Abstract: Textile industries produce a complex wastewater which is difficult to be treated. In this work, a catalytic degradation of wastewater effluent composed of sulphur black coloring agent discharged by industry was studied. UV lamp power, peroxide concentration, pH, and iron oxide catalyst were varied to determine the best conditions for oxidative treatment. Kinetic parameters were evaluated based on the reaction model proposed. In the absence of iron oxide catalyst, chemical oxygen demand (COD) and biological oxygen demand (BOD) degradation of up to 80% and 75%, respectively, were observed as resulting from using an H$_2$O$_2$ concentration of 0.61 moles/L, UV lamp power of 30 watts, and pH of 6. When using an iron oxide catalyst combined with UV light irradiation, the degradation rate could be increased significantly, while similar final COD and BOD degradation percentages resulted. It is found that the reaction rate order was shifted from first order to second order when using an H$_2$O$_2$/UV/Fe$_2$O$_3$ system. The results could be an alternative for treating textile industry wastewater, and the parameters obtained can be used for equipment scale-up.

Keywords: biochemical oxygen demand; chemical oxygen demand; Fenton reaction; wastewater effluent

1. Introduction

Textile industries produce wastewater which is considered dangerous for the environment. The combined waste from every process and stage can produce solutions with high chemical oxygen demand (COD), biological oxygen demand (BOD), thick color, and a total suspended solids (TSS) parameter which is alkaline [1]. It is reported that ~20% of dyes, which are the main component in wastewater effluent, are released to natural water environments [2–4]. Solutions with high COD and BOD can cause a rapid reduction in dissolved oxygen and are toxic to biological life if they are directly discharged into the environment. Furthermore, due to aesthetic concerns, the textile industry could face a serious challenge from the public to treat its dye effluent before releasing it to water bodies.

Traditional physical treatment can be used to treat wastewater effluent, with methods such as adsorption using activated carbon [5], ultrafiltration [6], ion exchange [7], and coagulation [8]. However, these treatments just transfer the pollutant to another phase, hence a further handling is needed. Destructive methods are an alternative approach, i.e., biological treatment using microorganisms and advanced oxidation processes (AOPs). Degradation by microorganism typically requires a large area and volume due to slow rates. Also, it is possible that dyes are adsorbed in the sludge, hence not degraded [9]. AOPs have the potential to be effective and efficient methods, since they can quickly destruct the contaminants, forming other acceptable constituents [10–12]. However, when the colorants are complexes, a modification of this process is necessary, like using photo assisted oxidation [13–15].
Fenton and photo-Fenton reactions have significant advantages compared to other advanced oxidation processes. Energy utilization is reduced due to the dark usage of cheap reagent hydrogen peroxide (H$_2$O$_2$) in a Fenton reaction. By adding iron, there will be more hydroxyl radical formation when H$_2$O$_2$ is mixed with wastewater following the reaction of Equation (1) [16].

$$Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+} + \cdot OH + H_2O$$

UV radiation can decompose H$_2$O$_2$ more efficiently and initiate photo-reduction of ferric to ferrous iron. Free solar radiation can be utilized to carry out the photochemical stages of the photo-Fenton reaction so that complete mineralization of organic compounds is possible in a short period of time [17]. The photo-Fenton reaction has been proven to be efficient in treating water contaminated with a variety of organic and biological pollutants and in organic synthesis [18].

In this work, a comprehensive study was performed to obtain the optimal conditions to treat a complex and real textile wastewater effluent based on sulphur black coloring agent using Fenton reaction assisted by UV light irradiation. UV lamp power, peroxide concentration, pH and iron oxide catalyst were adjusted and their effects on the degradation of sulphur black wastewater were studied. Because the photo-Fenton reaction is very complex, reaction models for the reaction rate prediction are based on empirical correlations. The reaction behaviors using only UV and combination of UV and iron oxide catalyst is presented. We demonstrate that with a good combination of different factors, it is possible to treat wastewater quickly and effectively.

2. Results and Discussion

2.1. Influence of UV Lamp Power on the DyeEffluent Degradation

UV lamp power is one of the factors that influences textile wastewater degradation. The lamp power was varied to 10, 20, and 30 watts. Figure 1 shows that with the usage of stronger UV lamp power, the degradation of textile wastewater will be greater, as can be seen from COD (Figure 1a) and BOD (Figure 1b) values. That is because the stronger the UV lamp power is, the faster the decomposition rate of H$_2$O$_2$ to OH radical will be. However, the increase of degradation seems not to be linear with increasing lamp power. There is only a slight change of degradation rates of COD and BOD with UV lamp powers of 10 and 20 watts. There is a deviation, that the BOD degradation rate at 30 min at 20 watts power was lower than the rate measured at 10 watts power. This is likely due to the limitations of measurement accuracy. When the UV lamp power was 30 watts, the degradation rates of COD and BOD were more powerful than those of 10 and 20 watts as shown by a strong decrease of COD and BOD values.

The influence of the research variable with the performance of oxidation reaction can be depicted from the reaction rate constant. The constant value of the reaction rate is the slope of the graph between −ln(1 − x) and reaction time. The relation between −ln(1 − x) and reaction time is shown in Figure 2a. The values of the constants used are summarized in Table 1. The higher the power of the UV lamp, the greater the value of the reaction rate constant. This can be seen from the UV lamp power of 30 watts, the reaction rate constant is 0.025 min$^{-1}$. UV radiation has photonic energy of sufficient strength to break the chemical bonds. Absorption of a photon provides the energy required to force electrons into higher energy states. Upon absorbing sufficient energy, electrons may be freed from an atom. Some of this released energy becomes heat, fluorescence, or activating light by chemicals that can lead to a reaction, which does not exist in lightless media.
Power of 30 watts can decompose and change hydrogen peroxide to hydroxyl radical optimally. This is a remarkable change of degradation that reached 78.91% in 60 min. Addition of higher concentrations in Table 1. The greater the UV lamp power, the faster the reaction rate. This is because the UV lamp energy prediction studied.

Energy power,

period photo

reaction complex seen when shown

Figure 3a,b depicts the correlation between radiation time and the degradation of COD and BOD. The correlation between lamp power with

\[
\text{BOD} = \frac{1}{10} \times \text{COD} + \text{BOD} \quad \text{and} \quad \text{BOD} = 2 \times \text{COD} + \text{BOD} + \text{BOD}
\]

Figure 2. (A) Correlation of \(-\ln(1 - x)\) and reaction time in UV lamp power variation. (B) Data fitted with a reaction model in the case of UV lamp power variation. Concentration of peroxide: 0.61 moles/L solution, pH 9.

Table 1. Kinetic parameters as a function of UV lamp power variation.

<table>
<thead>
<tr>
<th>UV Lamp Power, watt</th>
<th>(k', \text{ min}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.0070</td>
</tr>
<tr>
<td>20</td>
<td>0.0100</td>
</tr>
<tr>
<td>30</td>
<td>0.0250</td>
</tr>
</tbody>
</table>

The correlation between lamp power with \(k'\) value reviewed from COD degradation can be seen in Table 1. The greater the UV lamp power, the faster the reaction rate. This is because the UV lamp power of 30 watts can decompose and change hydrogen peroxide to hydroxyl radical optimally. This is marked by a 78.15% decrease of COD and a 70.45% decrease of BOD, with the \(k'\) value of 0.025 min\(^{-1}\).

2.2. Influence of Peroxide Concentration

Figure 3a,b depicts the correlation between radiation time and the degradation of COD and BOD. It is meant to find the optimum concentration of \(\text{H}_2\text{O}_2\) needed to degrade textile wastewater with the COD parameter. Without \(\text{H}_2\text{O}_2\), it is shown that there is no degradation because there is no hydroxyl radical formed without addition of hydrogen peroxide. But when \(\text{H}_2\text{O}_2\) is added with a concentration of 0.20 moles/L and 0.41 moles/L, there are some changes in the degradation, by about 19.97% and 46.85% in 60 min, respectively. When the concentration of \(\text{H}_2\text{O}_2\) added was increased to 0.61 moles/L, there was a remarkable change of degradation that reached 78.91% in 60 min. Addition of higher concentrations...
of H₂O₂ (0.82 moles/L and 1.02 moles/L) resulted in the degradation efficiency becoming less than before, (66.35% and 56.83%, respectively).

When the addition of H₂O₂ exceeded a concentration of 0.61 moles/L, it did not give more degradation efficiency. On the contrary, it resulted in lower efficiency, which made the degradation percentage lower too. This is because an excessive amount of *OH can react with H₂O₂ to produce *HO₂ which has a weaker ability to degrade organic compounds compared to hydroxyl radicals. Formation of *HO₂ reduces the amount of hydroxyl radical that is produced from photolysis reaction of H₂O₂ and UV light, where the *OH radical formed will react with H₂O₂ according to Equation (2) [14].

\[
*OH + H₂O₂ → *HO₂ + H₂O
\]

By the occurrence of this reaction, the hydroxyl radical produced is not proportional with the addition of H₂O₂ concentration. Therefore, it is understandable that the addition of higher H₂O₂ concentrations does not give a significant change of degradation percentage.

![Figure 3. (A) COD and (B) BOD degradation of textile wastewater with concentration of hydrogen peroxide variation.](image)

From Figure 4a, the reaction rate constant value increased with the increase of H₂O₂ concentration, which is because the amount of hydroxyl radical formed also increased as an oxidation agent. However, when the concentration of H₂O₂ exceeded 0.61 moles/L, the reaction rate constant decreased. As mentioned before, this is because an excessive amount of H₂O₂ concentration will form hydroperoxyl radicals (*HO₂) which are less reactive compared to hydroxyl radicals and result in a decrease of its reaction rate or its oxidation rate. The values of the reaction rate constant can be seen in Table 2 and with the reaction constraints, the data are well fitted with reaction model (Figure 4b). It can be concluded from the degradation of COD and BOD that the optimum reaction rate constant is 0.0250 min⁻¹.

**Table 2. Kinetic parameters of hydrogen peroxide concentration variation.**

<table>
<thead>
<tr>
<th>Hydrogen Peroxide Concentration, moles/L</th>
<th>(k', \text{ min}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.0010</td>
</tr>
<tr>
<td>0.2</td>
<td>0.0040</td>
</tr>
<tr>
<td>0.41</td>
<td>0.0120</td>
</tr>
<tr>
<td>0.61</td>
<td>0.0250</td>
</tr>
<tr>
<td>0.82</td>
<td>0.0160</td>
</tr>
<tr>
<td>1.02</td>
<td>0.0130</td>
</tr>
</tbody>
</table>
2.3. Influence of pH

To examine the effect of pH, reaction experiments were carried out in different pH levels but at a fixed concentration of H$_2$O$_2$ (0.61 moles/L) and lamp power (30 watts). Figure 5a shows degradation of COD over the reaction time. The results display that acidic pH is more favorable for dye degradation. As described in the literature [19], at higher pH (more OH$^-$) it is possible that hydroxyl reacts with peroxide to produce water and oxygen, hence finally, it will reduce the production of hydroxyl radicals. The reaction rate constant was evaluated based on the experimental data (see Figure 5b). In the acidic and basic regions, the values of $k'$ were ~0.0250 min$^{-1}$ and ~0.020 min$^{-1}$, respectively.

2.4. Influence of Iron Oxide Catalyst

Finally, the oxide catalyst was added to the reaction system to further promote the degradation of wastewater. The UV lamp power, H$_2$O$_2$ concentration, and pH were set to the optimal values of 30 watts, 0.61 moles/L and pH 6, respectively. As shown in Figure 6a,b the addition of Fe$_2$O$_3$ made the degradation of textile wastewater faster. The greater the concentration of Fe$_2$O$_3$ added, the greater was the degradation of COD and BOD. This is because Fe$_2$O$_3$ is functioning as a catalyst which able to decompose H$_2$O$_2$ to hydroxyl radicals, and it can further react with the organic compounds in the textile wastewater [20]. According to Koprivana and Kusic, the minimal concentration of
Fe$^{2+}$ or Fe$^{3+}$ required for the Fenton reaction is in the range 3–15 mg/L (0.05–0.3 mM) [21]. Hence, the concentration of catalyst in this work is enough to decompose pollutant in wastewater.

![Graph 6](image)

**Figure 6.** (A) COD and (B) BOD degradation of textile wastewater with concentration of iron (III) oxide catalyst variation. Conditions: pH 6, 0.61 moles/L concentration of H$_2$O$_2$, and 30-watt lamp power.

From the data observed, it is likely that, the reaction order changes with the addition of Fe$_2$O$_3$ catalyst. The data were fitted with reaction order one (Figure 7a) and order two (Figure 7b). It can be seen that the order two reaction is more precise to be used in this catalytic reaction. The change of the reaction order also showed that the reaction speed was increased by adding Fe$_2$O$_3$ catalyst to decompose H$_2$O$_2$ to hydroxyl radicals. The comparison of the values of the reaction rate constants between order one and order two can be seen in Table 3.

![Graph 7](image)

**Figure 7.** Fitting conversion data with reaction model order one (A) and order two (B). Conditions: pH 6, 0.61 moles/L concentration of H$_2$O$_2$, and 30-watt lamp power.

<table>
<thead>
<tr>
<th>Iron (III) Oxide Concentration, moles/L</th>
<th>First Order $k'$, min$^{-1}$</th>
<th>Second Order $k'$, L.(mg.min)$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>6 × 10$^{-4}$</td>
<td>0.0254</td>
<td>1.12 × 10$^{-5}$</td>
</tr>
<tr>
<td>1 × 10$^{-3}$</td>
<td>0.0255</td>
<td>9.71 × 10$^{-6}$</td>
</tr>
<tr>
<td>2 × 10$^{-3}$</td>
<td>0.0410</td>
<td>1.28 × 10$^{-5}$</td>
</tr>
</tbody>
</table>
3. Materials and Methods

3.1. Wastewater-Effluent Characteristics

Wastewater was obtained from textile industry located in Bandung, Indonesia. The sulphuric coloring agent was the main component. Before given treatment, the initial conditions of the waste were measured including COD, BOD, color, and pH parameters. The parameter measurement results can be seen in Table 4.

Table 4. Initial characteristics of sulphuric coloring agent of the textile industry.

<table>
<thead>
<tr>
<th>No.</th>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Color (TCU)</td>
<td>47,000</td>
</tr>
<tr>
<td>2</td>
<td>COD (mg/L)</td>
<td>9906</td>
</tr>
<tr>
<td>3</td>
<td>BOD₅ (mg/L)</td>
<td>3175</td>
</tr>
<tr>
<td>4</td>
<td>pH</td>
<td>9</td>
</tr>
</tbody>
</table>

3.2. Fenton Reactions

Up to 1000 mL of wastewater was placed in the reactor (shown in Figure 8) and then peroxide was added. The reaction was started when the UV lamp (254 nm) and stirrer were turned on. Samples were taken (as much as 50 mL) with radiation time 0, 10, 20, 30, 40, 50, and 60 min to analyze the COD and BOD. The experimental set-up and reaction conditions were based on reports of [22,23]. Variations of conditions were performed to evaluate the effects of reaction condition to degradation of dyes as follows.

(i) Hydrogen peroxide (H₂O₂) concentration variation: concentrations of hydrogen peroxide were set to 0.20; 0.41; 0.61; 0.82; and 1.02 moles/L while UV lamp was set to 30 watts;
(ii) Variation of UV lamp power: the UV lamp power was set to 10, 20, and 30 watts while peroxide concentration employed was 0.61 moles/L;
(iii) Variation of pH: pH was changed in the range of 5–9, while peroxide concentration employed was 0.61 moles/L and UV lamp power was 30 watts. pH was measured using a pH meter (Hanna Instruments, USA);
(iv) The effect of the reaction with Fe₂O₃ catalyst (phase: α-Fe₂O₃, particle size <5 µm, pro-analysis, from Merck, Germany): pH, peroxide concentration, and UV lamp power were set to 6, 0.61 moles/L, and 30 watts, respectively. Iron (III) oxide was added at the concentrations of 0.00063 moles/L, 0.00126 moles/L, and 0.00190 moles/L.

![Figure 8](attachment:image.png)
3.3. Sample Analyses

3.3.1. Determination of COD Values

The H$_2$SO$_4$ pro-COD was prepared by dissolving 1 g of AgSO$_4$ with 100 mL of H$_2$SO$_4$ 98%. Ferrous ammonium sulfate (FAS) 0.1 N was made by solving 39 g of (NH$_4$)$_2$SO$_4$.6H$_2$O with 20 mL of H$_2$SO$_4$ 98% and then distilled water was added until the volume was 1 L. The ferroin indicator was prepared by dissolving 1.485 g of phenanthroline monohydrate and 0.695 g FeSO$_4$.7H$_2$O with distilled water until the volume was 100 mL. Two screw cap tubes were provided, one was filled with 2 mL of distilled water and the other was filled with the sample. After adding 40 mg of HgSO$_4$, 3 mL of H$_2$SO$_4$ pro COD, and 1 mL of K$_2$Cr$_2$O$_7$ 0.25 N to the sample, it was then heated in the COD reactor for 2 h. After that, the sample was cooled down until room temperature, moved to a 100 mL Erlenmeyer flask, and three drops of ferroin indicator were added. The sample was titrated with FAS 0.1 N until an equivalent point or until the color changed to reddish brown. The volume of FAS needed was recorded.

The COD value was calculated by Equations (3) and (4).

\[
Normality = \frac{mL_{K_2Cr_2O_7} \times 0.1N}{mL_{FAS \, needed}} \tag{3}
\]
\[
COD = \frac{(V_{\text{blank titration}} - V_{\text{sample titration}}) \times (N_{FAS}) \times (8000) \times \text{(Dilution Factor)}}{2} \tag{4}
\]

3.3.2. Determination of BOD Values

As much as 25 mL of sample which had been incubated with Sanyo MIR-153 incubator was tested to get the initial BOD values and the pH was measured (about 6.5–7.5). If the pH was higher or lower, neutralization was performed. The temperature was set to be about 20 ± 1 °C, after the temperature was reached, as much as 40 mL of samples were put into BOD bottles with a magnetic stirrer and added with 100 mL of distilled water. Then the bottle was placed in the BOD unit, a seal was installed that had been given two drops of KOH 40%, and a cap was used to close the bottle. The BOD unit was connected to an electric current, and the motor was turned on. The screw cap of the pressure meter and the cap of the sample bottle were loosened up until about 30 min to get the temperature to 20 °C. After the temperature was reached, the screw cap of the temperature meter and the sample bottle’s cap were fastened. The mercury column was adjusted at zero points and the measurement time was started. The BOD values were determined on day five and entered in the datasheet.

The BOD was calculated by Equation (5).

\[
BOD_b = BOD_a \times n \tag{5}
\]

- $BOD_a$ = readable value, mg/L
- $BOD_b$ = actual BOD, mg/L
- $n$ = dilution factor.

3.4. Kinetic Models

The oxidation reaction with hydrogen peroxide was performed through three steps: (i) degradation reaction of hydrogen peroxide to hydroxyl free radicals with UV ray; (ii) reaction between COD and hydroxyl free radical; and (iii) degradation of COD* to other molecules as described in Equations (6)–(8) [11].

\[
H_2O_2 \overset{UV}{\rightarrow} ^\cdot OH \tag{6}
\]
\[
^\cdot OH + COD \rightarrow COD^* + H_2O \tag{7}
\]
The degradation reaction of hydrogen peroxide with UV ray is fast, so the determining reaction is the reaction between COD with hydroxyl radicals (Equation (7)). The reaction between COD and *OH is a one-way reaction. The reaction model is shown in Equation (9).

\[
(-r_{\text{COD}}) = k(C_{\text{COD}})^\alpha (C_{\text{OH}})^\beta
\]  

(9)

With:

\(-r_{\text{COD}}\) = Oxidation of COD reaction rate, (mg/L.minute)

\(K\) = Reaction rate constant, mg/(L.minute)/(mg/L)^{\alpha+\beta}

\(C_{\text{COD}}\) = COD concentration, (mg/L)

\(C_{\text{OH}}\) = Hydroxy radical concentration, (mg/L)

\(\alpha\) = COD concentration order reaction

\(\beta\) = Hydroxy ion concentration order reaction

By making excessive hydroxyl radicals relatively unchanged during the reaction, Equation (9) becomes Equation (10).

\[
(-r_{\text{COD}}) = k'(C_{\text{COD}})^\alpha
\]  

(10)

where \(k'\) is defined as Equation (11).

\[
k' = k(C_{\text{OH}})^\beta \approx k(C_{\text{OH}_0})^\beta
\]  

(11)

For order one reaction, or \(\alpha = 1\), Equation (10) becomes Equation (12).

\[
(-r_{\text{COD}}) = k(r(C_{\text{COD}})
\]  

(12)

where, \(-r_{\text{COD}}\) = Oxidation of COD reaction rate, (mg/L.minute);

\(k'\) = Reaction rate constant with \(C_{\text{OH}}\) relatively constant, (min\(^{-1}\));

\(C_{\text{COD}}\) = COD concentration, (mg/L).

Using mass balance and integration, we obtain Equation (13):

\[
-ln\left(\frac{C_{\text{COD}}}{C_{\text{COD}0}}\right) = k't
\]  

(13)

By defining conversion, \(x\), as Equation (14):

\[
x = \frac{C_{\text{COD}0} - C_{\text{COD}}}{C_{\text{COD}0}},
\]  

(14)

Equation (14) is inserted to Equation (13), hence:

\[
-ln(1-x) = k't
\]  

(15)

For order one reaction or \(\alpha = 2\), Equation (10) becomes Equation (16):

\[
(-r_{\text{COD}}) = k(r(C_{\text{COD}})^2
\]  

(16)

Using mass balance and integration, Equation (16) becomes Equation (17):

\[
C_{\text{COD}} = \frac{C_{\text{COD}0}}{1 + k'tC_{\text{COD}0}}
\]  

(17)

where, \(t\) = oxidation time, (minute) and \(k'\) = kinetics constant, (L.mg\(^{-1}\).min\(^{-1}\)).
4. Conclusions

An oxidative method assisted by UV light irradiation was carried out to treat textile wastewater based sulphur coloring agent. It was found that the optimal conditions without iron oxide addition were an H₂O₂ concentration of 0.61 moles/L, UV lamp power of 30 watts, and pH 6; from which COD and BOD degradations of up to 80% and 75% (respectively) resulted. In this condition, the reaction rate followed a first order reaction with k’ of 0.0250 min⁻¹. The addition of Fe₂O₃ could increase degradation rate significantly, while similar COD and BOD degradation percentages were obtained. When Fe₂O₃ was present, the reaction followed a second order reaction model.


Funding: The APC was funded by Publisher and Publication Board of Universitas Gadjah Mada.

Acknowledgments: In this section you can acknowledge any support given which is not covered by the author contribution or funding sections. This may include administrative and technical support, or donations in kind (e.g., materials used for experiments).

Conflicts of Interest: The authors declare no conflict of interest.

References
15. Wang, Q.; Pang, W.; Mao, Y.; Sun, Q.; Zhang, P.; Ke, Q.; Yu, H.; Dai, C.; Zhao, M. Study of the degradation of trimethoprim using photo-Fenton oxidation technology. *Water (Switzerland)* **2019**, *11*, 207. [CrossRef]


© 2019 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).