Study on Kinetic and Optimization of Continuous Advanced Oxidative Decolorization of Brilliant Reactive Red Dye

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Abstract

The azo dye brilliant reactive red K-2BP (λmax = 534 nm) is widely used for coloring textiles because of its low-cost and tolerance fastness properties. Wastewater treatment that contains the dye by conventional ways is usually inadequate due to its resistance to biological and chemical degradation. During this study, the continuous reactor of an advanced oxidation method supported the use of H₂O₂/sunlight, H₂O₂/UV, H₂O₂/TiO₂/sunlight, and H₂O₂/TiO₂/UV for decolorization of brilliant reactive red dye from the effluent. The existence of an optimum pH, H₂O₂ concentration, TiO₂ concentration, and dye concentration was taken from the batch reactor experiments. The best conditions were pH=3, H₂O₂ dosage = 500 ppm, TiO₂=100ppm and dye concentration=15 ppm. Under the most effective conditions, complete removal of the dye solution was achieved with different flow rates (10, 30, 60) ml/min. At flow rate of 10 ml/min, the percentage of decolorization were (80.47%, 84.65%, 89.42%, 77.5%) and at 60 mL/min (65.19%, 68.26%, 70.01%, 56.8%) for H₂O₂/sunlight, H₂O₂/UV, H₂O₂/TiO₂/sunlight and H₂O₂/TiO₂/UV respectively. Results of degradation information showed that the decolorization method was pseudo-first-order kinetics.

Keywords: Reactive Red, Photodegradation, advanced oxidation processes (AOP), Wastewater, Sunlight

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1- Introduction

Wastewater produced from the textile industry typically contains high concentrations of organic, inorganic materials, high COD, high pH and strong apparent color [1]. Dyes from coloring processes are the primary supply of color textile wastewater and it may cause serious environmental issues [2].

There are different types of treatment such as physical-chemical treatment included [coagulation-flocculation, adsorption on activated carbon and reverse osmosis] and biological treatment are used for removal toxic substance from wastewater. Biological treatment isn’t effective enough to remove dyes from effluent while physical-chemical treatment is not strong enough to decolor the dye so it generated a sludge and adsorbent regeneration are the principal weaknesses of those methods [3]. advanced oxidation processes (AOPs), that are considered a chemical treatment of wastewater and it is the most effective process for the removal of the organic pollutants [4]. AOPs are based on the generation of hydroxyl radical (OH*) that are capable of degrading the organic pollutants to carbon dioxide, water, and inorganic materials [5].

Various of AOPs include chlorination, ozonation, Fenton, photo-Fenton, photo-catalytic and wet-air oxidation [6]. H₂O₂/UV process is one of the advanced oxidation technique, hydrogen peroxide is photolysis to generate the OH* responsible for oxidation.

Hydroxyl radicals are attacked the organic molecules causing their destruction and mineralization. Also, another method is the photocatalyst with titanium dioxide that is a wide band gap semiconductor and it is used near-UV light of wavelength shorter than 380 nm or sunlight.

TiO₂ particles can form a paired electron (e⁻) and hole (h+), in the conduction band and valence band when it was the absorption of the ultraviolet radiation. The positive hole is seemingly ready to oxidize a water molecule to hydroxyl radical. The hydroxyl radical, in turn, is a powerful oxidant [7][8].

The processes of H₂O₂/UV, H₂O₂/TiO₂/UV treatment depends on many conditions that have an effect on the degradation of organic pollutants.

The conditions include the type and concentration of the organic materials, hydrogen peroxide concentration, TiO₂ amount, light source, pH, temperature, flow rate and reaction time [9].

The most important parameter is the dosage of H₂O₂ when its increased the formation of hydroxyl radical will be increased, therefore increasing the decolorization rate to optimal value then the H₂O₂ react with OH* and decreased in the decolorization rate [10]. pH plays a major role in the photocatalytic process.

The decolorization rate of azo dyes will increase with a decrease in the pH [11].
The photooxidation activity was the maximum decolorization rate under pH=6 and it was found to decrease when pH>6, it undergoes decomposition generating dioxygen and water lead to the less formation of OH* [12].

In the photocatalyst, the catalyst has a control on the process, when it’s increased in the quantity of it will increase in the number of active sites, that successively will cause increase the concentration of hydroxyl radical and superoxide radicals.

Also when the catalyst amount will increase higher than the optimum value, the rate of decolorization decreases because of the interception of the light by the suspension [13]. There are several studies in batch advanced oxidation, while limited studies in continuous processes conducted to remove the dye using solar energy.

Huang et al. [14] studied the parameter of adding the amount of hydrogen peroxide to remove the methyl orange from solution. The removal efficiency was increased with increase in H₂O₂ concentration. Zhiyong et al. [15] studied the addition of hydrogen peroxide with titanium dioxide Degussa P25 (0.5g/l) catalyst (1mM) to remove methyl orange solution under sunlight irradiation. Senthil Kumar et al. [16] reported that the increase in the concentration of OH* will cause the reduction of the hydrogen peroxide [17].

Ali [18] studied the continuous photo-catalytic reactor using TiO₂/UV process to treat wastewater solution, it showed that the rate of degradation of organic pollutants decreased with increase in the flow rate and increased with increasing the number of the UV lamp. The aim of this study is to treat the wastewater effluent from the textile factory in the north of Baghdad from the azo brilliant reactive red K-2BP by a continuous advanced oxidation process using (H₂O₂/UV, H₂O₂/sunlight, H₂O₂/TiO₂/UV, and H₂O₂/TiO₂/sunlight) and compare the results.

2- Experimental

The chemicals used in this study were brilliant reactive red that is employed in textile as a waste. H₂O₂ (50% w/w) was obtained from Merck. TiO₂ (P-25, 80% anatase, 20% rutile with particle size 30±5 nm) was used. H₂SO₄ and NaOH were used to modify the pH of the solutions. The continuous reactor composed of 2 layers of a glass reactor (80 x 30 x 1) cm. The depth between them is 4 mm. The upper layer glass was 6 mm thickness and the lower layer is a reflective mirror.

The solution passes between the two layers. Two liters of effluent introduced to the unit at optimum conditions, pH= 3, dye concentration= 15 ppm, H₂O₂= 500 ppm, and TiO₂ =100 ppm. These optimum conditions were taken from a prestudy of batch experiments.

The tests were conducted throughout the months of May and June with the temperature stable up to 35±3 C°.

The radiation intensity was measured employing a device sort (the daystar meter) that reads 494-565 watt/m² at 9 am, 680-705 watt/m² at 10 am and 775-805 watt/m² at 12 pm.

The processes (H₂O₂/UV, H₂O₂/sunlight, H₂O₂/TiO₂/UV, and H₂O₂/TiO₂/sunlight) for decolorization of reactive red dye from simulated solution were used. The concentration of red dye is measured by UV-Spectrophotometer at 534nm maximum of absorption. Fig. 1 and Fig. 2 show the sketch and photograph of a continuous reactor. The removal efficiency (%) was calculated using equation 1:

\[
\text{Removal efficiency (\%) = } \left(\frac{C_i - C_f}{C_i}\right) \times 100
\]

Where,

- \(C_i\) = the initial concentration of contaminants (dyes) in the samples wastewater (mg/l).
- \(C_f\) = the concentration (mg/l) after treatment.

Fig. 1. Sketch of a continuous system. (1) container tank (dye solution), (2) water pump, (3) valve, (4) flow meter, (5) chamber containing the photooxidation reactor, (6) UV lamp, (7) baffle (8) container tank (produced water treated).

Fig. 2. Photograph of Continuous reactor
3- Kinetic Analysis

The wastewater treatment of the textile that contains a dye is a complicated method involving several reactions. Therefore, approximate kinetics can be assumed for the removal of the dye in the effluents. The most color removal curves obey to the several investigators that are first or second order kinetics. The major color removal curves lead to the first order kinetic model [19]. The rate of kinetic for the first order reaction can be calculated from equation 2:

$$-\frac{dC}{dt} = KC$$  \hspace{1cm} (2)

Where,

\[ \frac{dC}{dt} = \text{the rate of change of dye concentration with a change of reaction time.} \]

\[ k = \text{the rate constant min}^{-1} \]

\[ C = \text{the concentration of dye at time t.} \]

Then the integration of equation (2) between t = 0 and t = t gives;

$$\ln \frac{[C]}{[C_0]} = kt$$  \hspace{1cm} (3)

Where: 

\[ C_0 = \text{Initial dye concentration at time t = 0.} \]

\[ C = \text{Dye concentration at time t.} \]

\[ k = \text{First order rate constant min}^{-1}. \]

\[ t = \text{Reaction time in minutes.} \]

4- Energy Requirement

The advanced oxidation treatment is directly affected by operation cost. To compare of reaction efficiencies that used parameter known as EE/O (electrical energy required to remove a pollutant by one order in one m³ of water or wastewater). EE/O calculated the electrical efficiency of an advanced oxidation process and allows for the comparison of various AOP methods. It is very required not only for several of AOPs also for economic analysis and comparison with conventional treatment. EE/O values are shown in equation 4 [20] [21].

$$EE/O = \frac{P(KW) \times t(\text{min.}) \times 1000}{V(L) \times 60 \log (\frac{C_0}{C})}$$  \hspace{1cm} (4)

Where: 

\[ P = \text{the power input to the system such as UV-lamp, generator of ozone, magnetic stirrer and water pump in kW.} \]

\[ t = \text{the reaction time in min.} \]

\[ V = \text{the volume of the wastewater in L.} \]

\[ C_0 = \text{the initial concentration of pollutant water at t = 0.} \]

\[ C = \text{the final concentration of pollutant water after treatment.} \]

5- Results and Discussion

The decolorization rate of dye depends on the optimum H₂O₂ concentration to generate the hydroxyl radicals that destroy the organic polluted [22].

The catalyst is also affected by advanced oxidation processes [23]. In the presence of photocatalyst (TiO₂), H₂O₂ or only H₂O₂, the pH is an optimizing parameter at acidic that got accelerated the rate of decolorization. On the other hand, an increase in irradiation time led to greater decolorization rate [24].

According to previous studies, a pre-study was conducted to find the optimum conditions of H₂O₂ concentration, TiO₂ amount, pH and dye concentration and it was found that [H₂O₂] = 500ppm, [TiO₂] = 100ppm, pH = 3 and dye concentration = 15ppm. Fig. 3, Fig. 4, Fig. 5 and Fig. 6 show the results of a continuous process for the four processes (H₂O₂/UV, H₂O₂/sunlight, H₂O₂/TiO₂/UV, and H₂O₂/TiO₂/sunlight) respectively at the optimum conditions. The flow rate to the reactor was adjusted according to the detention time dt=V/Q (volume/flow rate) [25]. When the flow rate increases (10, 30 and 60) ml/min the detention time (min) will be (150, 50 and 25) respectively. At each detention time, the same volume of wastewater had been treated but with different removal efficiencies. The treated volume is 1500 ml. The removal efficiency for four processes was (84.65%, 80.47%, 77.51%, and 89.42%) at the flow rate 10ml/min and (68.26%, 65.19%, 56.89%, 70.22%) at 60ml/min respectively. Increasing the flow rate the UV lamp or sunlight will be submerged in shorter time, therefore, decreases the amount of provided power for H₂O₂ to generate more hydroxyl radical.
photocatalyst the addition of H₂O₂ ensures many formations of OH⁺ radicals that can be destroyed organic pollutants, the results showed that H₂O₂/TiO₂/sunlight is better than H₂O₂/TiO₂/UV because sunlight contains a wavelength around 380nm that catalyst TiO₂ can be absorption this agrees with [26].

In the four advanced oxidation experiments, the kinetics model of red dye is represented as first-order reaction kinetics.

Table 1. The first-order reaction kinetics model for different advanced oxidation processes

<table>
<thead>
<tr>
<th>Methods</th>
<th>K (min⁻¹)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O₂/UV</td>
<td>0.0053</td>
<td>0.9174</td>
</tr>
<tr>
<td>H₂O₂/sunlight</td>
<td>0.0041</td>
<td>0.8635</td>
</tr>
<tr>
<td>H₂O₂/TiO₂/UV</td>
<td>0.0053</td>
<td>0.9992</td>
</tr>
<tr>
<td>H₂O₂/TiO₂/sunlight</td>
<td>0.0080</td>
<td>0.9863</td>
</tr>
</tbody>
</table>

7- Calculation of Electrical Energy Requirements

The advanced oxidation processes are required to spend energy for operating the equipment. In this study consist of four processes (H₂O₂/sunlight, H₂O₂/UV, H₂O₂/TiO₂/UV, and H₂O₂/TiO₂/sunlight) which is used a variable source of power like UV lamp and water pump. EE/O is the electrical energy per order of water or polluted water removal.

In the other hand, it means a powerful parameter and a measure of the degradation rates obtained in a very constant volume of wastewater as a function of the applied specific energy [20] [27].

Table 2 shows the comparison of energy requirements by various methods for the decolorization rate of brilliant reactive red dye at different flow rate dye. The energy required can be calculated from Eq. 4.

The results are apparent that the H₂O₂/UV and H₂O₂/TiO₂/sunlight processes most effective option of energy required and decolorization of dye.

Energy consumption of the advanced oxidation treatment increase with an increased in initial dye concentrations, flow rate and also with an increase in the applied dose [27].

Table 2. Comparison of the energy required by the different processes for the decolorization rate of brilliant reactive red dye at a different flow rate

<table>
<thead>
<tr>
<th>Reaction Conditions</th>
<th>Dye Conc.=15ppm, H₂O₂=500ppm, TiO₂=100ppm and pH=3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10 (ml/min)</td>
</tr>
<tr>
<td>Flow Rate</td>
<td></td>
</tr>
<tr>
<td>Methods of AOPS</td>
<td>Decolorization rate %</td>
</tr>
<tr>
<td>H₂O₂/UV</td>
<td>84.65</td>
</tr>
<tr>
<td>H₂O₂/Sunlight</td>
<td>80.47</td>
</tr>
<tr>
<td>H₂O₂/TiO₂/UV</td>
<td>77.51</td>
</tr>
<tr>
<td>H₂O₂/TiO₂/Sunlight</td>
<td>89.42</td>
</tr>
</tbody>
</table>
8- Conclusions

Brilliant Reactive Red Dye can be removed in all of the advanced continuous methods of oxidation that is used in this study, at a flow rate range from (10-60) ml/min and reaction time ranging from (25 – 150) min. However, the increase in the flow rate led to a decrease in the decolorization rate. The higher decolorization was required longer reaction time to generate hydroxyl radical that can destroy the organic substance. The results show that the H2O2/UV and H2O2/TiO2/UV processes can be efficiently used for removal of textile wastewater because H2O2 absorb the light <245nm and (TiO2 absorb the light <365nm. The maximum decolorization rate of dye may be achieved at acidic media (pH =3), a moderate concentration of H2O2, 150 min of UV irradiation and low flow rate by 10ml/min. The results indicated that sunlight is a suitable energy supply used in the photooxidation to remove organic substance due to its low cost and free availability.

References

دراسة أفضل ظروف باستخدام مفاعل مستمر لعملية الأكسدة المتقدمة لإزالة الصبغة الحمراء التفاعلية

الخلاصة

تستخدم صبغةazo صبغة نفاذة ذات اللون الأحمر والطول الموجي 534 نانومتر على نطاق واسع لصبغة المنسوجات بسب فعاليتها من حيث التكلفة وخصائص ثابتة ممتازة. وكثيراً ما تكون معالجة مياه الصرف الصحي المحتوية على هذه الصبغة بالطرق التقليدية غير كافية بسبب مقاومتها للتدهور البيولوجي والكيميائي.

في هذه الدراسة تم استخدام مفاعل مستمر للعملية الأكسدة المتقدمة تقوم على استخدام (H₂O₂/sunlight, H₂O₂/UV, H₂O₂/TiO₂/sunlight, H₂O₂/TiO₂/UV) لإزالة الصبغة الحمراء. وتم أخذ أفضل الظروف من حيث الأس الهيدروجيني ، تركيز بيروكسيد الهيدروجين، تركيز ثاني أوكسجين التيتانيوم وتركيز الصبغة من تجارب المفاعلات الدفعة (Batch reactor). وكانت أفضل ظروف الأس الهيدروجيني = 3، تركيز بيروكسيد الهيدروجين = 3ملغ/مل وتركيز الصبغة = 15ملغ/مل. تحت أفضل الظروف تم إزالة اللون للمحلول الحاوي على الصبغة مع معدل تدفق مختلف (10، 30، 60 مل/ دقيقة). في معدل تدفق 10 مل/ دقيقة، وبلغت نسبة إزالة اللون (78.42 %، 89.42 %، 77.5 %، 56.8 %) للعمليات الألكاتوى وعلى التوالي.

(H₂O₂/TiO₂/sunlight, H₂O₂/TiO₂/UV)