Comparative study of Fe\(^{2+}\)/H\(_2\)O\(_2\)/CuO/Vis and Fe\(^{2+}\)/H\(_2\)O\(_2\)/CuO for phenol removal in batik wastewater under visible light irradiation

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Abstract. Phenols contained in batik wastewater are harmful organic compounds. These compounds must go through proper treatment before being discharged into the environment. Therefore, phenol needs to be degraded before discharged into the environment. Fenton reagent which is made of hydrogen peroxide (H\(_2\)O\(_2\)) and Fe\(^{2+}\) ion can form hydroxyl radicals (•OH). This radical can degrade a compound through an oxidation process. CuO is a semiconductor photocatalyst with a narrow bandgap that can be activated under visible light irradiation. The purpose of this study was to determine the effect of visible light on the decomposition process of phenol in batik wastewater. The research was conducted by varying the concentration of H\(_2\)O\(_2\), FeSO\(_4\) and CuO weight, and pH of the solution. The result showed that visible light can accelerate and increase the formation of hydroxyl radicals so the phenol compound was optimally degraded. The decrease of phenol content in batik wastewater using Fe\(^{2+}\)/H\(_2\)O\(_2\)/CuO/Vis with the addition of H\(_2\)O\(_2\) 100 ppm, FeSO\(_4\) 1.0 g, CuO 1.0 g, a pH of 3, and irradiated with visible light for 5 hours resulted in the decrease of phenol content was 86.77%.

1. Introduction

Phenol is a dangerous organic compound contained in wax used during batik production. During batik production, there are soaking and rinsing steps that produce wastewater containing phenol [1]. If the wastewater containing phenol is immediately discharged into the environment, the aquatic environment will be polluted because of its toxicity. Due to its toxicity and persistence in the environment, phenol is considered as priority pollutants and included in the dangerous substances list of the US Environmental Protection Agency [2]. Discharging phenol containing wastewater without treatment may lead to serious health risks, therefore strict discharge limits for phenols for a sustainable environment was set [2]. The water purity standard set by US EPA was less than 1 ppb for phenol in surface water [3] with phenol toxicity levels of 9-25 ppm [4]. Moreover, the UAE government standards limit for phenol is 0.1 ppm [5]. Therefore, phenol-containing wastewater needs to be treated before discharge into the environment.

There are a lot of methods to treat phenol-containing wastewater, such as using metal oxide [5], electro-deposition method [6], and the Advanced Oxidation Processes (AOPs) method [1,7]. AOPs method is one of the most frequently used methods due to its harmless and eco-friendly characteristics, as well as gives carbon dioxide and water as the final results. AOPs were a system based on the powerful oxidative nature of •OH. The production of •OH radicals is initiated by reacting H\(_2\)O\(_2\) with a
ferrous ion (Fe$^{2+}$). This process is well known as Fenton reagent [7]. However, the combination of H$_2$O$_2$, ferrous ion, and visible light irradiation produces more hydroxyl radicals compared to the conventional Fenton method or photolysis and in turn, increases the rate of degradation of organic pollutants [8]. The mechanism of AOPs methods using Fenton Reagent was shown in Eq. 1 to 5 [8]:

$$\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \cdot\text{OH} + \text{OH}^- \quad (1)$$

$$\text{RH-X} + \cdot\text{OH} \rightarrow \text{oxidation product (CO}_2 + \text{H}_2\text{O}) + X^- \quad (2)$$

$$\text{H}_2\text{O}_2 \rightarrow 2 \cdot\text{OH} \quad (3)$$

$$\text{Fe(OH)}^{2+} + h\nu \rightarrow \text{Fe}^{2+} + \cdot\text{OH} \quad (4)$$

$$\text{Fe}^{2+} + \text{H}_2\text{O}_2 + h\nu \rightarrow \text{Fe}^{3+} + 2\cdot\text{OH} + \text{H}^+ \quad (5)$$

(RH-X= organic compound)

Copper (II) oxide (CuO) is an attractive photocatalyst because of its stability, easily obtained, and good absorption in the visible light spectrum. It is a p-type semiconductor with a narrow bandgap (E$_g$=1.2-2.0 eV) [1]. The mechanism of photodegradation is the electron jump to the conduction band left the holes that can interact with solvents (water) to form •OH. Hydroxyl radicals were active and stimulate decomposition processes [9,10]. Previously, Fenton/CuO photocatalyst has not been reported and used for photodegradation of the phenol contained batik wastewater before, hence the degradation of phenol containing batik wastewater using Fenton/CuO/Vis will be delivered in this research.

2. Methods

2.1. Effect of H$_2$O$_2$ Concentration
Batik wastewater sample was added with H$_2$O$_2$ solution with a variety of concentrations of 20, 40, 60, 80, 100, 120, 140, and 160 ppm. It was then stirred in a reactor for 8 hours. A total of 10 ml of the mixture was used to determine phenol contain using 4-amino antipyrine methods. The absorbance was measured using a UV-Vis spectrophotometer at a maximum wavelength of 506 nm. Determination of the percentage of phenol degradation was calculated using Eq. 6.

$$\%\text{Degradation} = \frac{C_f-C_i}{C_i} \times 100\% \quad (6)$$

where $C_i$ and $C_f$ were phenol concentrations before and after degradation processes, respectively.

2.2. Effect of FeSO$_4$$\cdot$7H$_2$O Weight
Batik wastewater sample was added with FeSO$_4$$\cdot$7H$_2$O powder with a variety of weights 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, and 1.6 g. It was then stirred in a reactor for 8 hours. A total of 10 ml of the mixture was used to determine phenol contain using 4-amino antipyrine methods. The absorbance was measured using a UV-Vis spectrophotometer at 506 nm.

2.3. Effect of Irradiation Time of the H$_2$O$_2$/FeSO$_4$ System
Batik wastewater sample was added with H$_2$O$_2$ solution and FeSO$_4$$\cdot$7H$_2$O powder at optimum concentration and weight. It was then stirred in a reactor for 8 hours. Every 1 hour, 10 ml of samples were taken to determine phenol contain using 4-amino antipyrine methods. The absorbance was measured using a UV-Vis spectrophotometer at 506 nm.

2.4. Effect of CuO Weight on Phenol Degradation
Batik wastewater sample was added with CuO powder with a variety of weights 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 1.0, and 1.5 g. It was then stirred in a reactor for 8 hours. A total of 10 ml of the mixture was used to determine phenol contain using 4-amino antipyrine methods. The absorbance of phenol content was measured using a UV-Vis spectrophotometer at 506 nm.
2.5. Effect of pH on Fenton/CuO and Fenton/CuO/Vis on Phenol Degradation
Batik wastewater sample was added with H$_2$O$_2$/FeSO$_4$·7H$_2$O/CuO at optimum concentration and weight. Subsequently, added H$_2$SO$_4$ and or NaOH, then stirred to obtain a solution with variations in pH of 3, 5, 7, 9, and 11. The mixture was irradiated under visible light during the optimum time. The concentration of phenol was determined and measured using a UV-Vis spectrophotometer at 506 nm.

3. Results and Discussion

3.1. Effect of H$_2$O$_2$ Concentration
The decrease in phenol concentration with and without the light irradiation was observed by varying the concentration of H$_2$O$_2$. The H$_2$O$_2$ system without a light was performed in a dim reactor. The effect of H$_2$O$_2$ and H$_2$O$_2$/Vis was shown in Fig. 1 (a). The optimum concentration of H$_2$O$_2$ is 100 ppm with the degradation ability for H$_2$O$_2$ and H$_2$O$_2$/Vis systems were 40.77% and 65.88%, respectively. Phenol content reduction with H$_2$O$_2$/Vis system is higher than ones. The reason is H$_2$O$_2$ in the H$_2$O$_2$/Vis system absorbs the energy from visible light which results in •OH radical and subsequently degrades phenol to CO$_2$ and H$_2$O molecules [7,12]. It indicated that the greater concentration of H$_2$O$_2$, the photogenerated •OH also increase, and lead to the decrease of the phenol content [8]. As shown in Fig. 1 (a), after the optimum concentration obtained, the low-percentage of phenol reduction was observed owing to the number of resulted in •OH radicals were much lower [8]. The more addition of the H$_2$O$_2$ concentration can react with •OH radical to form a hydroperoxyl (HO$_2$•) compound which is having lower oxidative properties than •OH [7]. The formation of HO$_2$• following the reaction in Eq. 7 and 8.

\[
\begin{align*}
\text{H}_2\text{O}_2 + \bullet \text{OH} & \rightarrow \text{HO}_2\bullet + \text{H}_2\text{O} \\
\text{HO}_2\bullet + \bullet \text{OH} & \rightarrow \text{H}_2\text{O} + \text{O}_2
\end{align*}
\]

3.2. Effect of FeSO$_4$ Weight Variation
As shown in Fig. 1 (b), the optimum weight of FeSO$_4$ was 1.0 g with phenol reduction for Fenton/Vis and Fenton systems were 82.95% and 62.46%, respectively. This suggested that with a higher weight addition of FeSO$_4$, the •OH production also enhances, and it stimulates the phenol content to decrease [8]. When the optimum weight is obtained (at 1.0 g of FeSO$_4$), the percentage of phenol reduction is slightly decreased because of the reduction of •OH formation. The Fe(II) ions can react with H$_2$O$_2$ and generate •OH and Fe(III) ions, then cycles were continued [7]. Besides, the photolysis mechanism of H$_2$O$_2$ compound which forms •OH may be also reserved for degrading phenol contains in batik.
wastewater. However, the higher Fe ions from FeSO$_4$ dissolution could generate the iron complex in the mixture. Therefore, due to the existence of the iron complex, which has strong radiation absorbing properties, the phenol degradation may only happen in the lower FeSO$_4$ weight addition [8].

3.3. Effect of Irradiation Time of the H$_2$O$_2$/FeSO$_4$ (Fenton) System on Phenol Degradation

The effect of irradiation time is shown in Fig. 2 (a). It clearly shows that the longer irradiation time, the higher phenol degradation could be achieved. Nonetheless, after the optimum time was reached at 5 h, the phenol degradation profiles were merely the same. The plenty of •OH radicals could stimulate the phenol degradation reaction so that the phenol content can be eliminated significantly over the long irradiation time. Nevertheless, during the phenol degradation process, another reaction could also occur in competition with other pollutants that exist in batik wastewater and form another complex [7,10]. Therefore, irradiation time more than 5 h closely showed similar trends. This concluded that the optimum time for degrading phenol is 5 h with a percentage of 84.76%.

![Figure 2](image.png)

**Figure 2.** Effect of visible light irradiation time (a) and CuO weight variation in the phenol degradation (b)

3.4. Effect of CuO Weight

Fig. 2 (b) shows the phenol content reduction by applying the CuO and CuO/Vis systems, respectively. According to Fig. 2 (b), the optimum weight for phenol degradation can be observed in the sample with 1.0 g of CuO powder. The percentage of CuO/Vis and CuO (without the light) systems were 31.53% and 8.03%, respectively. The higher the weight addition of CuO, the more hole (h$^+$) will be generated, and it stimulated the phenol content degradation to be high [1]. When the optimum weight is obtained, the percentage of phenol degradation is decreasing obviously. The more CuO could cause the mixture saturation. Besides, it will also cause the light scattering of the incident light while CuO powder was added exceeding the optimum weight [9]. Hence, the phenol degradation efficiency was significantly reduced. Semiconductor which has bandgap energy higher than 3.0 eV requires higher radiation, but under visible light, at least the bandgap energy should be or lower than 2.0 eV [9,12]. CuO semiconductor has narrow bandgap energy (E$_g$ = 1.2-2.0 eV) thus it can be activated by visible light [1]. Under the visible light irradiation, Wijaya and his co-authors stated that the •OH and •O$_2^-$ were further used in the phenol degradation following the reactions in Eq. 8-13 [12].

\[
\text{CuO} + \text{hv} \rightarrow \text{CuO} (e_{cb}^- + h_{vb}^+) \quad (8)
\]

\[
\text{CuO} (h_{vb}^+) + \text{H}_2\text{O} \rightarrow \text{CuO} + \text{H}^+ + \text{•OH} \quad (9)
\]
CuO (h\textsubscript{vb}+) + OH\textsuperscript{-} → CuO + •OH \hspace{1cm} (10)
CuO (e\textsubscript{cb} -) + O\textsubscript{2} → CuO + •O\textsubscript{2-} \hspace{1cm} (11)
•O\textsubscript{2-} + H\textsuperscript{+} → •HO\textsubscript{2} \hspace{1cm} (12)
phenol + (h+, •O\textsubscript{2-}, •OH) → CO\textsubscript{2} + H\textsubscript{2}O \hspace{1cm} (13)

3.5. Effect of pH on Phenol Degradation
The last step in this study was to determine the optimum pH condition using Fenton/CuO in a dim reactor and Fenton/CuO/Vis. The optimum pH condition is 3, as shown in Fig. 3. In the Fenton process, a report by Zhang et al (2019) explains that the organic pollutant of phenol was affected by the pH condition of wastewater [13]. Besides, at the low pH of phenol wastewater, the effect of OH\textsuperscript{-} trap by H\textsuperscript{+} tends to increase, therefore, the oxidation capacity of the Fenton process will be reduced significantly. Contrarily, Fe(III) ions were hydrolyzed and precipitated at a high condition of pH. Here, the catalytic capacity of Fe(III) was lower, as shown in Fig. 3. Based on the results, the optimum condition of phenol degradation was at a pH of 3 by 86.77%. This result was strictly similar to previous research [13]. Moreover, it stated that the optimum pH for organic pollutant degradation of phenol is ranging from 2 up to 4.

Figure 3. Effect of pH in the phenol degradation

4. Conclusion
Under visible light, the Fenton/H\textsubscript{2}O\textsubscript{2}/CuO system showed higher catalytic activity than in the dark condition. However, the Fenton/H\textsubscript{2}O\textsubscript{2}/CuO/Vis system exhibited an optimum condition at H\textsubscript{2}O\textsubscript{2} concentration of 100 ppm, FeSO\textsubscript{4} and CuO additions were 1.0 g, and pH of 3 with the percentage of phenol degradation of 86.77%. Hence, the visible light has an important role in enhancing significantly the phenol degradation of batik wastewater.

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