicals (13) or hydrogen ions (14) (Neppolian et al. 2002a) for the production of hydroperoxy radicals (12). Because there are many reactions taking place in the presence of H_2O_2, the photocatalytic degradation increases significantly.

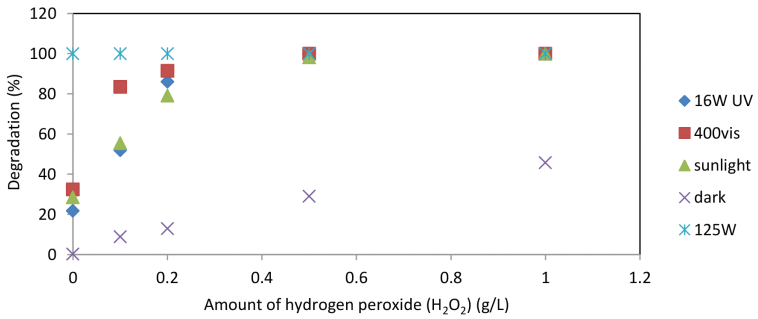

FIGURE 6. Influence of the amount of hydrogen peroxide in degradation of RB4 dye. Reaction conditions: amount of TiO_2= 1 g/L; initial dye concentration = 60 ppm; irradiation time = 40 min; light source =125 W UV lamp; stirring speed = 500 rpm; pH = 6

$$TiO_2\ (e_{CB}^-) + H_2O_2 \rightarrow TiO_2 + \cdot OH + OH^-. \quad (9)$$

$$TiO_2\ (e_{CB}^-) + O_2 \rightarrow TiO_2 + O_2^-. \quad (10)$$

$$O_2^- + H_2O_2 \rightarrow OH^- + \times OH + O_2. \quad (11)$$

$$O_2^- + H^+ \rightarrow HO_2\cdot \quad (12)$$

$$H_2O_2 \rightarrow 2\cdot OH. \quad (13)$$

$$H_2O_2 \rightarrow O_2^{2-} + 2H^+. \quad (14)$$

REUSABILITY

The economy of a photocatalytic reaction relies greatly on the number of times a catalyst can be reused without significant loss of photocatalytic efficiency (Chakrabarti & Dutta 2004). To examine reusability, the catalyst was filtrated and reused in a new reaction cycle without any treatment, such as calcination or washing. As shown in Figure 7, full degradation was achieved for the first two cycles. However, the degradation efficiency declined from 89% in the third cycle to 80% in the fifth cycle. This decrease in degradation efficiency may be caused by the adsorption of by-products such as photosensitive hydroxides or inorganic ions onto the catalyst surface. This problem was also encountered when working with photocatalysts such as zinc oxide (Hamlin et al. 1999). The accumulation of by-products on the catalyst surface blocks the surface TiO_2 active sites. Thus, fewer electrons will be excited from valence to conduction bands, leading to less production of hydroxyl radicals and superoxide ions. In addition, there is a possibility that the accumulated by-products scavenge hydroxyl radicals or form bonds that stabilize dye structures.

To reactivate the catalyst, the used TiO_2 was calcined at 550ºC to remove the unwanted by-products from the catalyst surface. This temperature is suitable to decompose most organic compounds, such as RB4 dye and its intermediates, to carbon dioxide (Rice et al. 1932). At the sixth cycle, degradation efficiency was recovered up to 95% (Figure 7). Although organic contaminants were removed from the catalyst surface, full degradation is still not achievable. This finding might be due to a partial change in the TiO_2 phase from anatase to rutile at high temperature. In addition, aggregation could also occur as a result of high temperatures, which could reduce the surface area available for reactions. Preliminary results show that the reusability of the catalyst was not attainable after calcinations and further investigation is in progress to understand the nature of the deactivation.

KINETIC STUDY OF THE PHOTOCATALYTIC OF TIO_2

The degradation of RB4 dye by pure anatase TiO_2 follows first-order kinetics (Figure 8) According to Neppolian et al. (2002a), the photodegradation of most organic compounds is described by pseudo-first-order kinetics (15) and (16).

$$r = -\frac{d[\mathrm{RB4}]}{dt} = k'[\mathrm{RB4}], \quad (15)$$

$$\ln\left(\frac{[\mathrm{RB4}]_t}{[\mathrm{RB4}]_0}\right) = -k't \ or \ \ln[\mathrm{RB4}]_t = -k't + \ln[\mathrm{RB4}]_0, \quad (16)$$

where k' is the first-order rate constant (min^{-1}), $[RB4]_t$ and $[RB4]_0$ are the concentration of the RB4 dye at time t and t =0, respectively. The correlation coefficient of 0.99 indicates that the photodegradation strongly follows pseudo-first-order kinetics. Pseudo-first-order kinetics is known to be associated with the Langmuir-Hinshelwood model at solid-liquid interfaces (Barka et al. 2009).

CONCLUSION

It is evident that RB4 dye (anthraquinone dye) is effectively degraded by nano-sized anatase TiO_2 under the irradiation of UV light. The combination of TiO_2 and H_2O_2 leads to a synergetic effect that increases photocatalytic activity. The addition of H_2O_2 also induces maximum RB4 degradation when using sunlight. The possibility of harnessing sunlight offers a cost-effective and practical solution to degrade RB4 in textile wastewater. In this study, the adsorption of the dye molecules is not a prerequisite for the degradation.

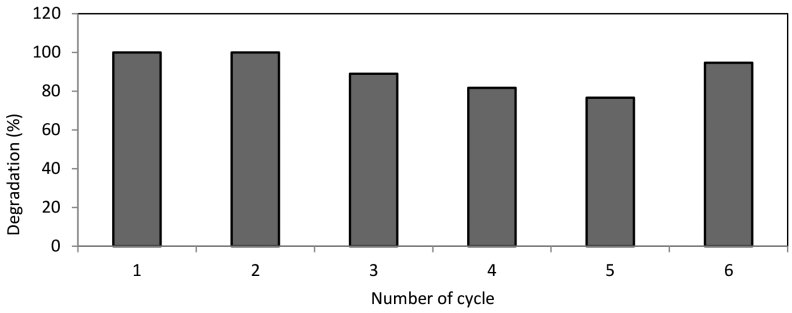

FIGURE 7. Reusability of titanium (IV) oxide. Reaction conditions: amount of TiO_2= 1 g/L; initial dye concentration = 60 ppm; irradiation time = 40 min; light source =125 W UV lamp; stirring speed = 500 rpm; pH = 6

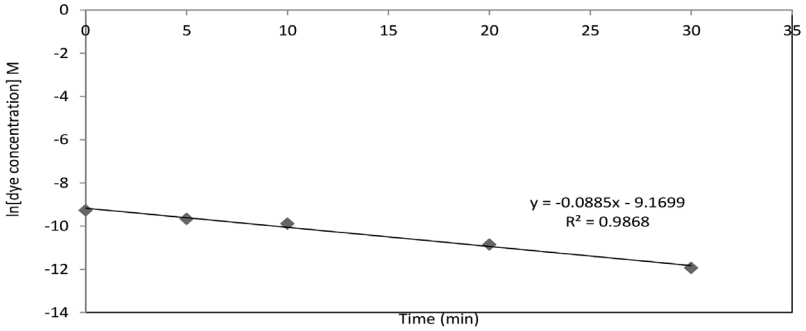

FIGURE 8. Kinetics of RB4 dye degradation. Reaction conditions: amount of TiO_2= 1 g/L; initial dye concentration = 60 ppm; light source =125 W UV lamp; stirring speed = 500 rpm; pH = 6

The hydroxyl radicals in the bulk solution are sufficient to completely degrade RB4 dye. The photodegradation kinetics follows pseudo-first-order kinetics and is dependent on the amount of TiO_2, pH, UV-light intensity, light source and H_2O_2 concentration.

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