Comparison between the photocatalytic degradation of single and binary azo dyes in TiO\textsubscript{2} suspensions under solar light irradiation
Ohm-Mar Min, Li-Ngee Ho, Soon-An Ong and Yee-Shian Wong

ABSTRACT
Textile industries discharge a large quantity of colored wastewater which is harmful to the ecosystem. In this study, two kinds of dyes were investigated: the mono azo Acid Orange 7 (AO7) and diazo Reactive Green 19 (RG19). The photocatalytic degradation of single (AO7, RG19) azo dye and binary (AO7 and RG19 mixture) azo dye aqueous solutions was photocatalyzed by commercial titanium dioxide (TiO\textsubscript{2}, P25) under solar light irradiation. The objectives of this study are to compare the photocatalytic degradation between single and binary azo dye aqueous solution and to study the various parameters such as the effect of different initial azo dye concentrations, different initial azo dye pH values, and compare the adsorption capacity of azo dyes with and without solar light irradiation, which influences the photocatalytic activities of single and binary azo dye aqueous solutions in a TiO\textsubscript{2} suspension. The results showed that photocatalytic degradation of AO7 and RG19 in a single azo dye aqueous solution was faster than a binary azo dye solution under the solar light irradiation process. Chemical oxygen demand results revealed that complete mineralization could be achieved for both AO7 and RG19 azo dyes under solar light irradiation within 22 hours.

Key words | adsorption capacity, azo dyes, mineralization, photocatalytic degradation, solar light, titanium dioxide

INTRODUCTION
Many chemicals, especially azo dyes, herbicides, and pesticides, are found in rivers and lakes (Akpan & Hameed 2009). Textile wastewaters are exceptionally colorful and have high chemical oxygen demand (COD). Azo dyes and dye-determined products are known to present serious carcinogenic effects (Behnajady et al. 2008). Various kinds of techniques have been investigated for biological, physical and chemical treatment of dye pollutants (Essawy et al. 2008; Abramian & El-Rassy 2009; Kulkar & Thakur 2014), chemical processes with flocculation, reverse osmosis, and adsorption onto activated carbon, etc. In these processes, the contaminants transfer from one phase to another (Uc 2010; Gopalapp et al. 2012).

Among the non-exclusive strategies, the propelled oxidation procedures are more productive and equipped for mineralizing an extensive variety of natural contaminants. The advanced oxidation process (AOP) is more efficient and capable of mineralizing a wide range of organic pollutants in wastewater treatment (Ay et al. 2009). Many techniques involve AOP methods such as the UV photolytic technique, the Fenton process, the photo-Fenton process, ozonation, sonolysis, photocatalysis, biodegradation and radiation induced degradation of dyes, respectively (Rauf et al. 2011). For this reason, the degradation of azo dyes was related to many efforts in various advanced oxidation methods (Zhang et al. 2005). The advantages of the photocatalytic process can be clarified as (1) complete mineralization, (2) no waste disposal problem, (3) low cost and (4) only mild temperature and pressure conditions are necessary (Mahmoodi et al. 2006).
There are many kinds of azo dyes, such as direct, acid, base, reactive, disperse, metal complex, mordant and sulfur dyes, which can be identified by the presence of one or more azo bonds (N=N) and which include over 50% of all textile dyes that are also individually used in many industries, such as the production of textiles, leather, plastic, paper, food and cosmetics (Sahoo et al. 2005; Divya et al. 2013). The decolorization of azo dye is attributed to the breakdown of azo bonds. Dye is degraded when it accepts an external electron donor, which is generated either biologically or chemically (Saratale et al. 2009). It can be demonstrated that azo dyes are textile wastewater and useful products for wastewater treatment. TiO2 is one kind of photocatalyst, which can have applications in several fields consisting of water splitting, antibacterial, selective oxidation, and the degradation of various pollutants. TiO2 is also a wide band gap semiconductor, 3.2 eV, which can be used as a photocatalyst for the successful treatment of organic and dye pollutants (Muruganandham & Swaminathan 2004; Sun et al. 2015). Moreover, TiO2 has high oxidation quality and can transform organic compounds into harmless compounds such as CO2 and H2O (Chatterjee & Dasgupta 2005).

Some researchers reported that the degradation efficiency for diazo dye was lower than that of mono azo dye (Tang & An 1995; Tanaka et al. 2000). In our previous studies we investigated the solar photocatalytic degradation of mono azo MO and diazo RG 19 in single and binary dye solution, where we have found that diazo RG with a higher number of sulfonate groups showed higher adsorbability and photodegradation rates than mono azo MO. In order to further confirm this phenomenon, we have investigated mono azo AO7 and diazo RG 19 in single and binary dye solution in this study. Thus, the objectives of the present study are to investigate the adsorption capacity of single and binary azo dye with and without solar light irradiation, and to study the effect of variables such as different initial concentrations of single and binary azo dye solutions under sunlight irradiation, as well as to evaluate the kinetic study of the photocatalytic degradation processes in single and binary azo dye solutions by using TiO2 as a photocatalyst.

MATERIALS AND METHODS

Materials

AO7 (Orange II, pure) is a mono azo dye that has 2-hydroxy and 1-naphthyl azo groups. AO7 was purchased from Acros Organics and used without purification. RG19 is a diazo and reactive dye which has 2-azo groups as the chromophoric moiety and 2-chlorotriazine groups. RG19 was bought from Sigma-Aldrich and also used without purification. The characteristics and chemical structure of AO7 and RG19 are shown in Table 1. Titanium dioxide (AEROXIDE TiO2 P-25) was purchased from Evonik industries with a purity >99.5%. It has a BET surface area of 50 m²/g and a median particle size of 21 nm. Ultra-pure water (pure lab option-Q, ELGA-DV 25) was used in the preparation and dilution of all samples for this research work.

Photocatalytic degradation process

The photocatalytic degradation of single and binary azo dyes aqueous solutions was evaluated under solar light irradiation. The stock solutions of single azo dyes (AO7, RG19) and binary azo dyes (an AO7 and RG19 mixture) were prepared in 1.0 g/L concentrations. The aqueous solution of single and binary aqueous solutions was conducted by 10 mg/L (5 mL diluted with 500 mL ultra-pure water), 30 mg/L (15 mL diluted with 500 mL ultra-pure water) and 50 mg/L (25 mL diluted with 500 mL ultra-pure water), respectively. The photocatalytic degradation of the single and binary azo dye aqueous solutions were placed in 500 mL beakers, sufficiently mixed with a magnetic stirrer and presented to solar light irradiation; 0.3 g (600 mg/L) of commercial TiO2 photocatalyst was added into the azo dye solutions, and the photocatalytic reaction was begun as the set up was placed under solar light irradiation for 6 hours.

Different pH mediums: acidic (pH 1), original–neutral (pH 6.8–7) and alkaline (pH 11) were investigated to evaluate the effects of pH on the solar photodegradation rate. For exploring the effect of pH, the solution’s pH was initially adjusted by adding 0.1 M (30.95 mL/L) hydrochloric acid (HCl) or 0.1 M (4 g/L) sodium hydroxide.
(NaOH) and by controlling with a pH meter (P11/BNC/Bante, UK). The pH values were modified by adding small amounts of 0.1 M HCl for pH 1 (acidic medium), and 0.1 M NaOH for pH 11 (alkaline medium). Before determining optimum pH, the experiments were carried out at a neutral pH of dye solution (pH 6.8). The experiment was conducted with 50 mg/L (25 mL diluted with 500 mL ultra-pure water) of commercial TiO$_2$ photocatalyst under solar light irradiation for 6 hours. The adsorption capacity of both single and binary of AO7 and RG19 can be calculated by using the following equation:

$$q_i = \frac{(C_0 - C_t) \cdot V}{m}$$

where $C_0$ is the initial dye concentration (mg/L); $C_t$ is the dye concentration at time (mg/L); $V$ is the volume of the solution (liter = l), and $m$ is the mass of the adsorbent (gram = g), respectively.

Samples of 20 mL were taken at interval times of 0, 0.5, 1, 1.5, 2, 3, 4, 5 and 6 hours. The water samples were filtered to eliminate the photocatalysts. The clear water samples were measured to determine the concentration of AO7 and RG19 by UV-Vis spectrophotometer (Hitachi U-2800, Japan). The maximum absorbance wavelength ($\lambda_{\text{max}}$) of AO7 and RG19 is given in Table 1.

### Table 1: The characteristics and chemical structure of acid orange 7 (AO7) and Reactive Green 19 (RG19)

<table>
<thead>
<tr>
<th>Type of azo dye</th>
<th>Chemical formula</th>
<th>Molecular structure</th>
<th>Molecular weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>AO7</td>
<td>C$<em>{16}$H$</em>{11}$N$_2$NaO$_4$S</td>
<td><img src="image" alt="Molecular structure of AO7" /></td>
<td>350.32</td>
</tr>
<tr>
<td>RG19</td>
<td>C$<em>{40}$H$</em>{23}$Cl$<em>2$N$</em>{15}$O$_{19}$S$_6.6$Na</td>
<td><img src="image" alt="Molecular structure of RG19" /></td>
<td>1,418.92</td>
</tr>
</tbody>
</table>

AO7: Acid Orange 7; RG19: Reactive Green 19.
were detected at 484 nm and 630 nm, respectively. The removal efficiency percentage of single and binary azo dyes was calculated by using the following equation:

\[
\text{Removal efficiency (\%) of azo dye} = \left(1 - \frac{C_t}{C_0}\right) \times 100 \%
\]  

(2)

where \( C_0 \) is the initial dye concentration and \( C_t \) is dye concentration after treatment at time intervals, respectively. The mineralization of azo dyes was checked through changes in the UV-Vis spectrum and COD. The water samples were filtered through 0.45 \( \mu \)m filter paper and subsequently analyzed for COD. The COD value was measured with a HACH DR2800 spectrophotometer. The mineralization percentage efficiency of the dyes was examined using the following equation:

\[
\text{Mineralization (\%)} = \left[1 - \frac{\text{COD}_{\text{t}}}{\text{COD}_0}\right] \times 100
\]  

(3)

where COD corresponds to time \( t \) and \( \text{COD}_0 \) corresponds to initial conditions. Figure 1 illustrates the mechanism for the charge transfer and separation that supports the photocatalytic activity of single AO7, RG19 and binary azo dyes aqueous solution using TiO₂ as photocatalyst under solar light radiation process. When TiO₂ is irradiated by sunlight, electrons are excited from the valence band to the conduction band, where photocatalytic decolorization of azo dye would occur. The electron that transfers to the conduction band of TiO₂ will react with \( O_2 \) to produce \( O_2^- \). Also, holes in the valence band of TiO₂ will react with \( H_2O \) or \( OH^- \) to produce active species such as \( OH^- \). The \( OH^- \) will further react with the azo dye to form carbon dioxide, water and other intermediate products. The mechanism for photocatalytic degradation of the dyes in this experiment is described as follows:

\[
\text{TiO}_2 \xrightarrow{\text{hv}} e_{\text{CB}} + h_{\text{VB}}^+
\]

At the conduction band

\[
e_{\text{CB}} + O_2 \rightarrow O_2
\]

(5)

\[
\text{HO}_2^- + H_2O \rightarrow H_2O_2 + HO^*
\]

(6)

\[
H_2O_2 \rightarrow 2HO^*
\]

(7)

At the valence band

\[
h_{\text{VB}}^+ + \text{OH}^- \rightarrow \text{OH}^*
\]

(8)

\[
\text{OH}^* + \text{azo dye} \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{intermediate products}
\]

(9)

**Kinetic study of dye concentration in single and binary azo dye aqueous solutions**

All single and binary water samples were analyzed using a UV-Vis spectrophotometer (Hitachi-U2800, Japan). The maximum wavelengths (\( \lambda_{\text{max}} \)) of AO7 and RG19 were 484 nm and 630 nm, respectively. The kinetics of photocatalytic reactions was characterized in the Langmuir–Hinshelwood model concerning the rate of photodegradation (\( r \)) and the organic compound concentration (\( C \)). The equation can be shown as follows:

\[
r = -\frac{dC}{dt} = \frac{kKC}{1 + KC}
\]

(10)

where \( r \) is the rate of photodegradation, \( C \) is the concentration of organic compound, \( k \) is the intrinsic rate constant, \( K \) is the adsorption equilibrium constant of dye on the catalyst particle, and \( t \) is the irradiation time.
rate expression equation, Equation (11), can be clarified into the pseudo first-order kinetics model and $k_{app}$ (h$^{-1}$) represented as an apparent first-order rate constant. The rate expression equation is then simplified into a pseudo-first order kinetic model by plotting $\ln\left(\frac{C_0}{C}\right)$ against $t$ and the $k_{app}$ value can be calculated from the slope of the plot:

$$\ln\left(\frac{C_0}{C}\right) = k_f t = k_{app} t$$  \hspace{1cm} (11)

**RESULTS AND DISCUSSION**

**Effects of removal efficiency of single and binary azo dye aqueous solutions**

The removal efficiency of 50 mg/L of single AO7, RG19 and binary azo dye aqueous solution suspended with 0.3 g of TiO$_2$ were investigated with and without solar light irradiation for 6 hours. Figure 2 shows that the removal efficiency of the concentration of single AO7 and RG19 were 44 and 39 mg/L without sunlight irradiation, and complete decolorization was achieved for both single azo dyes under the solar light irradiation process. The results show the concentration of 48 mg/L and 41 mg/L of AO7 and RG19 in binary solution without solar light irradiation and also examined the concentrations of 5.1 mg/L and 1 mg/L of AO7 and RG19 in binary solution under solar light irradiation, respectively. The results showed that under solar light irradiation it was easier to decolorize than without solar light irradiation for each azo dye aqueous solution in this study. Under the solar light irradiation process, the degradation of organic matter in the azo dye solution is started by the photo excitation of the semiconductor, emulated by the formation of electron-hole pairs on the surface of the catalyst. The mechanism of photocatalytic degradation of an azo dye is described by nitrogen to nitrogen double bonds (N=N). The azo-dye color is determined by the azo bonds and their related chromosphere and auxochromes. Azo bonds, which can be oxidized by positive hole or hydroxyl radical or reduced by electron in the conduction band, are the most active bonds in azo-dye molecules (Gopalapp et al. 2012). In this process, decolorization of the azo dyes decreased after 30 minutes due to adsorption on the surface of the TiO$_2$. The adsorption capacity ($q_i$) of single and binary RG 19 was 18.33 and 15 mg/g, and that of single and binary AO7 was 10 and 3.33 mg/g without solar light irradiation after 6 hours. Moreover, the adsorption capacity ($q_i$) of single and binary RG 19 was 83.33 mg/g and 81.67 mg/g and that of single and binary AO7 was 83.33 mg/g and 74.83 mg/g under solar light irradiation after 6 hours, respectively.

**Effect of different initial concentrations of single and binary azo dye aqueous solutions**

The different initial concentrations of RG19 and AO7 in single and binary aqueous solutions investigated in this study were 10, 30 and 50 mg/L with 0.3 g of TiO$_2$ as catalyst. The concentrations of dyes in single and binary solutions were analyzed with a UV-Vis spectrophotometer, and the measurements of all samples were obtained by absorption spectra at their maximum wavelengths ($\lambda_{max}$) of 484 nm for AO7 and 630 nm for RG19. Figure 3(a) illustrates the photocatalytic degradation of a single RG19 solution. The results showed that 10 mg/L of dye solution can be decolorized more easily than 50 and 30 mg/L of dye solution at different initial concentrations. The decolorization rate is concerned with the possibility of hydroxyl radicals forming on the surface of the TiO$_2$, which also react with dye molecules. When the initial dye concentration increased, the dye ions and the photo path-length entering the solution decreased in the active sites of TiO$_2$ (Song et al. 2008). When the initial concentration of dye increased, more dye molecules were adsorbed on the surface of the TiO$_2$ particles under solar light reaction. As reported by Jain & Shrivastava (2008) and Wang et al. (2008), the photodegradation rate decreased with an increase in initial dye concentration, because for a fixed catalyst amount, the number of active sites remained the same. However, the number of substrate ions accommodated in the inter-layer space increased with the increase in dye concentration, hence the degradation rate decreased. Therefore, the catalytic reaction efficiency reduced due to the decrease of OH* and O$_2^*$ free radicals. Moreover, Ong et al. (2012) found that when the amount of TiO$_2$ increased, the photodegradation
rate also increased under solar light irradiation. Rauf et al. (2011) observed that the initial concentration of dye is an important factor in the photocatalytic reaction. The researcher also mentioned that more organic substances were adsorbed on the surface of TiO$_2$ when the azo dye concentration increased. Therefore, the degradation percentage is low due to lower numbers of photons reaching the photocatalyst surface, and the production of OH becomes slow. The degradation percentage decreases with an increased dye concentration while maintaining a fixed amount of catalyst. Moreover, hydroxyl radical formation will be slower and a lower degradation percentage is obtained. Therefore, it can be concluded that when the dye concentration increased, the degradation rate decreased.

Figure 3(b) shows the different initial dye concentrations of single AO7 solutions under solar light irradiation. It was found...
that the highest photocatalytic degradation was obtained with the lowest initial dye concentration (10 mg/L). However, the photocatalytic degradation efficiency of AO7 was lower than that of RG19. As reported by Ong et al. (2013), RG19, with a higher number of sulfonic groups, can contribute to a higher adsorption capacity on the surface of TiO2 compared to that of the MO, with a lower number of sulfonic groups.

Figure 3(c) shows the effect of different initial dye concentrations of binary azo dye solutions under solar light irradiation. It can be found that the decolorization rate of both azo dyes is lower than single solutions due to the effect of adsorption of dye molecules, but the degradation rate of RG19 is higher than AO7 in binary dye solution because of retarding and competition effects occurring on the photodegradation of azo dyes in binary solutions (Juang et al. 2010). When the dye concentration increased, fewer photons could reach the catalyst surface, and hydroxyl radical production lessened in the binary solution (Mahmoodi...
et al. 2006). It can be mentioned that the competition of azo dyes depends on the structures of the sulfonic groups. RG19 has higher sulfonic groups, and it can be more easily decolorized than AO7 in both single and binary solutions.

**Effect of different initial pH values of single and binary azo dye aqueous solutions**

The effects of pH on the degradation of single and binary solutions were examined under solar light irradiation.

*Figure 4(a)* represents different pH mediums of single RG19 solutions on TiO$_2$ suspensions. It was observed that more rapid decolorization under an acidic medium (pH = 1) than neutral (pH = 6.8) and alkaline (pH = 11) mediums is due to more efficient generation of hydroxyl radicals by the surface of the TiO$_2$. The different pH conditions of the dye solution are related to the photodegradation efficiency of dyes, and this is an important parameter for the reaction occurring on the TiO$_2$ surface. Different pH solutions can determine the surface charge of the TiO$_2$, and can also

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**Figure 4** | Photocatalytic degradation of different initial pH values of (a) RG19, (b) AO7 and (c) binary azo dye aqueous solution using TiO$_2$ under solar light irradiation (pH = 1, 6.8, 11, concentration – 50 mg/L, TiO$_2$ – 600 mg/L).
change the potential of catalytic reactions. Sahoo et al. (2005) studied pH ranges from pH 3–15, and mentioned that the zero point charge (pHpzc) occurs at pH 6.6. Juang et al. (2010) investigated different pH values (pH 4.5 and 8) for the single (AO7, RR2) and binary azo dye aqueous solutions on a commercial TiO2 suspension. They reported that the point of zero charge (pHpzc) is between pH 6.2 and 6.6. It can be assumed that the point of zero charge (pHpzc) is at pH 6.6 in this study. The surface of the TiO2 photocatalyst will be positively charged at an acidic medium (pH < pHpzc), negatively charged at an alkaline medium (pH > pHpzc) and neutral at pH = pHpzc, respectively. Under an acidic or alkaline medium, the titanium surface can be protonated or deprotonated and the reactions will occur on the surface according to the following:

\[ \text{TiOH} + \text{H}^+ \rightarrow \text{TiOH}_2^+ \] (12)

\[ \text{TiOH} + \text{OH}^- \rightarrow \text{TiO} + \text{H}_2\text{O} \] (13)

Equation (12) represents the acidic medium, and in this reaction the titanium surface will remain positively charged. Conversely, it will be negatively charged under an alkaline medium; Equation (13) (Konstantinou & Albanis 2004). The adsorption on the surface of TiO2 depends on the nature of the dye in low or highly acidic and alkaline media. As shown in Figure 4(a), enhanced photocatalytic degradation could be observed under an acidic medium (pH = 1) in RG19 because of the formation of hydroxyl radicals, and the reaction can be described by the following equations:

\[ e_{C_B} + O_2(\text{ads}) \rightarrow O_{2(\text{ads})}^* \] (14)

\[ O_{2(\text{ads})}^* + \text{H}^+ \rightarrow \text{HO}_2^* \] (15)

\[ 2\text{HO}_2^* \rightarrow \text{O}_2 + \text{H}_2\text{O}_2 \] (16)

\[ \text{H}_2\text{O}_2 + \text{O}_{2(\text{ads})}^* \rightarrow \text{OH}^* + \text{OH}^- \] (17)

In an acidic medium, reduction by electrons in the conduction band is essential in the degradation of dyes because of the reductive cleavage of azo bonds. Moreover, the acidic medium preferred the adsorption of dye onto the TiO2 surface, and the photodegradation efficiency of the process increased (Daneshvar et al. 2003). Similar results can be found in the photocatalytic degradation of single AO7 solutions (Figure 3(b)) and binary solutions (Figure 3(c)), respectively. The photocatalytic degradation efficiency under acidic conditions for single and binary RG19 is 100% and 98%, respectively, after 2 hours under solar light irradiation. At the same intervals, the photodegradation efficiency of AO7 is 96% in single and 84% in binary acidic solution. A similar phenomenon could be observed in this study, where the photodegradation performance of RG19 is better than AO7. The higher number of sulfonic groups of RG19 can contribute to a higher absorbability and photodegradation rate (Ong et al. 2013).

**Kinetics study for photocatalytic degradation of single and binary azo dye aqueous solutions**

Tables 2 and 3 show the \( k_{app} \) values for the photocatalytic degradation of single and binary azo dye aqueous solutions.

**Table 2** | Kinetic photodegradation degradation of different initial concentrations of single RG19, AO7 and binary azo dye aqueous solutions using TiO2 under solar light irradiation (pH = 6.8, concentration = 10, 30, 50 mg/L, TiO2 = 600 mg/L)

<table>
<thead>
<tr>
<th>Concentration (mg/L)</th>
<th>( k_{app}/h )</th>
<th>( R^2 )</th>
<th>( k_{app}/h )</th>
<th>( R^2 )</th>
<th>( k_{app}/h )</th>
<th>( R^2 )</th>
<th>( k_{app}/h )</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>4.69</td>
<td>0.99</td>
<td>2.07</td>
<td>0.89</td>
<td>3.29</td>
<td>0.96</td>
<td>2.90</td>
<td>0.81</td>
</tr>
<tr>
<td>30</td>
<td>3.69</td>
<td>0.96</td>
<td>0.87</td>
<td>0.98</td>
<td>2.91</td>
<td>0.94</td>
<td>0.68</td>
<td>0.99</td>
</tr>
<tr>
<td>50</td>
<td>2.40</td>
<td>0.83</td>
<td>0.59</td>
<td>0.91</td>
<td>0.64</td>
<td>0.81</td>
<td>0.39</td>
<td>0.98</td>
</tr>
</tbody>
</table>

Conc: initial concentration of azo dye; AO7: Acid Orange 7; RG19: Reactive Green 19; \( k \): apparent rate constant; h: hour; \( R^2 \): relative coefficients value.

**Table 3** | Kinetic photodegradation degradation of different pH values of single RG19, AO7 and binary azo dye aqueous solutions using TiO2 under solar light irradiation (pH = 1, 6.8, 11, concentration = 50 mg/L, TiO2 = 600 mg/L)

<table>
<thead>
<tr>
<th>pH</th>
<th>( k_{app}/h )</th>
<th>( R^2 )</th>
<th>( k_{app}/h )</th>
<th>( R^2 )</th>
<th>( k_{app}/h )</th>
<th>( R^2 )</th>
<th>( k_{app}/h )</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6.68</td>
<td>0.94</td>
<td>0.98</td>
<td>0.99</td>
<td>2.70</td>
<td>0.84</td>
<td>0.60</td>
<td>0.98</td>
</tr>
<tr>
<td>6.8</td>
<td>2.43</td>
<td>0.83</td>
<td>0.56</td>
<td>0.92</td>
<td>0.63</td>
<td>0.99</td>
<td>0.38</td>
<td>0.99</td>
</tr>
<tr>
<td>11</td>
<td>1.17</td>
<td>0.87</td>
<td>0.32</td>
<td>0.95</td>
<td>0.30</td>
<td>0.99</td>
<td>0.26</td>
<td>0.99</td>
</tr>
</tbody>
</table>

AO7: Acid Orange 7; RG19: Reactive Green 19; \( k \): apparent rate constant; h: hour; \( R^2 \): relative coefficients value.
of different concentrations (50, 30 and 10 mg/L) and different pH (1, 6.8 and 11) media, respectively. The values of photodegradation pseudo first order rate constants for different concentrations of dyes calculated from the linear plots of $\ln \frac{C}{C_0}$ against irradiation time and slope $k_{app}$ (apparent constant) and $R^2$ can be calculated from Equation (11). The pseudo first order constant values obtained for RG19 are greater than that of the AO7 solution. The $k_{app}$ values for RG 19 are larger than that of the AO7. By comparing $R^2$ values from the slopes, it is found that the Langmuir model could describe the isotherm well at an acidic medium (pH = 1) in both single and binary RG19 aqueous solutions. The higher $R^2$ values were obtained in both the RG19 single and binary solutions of the lowest initial concentration (10 mg/L) and in an acidic medium (pH = 1). The high degradation efficiency observed in the RG 19 aqueous solution could be attributed to the fast decomposition of hydrogen peroxide, which produces the hydroxyl radicals. From Table 1, RG19 has a diazo bond and six sulfonic groups. Compared with AO7, RG19 has more azo bonds and higher numbers of sulfonic groups. In this study, the decolorization rate of the dye with a diazo bond (RG19) is faster than that of the dye with a mono azo bond (AO7). This can be proved through similar research by Khalik et al. (2014), who reported that RG19, with the highest number of sulfonic groups, had the highest photodegradation rate in the azo dye study. Moreover, Wang (2000) found that the azo dye with four sulfonic groups has a higher photodegradation rate than that with three sulfonic groups.

Hydroxyl radicals are generated on the surface of TiO$_2$ where the photocatalytic degradation of the azo dyes also occurred. Hence, at an acidic medium (pH = 1), the electrostatic attraction of the positively charged TiO$_2$ surface with the dye led to strong adsorption of the dye molecules on the surface of the TiO$_2$ (Sohrabi & Ghavami 2008). The adsorption capacity of RG 19 is 83.33 and 82.17 mg/g and the adsorption capacity value of AO7 is 82.5 and 82 mg/g in single and binary aqueous solution respectively, at initial concentrations of 10 mg/L within a 2 hour time interval. While under acidic conditions (pH = 1), the adsorption capacity of RG 19 is 83.33 mg/g and 81.83 mg/g, and the adsorption capacity value of AO7 is 70 mg/g and 68.33 mg/g in single and binary aqueous solution, respectively. The results show that the adsorption capacity of RG 19 was higher than AO7 at the lowest concentration (10 mg/L), and at pH 1 in single and binary azo dye solutions. When the single RG19 concentration increased from 10 to 50 mg/L, the apparent rate constant decreased from 4.69 to 2.40 per minute. In the single AO7 solution, the apparent rate values decreased from 2.07 to 0.59 per minute when the concentration increased from 10 to 50 mg/L. When the concentrations of the binary solutions increased, the $k_{app}$ obtained decreased because of the lower adsorption of dye molecules in the binary dye solution. When the concentrations of the binary solutions increased, the $k_{app}$ values decreased because the higher dye concentration can be decolorized more than lower dye concentration.

UV-Vis spectrum analysis

The photocatalytic degradation of 30 mg/L of single and binary azo dye aqueous solution suspended by 0.5 g of TiO$_2$
under sunlight irradiation was investigated by UV-Vis spectroscopy as shown in Figure 5. Figure 5(a) shows the UV-Vis spectrum of photodegradation of RG19, where peaks at 268, 325 and 630 nm can be observed in the visible region. The adsorption peak at 630 nm is associated with the azo bond (\(-\text{N}==\text{N}-)\). The azo peak of RG19 significantly decreased due to the azo bond and can be easily broken down under sunlight, which shows that it is the most active site for oxidation attack by hydroxyl radicals (Khataee et al. 2013). The peaks at 268 nm and 325 nm are attributed to the benzene and naphthalene rings, respectively. As reported by Bansal et al. (2010), a decrease at the peaks at 268 and 325 nm is due to the breakdown of the azo bond in the first period followed by the formation of two aromatic rings, which led to the adsorption intensity increase at the benzene and naphthalene peak (Stylidi et al. 2003). After 6 hours, all peaks disappeared because of the complete decolorization in solar light irradiation. As shown in Figure 5(b), peaks at 228, 310 and 484 nm in the visible region could be found in the spectrum of AO7. The peak at 484 nm is the maximum absorption peak which relates to the azo bond (\(-\text{N}==\text{N}-)\). The peaks at 228 nm and 310 nm could refer to the benzene and naphthalene rings, respectively (Bansal et al. 2010). The absorption peak is slightly decreased in this process because of the breakdown of the azo bond in AO7 solution. Figure 5(c) shows the UV-Vis spectrum of the binary solution under the sunlight irradiation process. Peaks at 630, 484, 310, 268 and 228 nm could be observed. The peaks at 630 and 268 nm represent the RG19 solution, whereas peaks appearing at 484, 310 and 228 nm are assigned to the AO7 solution. The binary solution shows a lower degradation rate than the single solution because two azo dyes in binary solution would compete to adsorb and react on the active sites of the surface of the TiO2 (Damodar et al. 2009).

**Mineralization of azo dyes**

Figure 6(b) demonstrates the mineralization percentage within the photocatalytic degradation of AO7 and RG19, and the mineralization rate can be estimated (Equation (3)) from Figure 6(a) COD results. The COD examination is widely utilized as an effective technique to quantify the organic strength of wastewater, and it is focused around the amount of oxygen needed to oxidize the organic matter to CO_{2} and H_{2}O (Jain & Shrivastava 2008). The photocatalytic experiment was prepared by using 50 mg/L of azo dye aqueous solution (1,000 mL) on 0.6 g (600 mg/L) of TiO2 suspension under solar light irradiation for 22 hours, and the samples were collected at set time intervals for COD tests. It was found that AO7 and RG19 were completely mineralized after 4 and 12 hours under solar light irradiation. In addition, the complete decolorization of single AO7 and RG19 (Figure 2) occurred within 2 and 5 hours under the solar light irradiation process. The time
intervals for COD analysis were longer, contrasted with photocatalytic activity, in order to ensure the complete mineralization of the azo dyes. This may be due to the formation of intermediate products and intensity in the middle of intermediates and parent dye molecules in the photocatalytic degradation process (Nishio et al. 2006). The results showed that the photocatalytic activity of RG19 was slightly higher than that of AO7. From the COD results, it is clearly demonstrated that the photocatalytic process can completely mineralize the parent azo dye and its intermediate products. This was also mentioned by Stylidi et al. (2005), who used TiO2 as a catalyst to examine the pathways of solar light-induced photocatalytic degradation towards azo dye. It can be observed that the COD values of AO7 and RG19 dropped significantly after 1 and 7 hours of solar light irradiation. The intermediate products can be oxidized and mineralized to produce several inorganic ions, for example, carbon dioxide (CO2), water (H2O), nitrates ion (NO3–), natrium ion (Na+), sulfate ion (SO42–) and hydrogen ion (H+) (Khalik et al. 2014).

CONCLUSION

The photocatalytic degradation of mono azo AO7 and diazo RG19 azo dyes of single and binary azo dye aqueous solutions were photocatalyzed under solar light irradiation. The results demonstrated that under solar light irradiation there were higher adsorption capacities than without solar light irradiation because the degradation of organic matter in azo dye solution is started by the photo excitation of the semiconductor, emulated by the formation of electron-hole pairs on the surface of the catalyst under solar light irradiation. The results showed that under an acidic medium (pH = 1), both RG19 and AO7 were more easily decolorized than under neutral and alkaline media, due to the more efficient generation of hydroxyl radicals by the surface of the TiO2. The highest relative coefficients (R2) value could be obtained in both RG19 single and binary solutions at the lowest initial concentration (10 mg/L) and in an acidic medium (pH = 1). The comparison between single and binary solutions found that diazo RG19 had a significantly higher degradation efficiency than mono azo AO7 in this study. This might be ascribed to the higher number of sulfonic groups in diazo RG19 compared to that of the mono azo AO7. From UV-Vis and COD analysis, it was proven that the mono azo (AO7) and diazo (RG 19) dyes can be completely mineralized under solar light irradiation.

REFERENCES


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