Optimization of photocatalytic degradation of real textile dye house wastewater by response surface methodology
Sayed Mohammad Bagher Hosseini, Narges Fallah and Sayed Javid Royaee

ABSTRACT
This study evaluates the advanced oxidation process for decolorization of real textile dyeing wastewater containing azo and disperse dye by TiO$_2$ and UV radiation. Among effective parameters on the photocatalytic process, effects of three operational parameters (TiO$_2$ concentration, initial pH and aeration flow rate) were examined with response surface methodology. The F-value (136.75) and p-value < 0.0001 imply that the model is significant. The ‘Pred R-Squared’ of 0.95 is in reasonable agreement with the ‘Adj R-Squared’ of 0.98, which confirms the adaptability of this model. From the quadratic models developed for degradation and subsequent analysis of variance (ANOVA) test using Design Expert software, the concentration of catalyst was found to be the most influential factor, while all the other factors were also significant. To achieve maximum dye removal, optimum conditions were found at TiO$_2$ concentration of 3 g L$^{-1}$, initial pH of 7 and aeration flow rate of 1.50 L min$^{-1}$. Under the conditions stated, the percentages of dye and chemical oxygen demand removal were 98.50% and 91.50%, respectively. Furthermore, the mineralization test showed that total organic compounds removal was 91.50% during optimum conditions.

Key words | advanced oxidation process, photocatalytic degradation, real textile wastewater, surface response method, TiO$_2$/UV

INTRODUCTION
After the industrial revolution, a wide range of aromatic contaminants, such as halogenated aromatics and nitro aromatics, which are known as xenobiotic compounds, entered the environment. Synthetic dyes, especially azo dyes, are such materials, which are used in the textile industry on a large scale. Diffusion of these toxic and mutagenic substances into the environment even at low concentration causes cancer (Bisschops & Spanjers 2005). Furthermore, these compounds absorb sunlight and decrease the influence of sunlight to the water depths. So, they affect the photosynthesis of aquatic plants, which consequently lowers the level of dissolved oxygen (DO) in water and raises the temperature (Vilar et al. 2011). Therefore, dye effluents must be treated completely before entering the environment. There are some common methods for treating dye wastewater, such as adsorption on activated carbon (Ahmad & Hameed 2010), coagulation/flocculation followed by sedimentation or dissolved air flotation (Riera-Torres et al. 2010; Khouni et al. 2011) and reverse osmosis. These processes just transfer pollutants from one phase to another rather than eliminating them from the water matrix (Alaton et al. 2002). Although physical methods have the ability to remove dye in a short time, they have some shortcomings, such as high energy consumption, high costs and the necessity of a second treatment method due to the transferring of contaminants from one phase to another phase (Sudarjanto et al. 2006; Fallah et al. 2010; Keramati et al. 2014a). Moreover, biological methods require too much time and space for treating a high volume of effluents and face problems such as activated sludge disposal (Keramati et al. 2014a).

In recent years, an advanced oxidation process based on heterogeneous photocatalysts, especially the photocatalyst titanium dioxide (TiO$_2$), has been introduced as an efficient method. It has several advantages, such as availability, low cost, chemical stability and the ability to remove a variety of contaminants even until the mineralization stage in environmental conditions (Giri et al. 2010; Ram et al. 2012;
Divya et al. 2013; Asaithambi et al. 2014; Keramati et al. 2014a, 2014b; Pishkar et al. 2014). Also, based on the characteristic of catalysts, these materials remain at the end of the process without being consumed and have the potential to be reused and revived. Most studies on the photocatalytic treatment of textile wastewater have been done on synthetic wastewater containing one azo dye and also have been done by the classical method, in which, by keeping a series of parameters constant, the effect of one parameter is examined, which needs more time and effort. To solve these problems and a closer look at the present work, the statistical design method has been used (Sudarjanto et al. 2006). Furthermore, during the experiments there are some operational parameters which affect the process simultaneously. So considering the effect of all affecting parameters at the same time could help the researchers to recognize the process better. For this purpose, the Box-Behnkken method was selected for this study, which is a quadratic polynomial independent design approach based on response surface method (RSM) of sub-fractional factorial design. This method is beneficial for modeling and analysis of process response influenced by several variables. Its target is optimization and interpolation for other unexamined points and a correct estimation of probable response at those points (Box & Wilson 1951; Gardiner & Gettinby 1998).

Furthermore, during the experiments there are some operational parameters which affect the process simultaneously. So considering the effect of all affecting parameters at the same time could help the researchers to recognize the process better. This study focuses on the treatability of real dye house wastewater containing azo, dispersed, acidic or basic dye at different concentrations by using the photocatalytic degradation process, which has not been applied previously. Another aim of this research was to correlate and analyze the photocatalytic degradation of real dye house wastewater in regard to the simultaneous effects of three operating variables (aeration rate, amount of catalyst and pH) and one response (dye removal) by RSM with the goal of 100% dye removal, which has not yet been reported in preceding research.

MATERIALS AND METHODS

Chemicals and reagents

Wastewater was obtained from a textile dyeing factory located in the industrial zone of Eshtehard town, Iran, which is under the supervision of industrial towns of Alborz province. The company has several dyeing batch reactors. Discharge wastewater volume of this factory was approximately 250 (m³/day) and its chemical composition varied depending on the characteristics of the fiber material being dyed and the stage (e.g. dyeing, washing and drying) of the dyeing process. The industrial dye bath consisted of a mixture of dyes including: Reactive Black 5, Reactive Red 195, Reactive Blue 222, Reactive Yellow 145, Disperse Red 167, Disperse Yellow 211, Disperse Red 60, 152 and 153, Disperse Blue 56 and 60. In the textile dyeing factory, prior to the disposal into the industrial sewage system, the effluent wastewater was collected in three basins in series (each with a capacity of 150 m³). All the wastewater samples used in the present study were obtained from the last basin using the grab sampling method. The wastewater was kept at 4 °C (Balcioglu & Arslan 1998). Indeed, right after the used wastewater was transferred to the laboratory, it was maintained in a refrigerator, which caused decrease of microorganisms’ activity in the wastewater. Also, UV light causes inactivity of microorganisms.

The characteristics of the wastewater are as follows:

pH = 9.8, Color = 220 SU (Standard Unit), chemical oxygen demand (COD) = 1200 mg L⁻¹, total dissolved solids (TDS) = 8200 mg L⁻¹

Titanium dioxide (TiO₂) p-25 was obtained from Degussa Company (Germany). The characteristics of TiO₂ were Brunauer–Emmett–Teller (BET) surface area 50 ± 15 m² g⁻¹, average particle size 21 nm and 80/20 anatase/rutile ratio. H₂SO₄ and NaOH in analytical grade were used for pH adjustment.

Photocatalytic degradation procedures

The photocatalytic reactions were done in a double-layer cylindrical slurry reactor made of stainless steel. To maintain a constant temperature, water was used as the cooling fluid. The light source was provided using eight UV-C 16-watt lamps manufactured by Philips, which were installed in the reactor using eight holders made of quartz. In order to mix the reaction solution, a blade mixer with three rowing-like blades, which rotates with an electromotor, was used. The oxygenation of the solution was provided by blowing with the help of an aeration pump manufactured by Hailea Company (China) with 35 L min⁻¹ capacity and injected by a ring sparger into the system. The schematic diagram of the reactor is shown in Figure 1.
For a typical run, 2 L of textile wastewater was introduced into the reactor. The initial pH (as value listed in Table 1) adjustment was conducted with 0.10 M H₂SO₄ and 0.10 M NaOH, and the required amount of TiO₂ powder (from 0.20 to 3 g L⁻¹) was added according to the experimental design. Prior to photocatalytic experiments, adsorption and photolysis studies were carried out. All experiments were conducted at room temperature, at atmospheric pressure and in batch operation. Samples for analyses were withdrawn at regular time intervals during the UV irradiation time and centrifuged to remove TiO₂ particles immediately before analysis. Total volume of the withdrawn samples was less than 4% (by volume) of the suspension.

The operational parameters’ range is shown in Table 1.

**Analysis**

Since the tested wastewater was real wastewater of the textile industry, in order to determine the amount of color, the initial dye solution and samples were scanned using a UV-Vis spectrophotometer (Model v-550) manufactured by Jasco (USA) after centrifugation and separation of the particles of TiO₂ in the range of 200–800 nm. The absorption curve was plotted for this range. The area under the plotted absorption curve in the visible light range, i.e. 400–800 nm, was determined as a criterion of the amount of color in SU units using relevant software (Chinwetkitvanich et al. 2000; Panswad et al. 2001).

COD was determined at 605 nm on a photometer (Jasco Model v-550) using standard COD digestion solutions in the range 100–1,500 mg L⁻¹. Due to the high concentration of chloride ion in the effluent, dilution was used to reach the limit (APHA 1998).

**Response surface methodology**

In the present work, the Design Expert® (7.3.1) software was used for statistical analysis of data. RSM based on Box-Behnken was used to examine the effect of operational parameters and interactions between them and determine the optimum conditions for decolorization of dye. Seventeen experiments were conducted based on the same design. Percentage of dye removal was chosen as response variable.

In most degradation studies by the UV/TiO₂ system, it has been shown that degradation rate is dependent on aeration rate, amount of catalyst and pH (Thakur et al. 2010; Keramati et al. 2014a). In our study, the parameters were investigated as well as the interactions between them. To select the level of parameters, initial experiments were carried out, in which the methodology of determination of these parameters will be explained in the next section.

**RESULTS AND DISCUSSION**

**Evaluation of dye adsorption rate by TiO₂**

In order to evaluate the decolorization efficiency through dye adsorption on TiO₂ surface, different concentrations of catalyst were mixed well by a mixer at different pH in darkness. Figure 2 shows the effluent decolorization over time by adsorption in different conditions (pH = 5 and TiO₂ = 3 g L⁻¹, pH = 5 and TiO₂ = 1.60 g L⁻¹, pH = 7 and TiO₂ =
0.20 g L\(^{-1}\)). As observed, in the first half hour, the solution was balanced and no significant change in the decolorization rate was seen. Thus, in all the next experiments the solution was mixed in darkness for 30 min and then the light radiation began. Table 2 shows the decolorization rate by TiO\(_2\) adsorption in different conditions. As is expected, the adsorption efficiency increases with the increase of catalyst concentration and consequently the increase of its surface.

### Determination of operational parameters level

**Aeration rate/catalyst loading/pH**

To test the role of dissolved O\(_2\) in the photocatalytic degradation process, 2 L of wastewater was aerated at different air flow rates (from 0.25 to 2.50 L min\(^{-1}\)). Then the DO concentration was measured. The role of O\(_2\) during photocatalytic processes has long been debated. Although O\(_2\)’s electron scavenging character is well documented, the roles of its reduction products (e.g. HO\(_2\)) are questionable. There is evidence for and against the importance of these species. It is noteworthy that not only O\(_2^•\)/HO\(_2^•\), but also dissolved O\(_2\), can react with radicals formed during the degradation process. In a UV light/TiO\(_2\) system, almost all active species are generated following the reaction in which oxygen captures the e\(_{cb}\). Oxygen is an indispensable reactant to generate active oxygen radicals, including singlet oxygen (\(^1\)O\(_2\)), hydroxyl radical (OH\(^•\)), superoxide radical (HO\(_2^•\) or O\(_2^•\)), and hydrogen peroxide (H\(_2\)O\(_2\)) (Chatterjee & Mahata 2001). Therefore, oxygen is very important in photocatalytic reactions induced by UV light. It not only scavenges e\(_{cb}\) to effectively prevent the recombination of e\(_{cb}\) and H\(^+\), but is also the predominant reactant to generate active species. As represented in Table 3, in which the amounts of DO at different aeration rates are shown, by increasing the aeration rate up to 1 L min\(^{-1}\), the concentration of DO was increased, but by increasing the aeration rate from 1 to 2.50 L min\(^{-1}\), the amount of DO concentration was not changed. According to the obtained results, the range 0.25 to 1.50 L min\(^{-1}\) of aeration rate was selected as the optimum limited.

The effect of TiO\(_2\) concentration on decolorization efficiency has been shown in Figure 3(a). As seen, increasing the amount of catalyst from 0.20 to 2 g L\(^{-1}\) leads to increase of the decolorization, though decolorization meets a small decline by increasing catalyst concentration from 2 to 3 g L\(^{-1}\). Finally, the desired level was selected in the range 0.20 to 3 g L\(^{-1}\). Vaiano et al. (2016) also have studied the effect of catalyst dosage for degradation of patent blue V dye using Au-TiO\(_2\) and stated that by increasing catalyst dosage to up to 9 g L\(^{-1}\), the amount of decolorization total organic compounds removal increased, but when the concentration of catalyst was increased from 9 to 12 g L\(^{-1}\),

**Table 2** | The effect of TiO\(_2\) concentration and pH on decolorization of the textile wastewater by adsorption process after 30 min

<table>
<thead>
<tr>
<th>TiO(_2) concentration (g/L)</th>
<th>pH</th>
<th>Decolorization</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>3</td>
<td>0.155</td>
</tr>
<tr>
<td>1.6</td>
<td>3</td>
<td>0.380</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>0.625</td>
</tr>
<tr>
<td>0.2</td>
<td>5</td>
<td>0.271</td>
</tr>
<tr>
<td>1.6</td>
<td>5</td>
<td>0.355</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>0.437</td>
</tr>
<tr>
<td>0.2</td>
<td>7</td>
<td>0.227</td>
</tr>
<tr>
<td>1.6</td>
<td>7</td>
<td>0.215</td>
</tr>
<tr>
<td>3</td>
<td>7</td>
<td>0.447</td>
</tr>
</tbody>
</table>

**Table 3** | The effect of aeration rate on DO concentration of textile wastewater (without adding catalyst and UV irradiation)

<table>
<thead>
<tr>
<th>Aeration rate (L/min)</th>
<th>DO concentration (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>6.62</td>
</tr>
<tr>
<td>0.5</td>
<td>7.05</td>
</tr>
<tr>
<td>0.75</td>
<td>7.12</td>
</tr>
<tr>
<td>1</td>
<td>7.18</td>
</tr>
<tr>
<td>1.5</td>
<td>7.18</td>
</tr>
<tr>
<td>2</td>
<td>7.18</td>
</tr>
<tr>
<td>2.5</td>
<td>7.18</td>
</tr>
</tbody>
</table>
the decolorization and the mineralization of the dye decreased. Possibly, the increase in the catalyst dosage over the optimum value resulted in a decreased light penetration through the solution because of the increased opacity of the aqueous suspension (Vaiano et al. 2016).

To determine the level of pH, two values of pH were examined at 2 g L$^{-1}$ TiO$_2$ concentration and 1.50 L min$^{-1}$ aeration rate. After 120 min, the maximum decolorization efficiencies of raw wastewater with pH equal to 9.80 and 3 were 40% and 80%, respectively (Figure 3(b)). The optimum range of pH was selected from 3 to 7.

**Statistical analysis**

The values of three operational parameters and one response for all 17 runs by Box-Behnken design are seen in Table 4. Based on the results, a quadratic equation was presented by the software to predict the experiments. This equation includes a set of coefficients and coded factors described as follows:

$$Y = 0.83 - 0.020 A + 0.20 B + 0.062 C + 0.035 AB + 0.030 AC - 0.12 B^2 - 0.035 C^2$$  \hspace{1cm} (1)

Variables A, B, C are pH, concentration of catalyst and aeration flow rate, respectively. It can be seen from the equation that there is an interaction between (A, B) and (A, C), while the interaction between (B, C) is small, so it was deleted from the equation. According to Figure 4, which shows the actual results obtained from experiments against prediction values of software, the designed equation covers a large area of the experiments properly.

The success and proportion of the model examined by variance analysis are shown in Table 5. The F-value (136.75) and p-value <0.0001 imply that the model is significant. There is only a 0.01% chance of occurrence of the model F-value due to noise. The lack of fit F-value of 1.86 is not significant relative to the pure error. For a model to be successfully used for prediction, the lack of fit should be not significant. The ‘Pred R-Squared’ of 0.95 is in reasonable agreement with the ‘Adj R-Squared’ of 0.98, which confirms the adaptability of this
model (Sudarjanto et al. 2006). So, it can be concluded that the obtained model is adequate to describe the relationship between the decolorization efficiency and operational factors for degradation of real textile dye by the photocatalytic process.

Effect of parameters and interactions between them

In Figures 5 and 6, the three-dimensional response surface and interaction plots of the textile wastewater decolorization for two pairs of factors are displayed: pH vs. TiO₂ concentration, AB (Figure 5(a) and 5(b)) and pH vs. aeration, AC (Figure 6(a) and 6(b)).

Figure 5(a) and 5(b) show the interaction of pH and concentration of TiO₂ in the average aeration, i.e. 0.88 L min⁻¹. As is shown, decolorization increases by increasing the concentration of catalyst, which is a natural characteristic of heterogeneous photocatalysts (Rauf et al. 2011). By increasing the catalyst’s concentration, in fact, the surface area and number of active sites of catalyst increase, and thus the dye adsorption and formation of free radicals, which degrade the dye, increase (So et al. 2002; Pekakis et al. 2006; Hussein & Abass 2010). As the effect of concentration of TiO₂ was expressed as a quadratic model with a negative coefficient in Equation (1), as shown in Figure 5(a), the related curve formed like a parabola with a maximum value. It is evident that at the end of the process, there is a certain concentration of catalyst after which the degradation of dye does not increase or probably decreases (Muruganandham & Swamianathan 2006; Toor et al. 2006; Nikazar et al. 2010). This phenomenon may be due to staining of the solution, resulting in a decrease in light penetration into the reactor and blocking and scattering of resulting light. However, the catalyst aggregation at high concentrations and subsequently the decrease in number of active sites should not be ignored. Similar results were confirmed by others in similar scenarios (Konstantinou & Albanis 2004; Herrmann 2005; Saquib et al. 2008a; Sun et al. 2008; Rauf et al. 2011). But the effect of pH is slightly more complicated. As can be observed from Figure 5, at a low concentration of catalyst, the decolorization decreases with increase of pH, but a reversed mode was observed at high concentration of catalyst. Similar results were reported by Keramati and her co-workers in

Table 5 | ANOVA for the response surface quadratic model

<table>
<thead>
<tr>
<th>Source</th>
<th>Sum of squares</th>
<th>df</th>
<th>Mean squares</th>
<th>F-value</th>
<th>p-value</th>
<th>Prob &gt; F</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>0.44</td>
<td>7</td>
<td>0.063</td>
<td>136.75</td>
<td>&lt;0.0001</td>
<td>Significant</td>
<td></td>
</tr>
<tr>
<td>A-pH</td>
<td>3.120E-003</td>
<td>1</td>
<td>3.120E-003</td>
<td>6.75</td>
<td>0.0288</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B-TiO₂</td>
<td>0.33</td>
<td>1</td>
<td>0.33</td>
<td>723.09</td>
<td>&lt;0.0001</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-Air</td>
<td>0.030</td>
<td>1</td>
<td>0.030</td>
<td>65.74</td>
<td>&lt;0.0001</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AB</td>
<td>4.970E-003</td>
<td>1</td>
<td>4.970E-003</td>
<td>10.76</td>
<td>0.0095</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AC</td>
<td>3.660E-003</td>
<td>1</td>
<td>3.660E-003</td>
<td>7.92</td>
<td>0.0202</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B₂</td>
<td>0.059</td>
<td>1</td>
<td>0.059</td>
<td>126.91</td>
<td>&lt;0.0001</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₂</td>
<td>5.278E-003</td>
<td>1</td>
<td>5.278E-003</td>
<td>11.42</td>
<td>0.0081</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Residual</td>
<td>5.521E-003</td>
<td>7</td>
<td>5.031E-004</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lack of Fit</td>
<td>2.906E-003</td>
<td>5</td>
<td>5.812E-004</td>
<td>1.86</td>
<td>0.2846</td>
<td>Not significant</td>
<td></td>
</tr>
<tr>
<td>Pure Error</td>
<td>1.253E-003</td>
<td>4</td>
<td>3.133E-004</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cor Total</td>
<td>0.45</td>
<td>16</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
photocatalytic degradation of styrene in aqueous phase under a UV/TiO\(_2\) system (Keramati et al. 2014a). Studies indicate that pH can affect the photocatalytic process in several ways. First, varying pH can change the charge of both catalyst surface and dye molecules with ionizable functional groups. Therefore, varying pH can affect the adsorption of dye molecules on the catalyst surface, which is a key step in the photocatalytic process (Wu 2008; Silva & Faria 2009).

Second, due to the reaction of hydroxide ion (OH\(^-\)) and positive hole, hydroxyl radicals can be produced. Thus, alkaline conditions could favor the formation of the hydroxyl radicals and improve degradation. Third, TiO\(_2\) particles tend to aggregate in acidic conditions, and this decreases the usable surface for dye and photon adsorption (So et al. 2002).

The zero charge point of TiO\(_2\)-P25, P\(_{zc}\) was reported between 6.25 and 6.80 by Degussa company (Loannis & Triantafylllos 2004; Saquib et al. 2008a; Rauf et al. 2011). In alkaline and acidic conditions, the titanium surface can be protonated or deprotonated. Therefore, the TiO\(_2\) surface will have positive charge at pH < P\(_{zc}\) and negative charge at pH > P\(_{zc}\). Thus, at low concentration of catalyst, a greater effect of first impact was seen in the photocatalytic process. It means that in the acidic range, considering the positive surface charge of the catalyst in this pH range, most adsorption occurs for the dye molecules which have negative functional groups, but at high concentration of the catalyst, the other two effects of pH on the process will be more highlighted. First, in the acidic range, a greater aggregation of TiO\(_2\) particles will occur, and as a result the reduction in active surface area of catalyst will decrease the decolorization. Secondly, by measuring the pH at the end of the photocatalytic process, for the reaction conditions with initial pH equal to 7, we observe an entry into the alkaline range. Therefore, we will see the share of the second effect increase, and as we have more active sites at pH = 7 in high concentration of catalyst versus acidic pH, there is an opportunity for the second effect to react (Saquib et al. 2008b).

Figure 6(a) shows the effect of aeration and its interaction with pH at the average concentration of catalyst, TiO\(_2\) concentration = 1.60 mg L\(^{-1}\). What is observed is that the increase of aeration rate causes decolorization to be enhanced, but there is a maximum limit for aeration rate after which no more decolorization was seen. It seems that the solution was saturated with oxygen, which depends on oxygen consumption. Based on Figure 6(b), which indicates the interaction of two factors, it can be observed that at the lower limit of aeration, the decolorization decreases with the increase of pH, and at the upper limit of aeration, the decolorization increases with the increase of pH. Oxygen is very important in photocatalytic reactions induced by UV light. It not only scavenges e\(_{cb}\) to effectively prevent the recombination of e\(_{cb}\) and H\(^+\), but is also the predominant reactant to generate active species (Fujishima et al. 2008; Royaee & Sohrabi 2010).

Figure 7 shows the variation of oxygen consumption by changing the pH. Maximum oxygen consumption increases with increase of pH and the maximum aeration moves to larger numbers. This reflects an increase in the degradation of dye.

On completion of the above description, there are three states for dye degradation based on the mechanism of the photocatalytic process: (1) dye absorption by photocatalyst and direct degradation of dye, (2) hydroxide ion absorption
on the catalyst surface and the formation of OH⁻ (free radicals) and dye degradation by them, and (3) molecular oxygen absorption on catalyst surface and formation of peroxide ion radicals and formation of OH⁻, which causes dye degradation.

Thus, dye and hydroxide ion and molecular oxygen are in competition for being adsorbed by catalyst, and as mentioned before, dye adsorption changes dramatically with pH variations. At acidic pH ($\text{pH} < \text{pH}_{\text{ZPC}}$), the catalyst surface is highly positively charged, and increasing it toward $\text{pH}_{\text{ZPC}}$, the surface charge goes toward neutral and negative. On the other hand, the used wastewater is negatively charged mostly with ionic groups.

With increasing pH, the dye absorption of photocatalyst decreases. However, the photocatalyst level remains constant and even increases due to aggregation condition removal. In this case, the opportunity for the adsorption of hydroxide ion and DO will increase. In particular, molecular oxygen with no charge has more opportunity for being adsorbed on the surface with negative charge, and increasing the aeration rate increases the absorption of molecular oxygen and thus improves the effectiveness of the related reaction. Thus, with increasing pH, the efficiency of dye removal rises due to direct dye degradation, and the reaction effect of molecular oxygen increases. While at minimum aeration (0.25 L min⁻¹) a slight increase in the efficiency is seen due to the lack of molecular oxygen, but not to an extent that reverses the dye removal slope of Figure 6(b).
But in maximum aeration and with the presence of sufficient oxygen, the contribution of the related reaction increases and the slope of the dye removal diagram is reversed.

Software optimization of process and comparison with experimental results

The main objective of this study is to find the optimum conditions of parameters in order to achieve the maximum decolorization of the real textile wastewater based on the experimental results. On this basis, the numerical optimization was performed by design expert software. Choosing 100% decolorization as a target and selecting independent parameters in experimental ranges, pH = 7, concentration of $\text{TiO}_2$ 3 g L$^{-1}$ and aeration rate = 1.50 L min$^{-1}$ were determined as optimum conditions. 98% wastewater decolorization was predicted in optimum conditions by software. The experiment was done in optimum conditions to compare the predicted optimum value with the actual value and check the presented model. The resulted decolorization is 99%, which is well compatible with the predicted value and indicates that the presented model can describe the wastewater decolorization well using the studied parameters.

Mineralization assessment

COD analysis has been used to evaluate the degradation performance and mineralization of dye in studied wastewater. During the photocatalytic process, it is possible that the dye molecule breaks and produces intermediate substances which are more dangerous than the first dye. So, the examination of mineralization is very important. Thus, samples were taken from the run at specified time intervals and COD testing was done. These results show that the photocatalytic process of dye degradation has been very successful and 91.50% mineralization was achieved in 2.50 h.

CONCLUSION

The photocatalytic degradation of real textile wastewater in a slurry reactor was investigated. The initial pH of reaction mixture, $\text{TiO}_2$ concentration and aeration were evaluated via Box-Behnken design based on response surface methodology.

In order to reach the maximum decolorization, optimal amounts of variables were achieved as follows: $\text{TiO}_2$ concentration = 3 g L$^{-1}$, initial pH = 7 and aeration rate = 1.50 L min$^{-1}$. In these conditions, 98% decolorization was predicted. By performing experiments in optimum conditions, 99% decolorization was achieved, which matches the software prediction. Also, the removal percentage of COD (91.50%) shows the successful mineralization of textile wastewater by the photocatalytic process. In this paper we tried to investigate the efficiency of a batch photocatalyst process in treating a real textile wastewater, but it is necessary to investigate the efficiency of a continuous photocatalyst process with stabilization, recovery or separation of catalyst in future research.

ACKNOWLEDGEMENTS

The authors wish to thank Alborz Industrial Park Company for financial support.

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First received 24 January 2016; accepted in revised form 20 April 2016. Available online 23 May 2016