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Characterization and Treatment Pharmaceutical Wastewater by Photo-Fenton Process

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ABSTRACT

The characteristics of the PT X pharmaceutical wastewater influent were a pH of 7.18, a COD of 384 mg/L, and a red-brown color. The Chemical Oxygen Demand (COD) has not met the quality standards based on the Ministry of Environment and Forestry Regulation No. 5 of 2014. The red-brown color was caused by wastewater containing rifampicin as a component of the tuberculosis drug. The objectives of this study were treating the real pharmaceutical wastewater to reduce COD and color by varying the molar ratio of the Fenton reagents and to identify the influence of the neutralization process. The Fenton reagents were $FeSO_4.7H_2O$ and H_2O_2 with a molar ratio of 1:1.5, 1:2, and 1:3. The process was conducted with the help of UV light and acidic conditions. The photo-Fenton process produced residues, which can be neutralized by using 0.1 NaOH solution and coagulated by using NaCl. The neutralization process successfully decreases the amount of Fe, H_2O_2, and COD on liquid. The results showed that the best molar ratio is 1:2, which can be seen from the removal efficiency of organic compounds of 89.58%, and the color decrease is seen from the decrease in absorbance value.

Keywords: wastewater, photo-Fenton, UV light, COD, color

1. INTRODUCTION

Water bodies are frequently contaminated by nonbiodegradable organic compounds and toxic components from industrial wastewater. One of the contributors is the pharmaceutical industry. PT X has influent wastewater that does not meet the quality standard. The characteristics of its wastewater were a pH of 7.18, a COD of 384 mg/L, and a red-brown color. According to the Ministry of Environment and Forestry Regulation No. 5 of 2014, the quality standards of pharmaceutical wastewater are pH of 6-9, COD value of 150 mg/L, and clear physical color [1].

The cause of red-brown color comes from the content of rifampicin, which is used as a tuberculosis drug [2]. Rifampicin is a crystalline powder that is red-brown and optimally soluble at acidic conditions [3]. To purify the color and reduce organic compound of wastewater, the photo-Fenton process was used, breaking down organic compounds using hydroxyl radicals ($OH^{\bullet}$). Hydroxyl radicals are obtained from the reaction of Fenton reagents in the form of $FeSO_4.7H_2O$ and H_2O_2, as shown in equations 1 and 2.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\bullet} + OH^{-} \quad (1)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + OH^{\bullet} + OH^{-} \quad (2)$$

The photo-Fenton is an enhancement of the Fenton reaction that uses near UV to visible light to enhance hydroxyl radicals generation and quickly convert Fe^{3+} back to Fe^{2+}. The reaction can be seen in equation 3-5 [4]. This conversion of Fe^{3+} back to Fe^{2+} results in a lower amount of Fe required for the photo-Fenton than the Fenton process.

$$H_2O_2 + \text{light} \rightarrow 2\ OH^{\bullet} \quad (3)$$

$$Fe^{3+}(OH^{-}) + \text{light} \rightarrow Fe^{2+} + OH^{-} \quad (4)$$

$$H_2O_2 + Fe^{3+} + \text{light} \rightarrow Fe^{2+} + OH^{\bullet} + H^{+} \quad (5)$$

The photo-Fenton proces has been used by several researchers to treat wastewater for the pharmaceutical sector. Natividad et al.[5] have treated effluent of wastewater treatment containing paracetamol and obtained degradation of organic compounds close to 100% at acidic pH

(2.7). Ozturk et al. [6] have treated real wastewater containing Diclofenac. The study results showed that the optimum conditions of pH 2.87, 4.38 gram H_2O_2/L, and 0.297 gram $FeSO_4$/L, respectively. Bambague et al. [7] treated real wastewater containing twenty-two pharmaceutical compounds, resulting in removal efficiencies between 24.2 and 56%.

This study conducted an experiment to treat real wastewater containing rifampicin using the photo-Fenton process. The purposes of this study were to reduce COD and color by varying the molar ratio of the Fenton reagents and to identify the influence of the neutralization process.

2. MATERIALS AND METHODS

2.1 Materials

The materials used in the study were influent wastewater of PT X, H_2O_2, $FeSO_4.7H_2O$, H_2SO_4, NaCl, NaOH, HNO_3, HCl, and KSCN. All materials were pro analysis and purchased from Merck company.

2.2 Experimental procedure

2.2.1 Preparation for Fenton Reagent

Fenton reagents consist of $FeSO_4.7H_2O$ and H_2O_2. Five hundred milligrams of $FeSO_4.7H_2O$ were mixed with a 35% H_2O_2 solution. The amount of H_2O_2 solution varied with the molar ratio $FeSO_4.7H_2O$ to H_2O_2 of 1:1.5, 1:2, and 1:3.

2.2.2 Photo-Fenton Process

The photo-Fenton process involved reacting the Fenton reagents with wastewater. In the first process, the wastewater's pH was adjusted to 3, and then Fenton reagents were added. The mixture was placed in a UV light cabinet and stirred for 240 minutes. After that, the liquid was analyzed to identify the COD and color parameters.

2.2.3 Neutralization Process

The neutralization process aimed to reduce the residue that was left over after the photo-Fenton process. The sample was adjusted to neutral by adding 0.1 M NaOH solution (first phase) and then one gram of NaCl to coagulate the residue (second phase). The neutralization process was carried out for 120 minutes. After the neutralization process, the treated wastewater was analyzed to identify the decrease in COD, color, Fe residue, and H_2O_2 residue.

2.3 Methods of analysis

2.3.1 COD Analysis

The COD value of initial and treated wastewater was analyzed. A sample of 2.5 ml was placed into a Hach tube and 1.5 ml of dichromate reagent and 3.5 ml of sulfate reagent were added. Then, the mixture was heated by using a Hach digester for 2 hours at 150 °C. After that, the mixture was added with ferroin indicator and titrated with 0.1 N FAS until the mixture changes color to reddish-brown.

2.3.2 Color Analysis

The color of treated wastewater was analyzed using the spectrophotometry UV-VIS method. The first step was to determine the optimum wavelength. Furthermore, the absorbance of sample was measured by measuring at the maximum wavelength.

2.3.3 Fe Analysis

The Fe content of treated wastewater was analyzed by spectrophotometry UV-VIS method referring to the procedure of Suryani et al. [8]. The calibration curve was made by plotting the absorbance value versus the concentration of a standard solution (0.2, 0.5, 1, 1.5, 2, 2.5, 3, 4, 6, and 10 mg /L). The standard solution was diluted 100 ppm Fe solution with 0.05 M HNO_3 solution. Then, 5 ml standard solution was mixed with 2 ml of 4 M HCl solution and 5 ml of 2 M KSCN solution and left to sit for 15 minutes. Fe concentration was determined by measuring absorbance and then the value was plotted on callibration curve.

2.3.4 H_2O_2 Analysis

The H_2O_2 content of treated wastewater was analyzed by the metavanadate method, referring to Nogueria et al. [9]. H_2O_2 concentration was determined by measuring absorbance at a wavelength of 450 nm and then the value was plotted on callibration curve.

2.4 Data Analysis

The data was taken once without replication. The removal efficiency of organic compound and color were calculated using the following formula.

$$\text{removal efficiency} = \frac{\text{initial value} - \text{final value}}{\text{initial value}} \times 100\% \quad (6)$$

3. RESULTS AND DISCUSSION

3.1 Characteristics of Pharmaceutical Wastewater

The main parameters, such as COD, pH, and color of pharmaceutical wastewater, were analyzed, and the findings are compiled in Table 1. According to the COD result, there were a lot of organic compounds in the wastewater (384 mg/L). According to the Environment and Forestry Regulation No. 5 of 2014 [1], the COD of its wastewater does not meet the quality standard (150 mg/L). One more significant point was the red-brown color of the wastewater, indicating that it still contains a pharmaceutical component (rifampicin).

Table 1. Characteristics of Influent of Pharmaceutical Wastewater

Parameter	Value
COD (mg/L)	384
pH	7.18
Color	Red-brown

3.2 Photo-Fenton Process

The experiment utilized Fenton reagents and UV light that can break down organic compounds in wastewater. The COD results are illustrated in Figure 1. The influence of the molar ratio of Fenton reagents was studied by varying the molar ratio of $FeSO_4.7H_2O$ to H_2O_2 of 1:1.5, 1:2, and 1:3 at a constant pH of 3. At a pH of 3, rifampicin can be dissolved and can be broken down. According to the findings, the photo-Fenton process reduced COD by reacting organic compounds with hydroxyl radicals, yielding harmless product [10]. The highest COD reduction was achieved at a molar ratio of $FeSO_4.7H_2O$ to H_2O_2 of 1:3. This finding is align with the results of Rahmawati et al [11]. At a molar ratio of 1:3, the amount of H_2O_2 was greater than the other ratios, so greater amount of hydroxyl radicals formed resulted in the increasing degradation of organic compounds. However, the amount of H_2O_2 should not be excessive because H_2O_2 will react with hydroxyl radicals to form $HO_2\bullet$, which is less reactive [12].

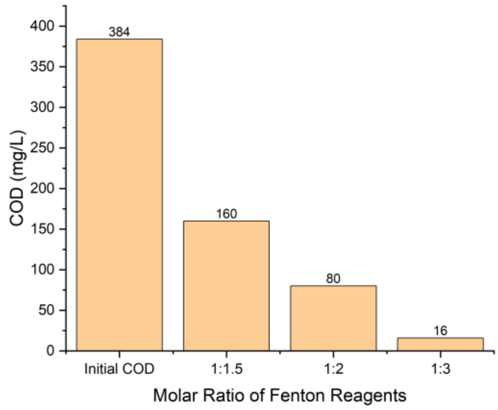

Figure 1. Influence of Molar Ratio of $FeSO_4.7H_2O$ to H_2O_2 on COD

To identify the influence of the molar ratio of Fenton reagents on color, the treated wastewater of the photo-Fenton process was measured its absorbance by using spectrophotometry UV-VIS. The absorbance results are illustrated in Figure 2. Similar to the result of COD, the highest color removal was achieved at a molar ratio of 1:3. The color removal is influenced by the amount of H_2O_2 because H_2O_2 is the source of hydroxyl radicals during the process. The introduction of UV light also contributes to the breakdown of colors in wastewater by producing photocatalytic oxidation reactions that can degrade the color [13]. Figure 3 shows the difference of color between wastewater before and after treatment by the photo-Fenton process.

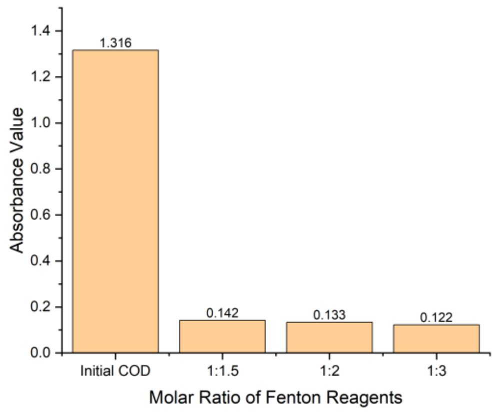

Figure 2. Influence of Molar Ratio of $FeSO_4.7H_2O$ to H_2O_2 on Absorbance Value

(a) (b)

Figure 3. Color of Pharmaceutical Wastewater (a) Before, (b) After Treatment of Photo-Fenton Process

3.3 Neutralization Process

The next process is the neutralization process to reduce Fe and H_2O_2 residues. The first phase of the neutralization process was carried out by increasing the pH using 0.1 M NaOH solution so that the pH was neutral, which was a requirement for the second phase of the neutralization process. The second phase was carried out by adding NaCl to coagulate the residue. The effect of the neutralization process on Fe and H_2O_2 residues is shown in Figures 4 and 5. It is clear from these figures that the neutralization process can decrease the amount of Fe and H_2O_2. NaCl reacts with Fe^{3+} to produce $FeCl_3$ to reduce the Fe and H_2O_2 residues [14]. The neutralization process occurs when $FeCl_3$ binds Fe and H_2O_2 residues and then produces deposits. This neutralization process is the last stage before wastewater is discharged into the environment.

Based on Figure 6, results indicated that neutralization was successful in reducing COD at molar ratios of 1:1.5 and 1:2. NaCl functions as a coagulant, so it can bind organic compounds to settle downwards and lower COD [15]. At molar ratio of 1:2, the removal efficiency of organic compound is 89.58%, and the decrease in the absorbance value indicated that the sample's color is 89.89%. Whereas, at a molar ratio of 1:3, the result of COD increased due to not all of NaCl being reacted with Fe^{3+}, resulting in additional residues sourced from inorganic compounds in the form of NaCl.

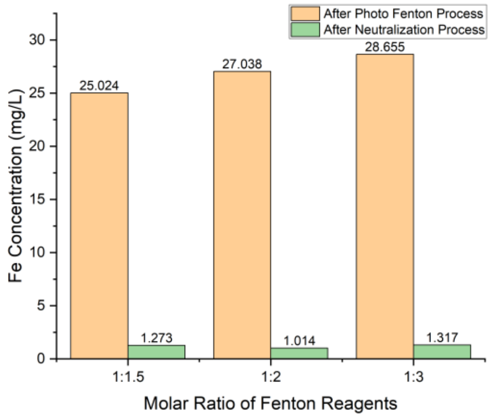

Figure 4. Influence of Neutralization Process on Fe Concentration

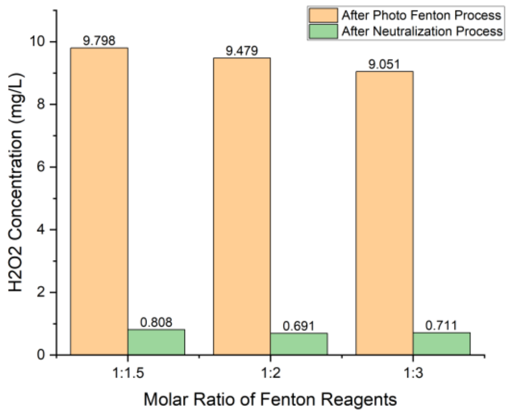

Figure 5. Influence of Neutralization Process on H_2O_2 Concentration

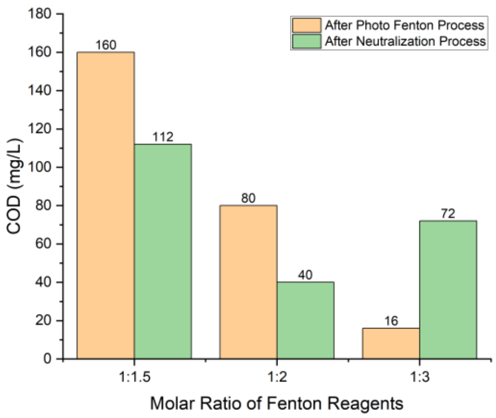

Figure 6. Influence of Neutralization Process on COD

CONCLUSION

The photo-Fenton process was successful in treating pharmaceutical wastewater containing rifampicin. The Fenton reagents used $FeSO_4.7H_2O$ and H_2O_2 to build hydroxyl radicals. UV light contributes to improving the degradation of organic compounds. The neutralization process can decreases the amount of Fe, H_2O_2, and COD on liquid. The best molar ratio of Fenton reagents was obtained at a ratio of 1:2. The removal efficiency of organic compound is 89.58%, and the decrease in the absorbance value indicated that the sample's color is 89.89%.

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CONFLICT OF INTEREST

No potential conflict of interest was reported by the author(s).

CREDIT AUTHORSHIP CONTRIBUTION STATEMENT

Endang Kusumawati: conceptualization, methodology, writing—original draft, resources, and editing, supervision.
Bunga Liswandila: investigation, data curation.
Erisca Saputri: methodology, writing-review editing.
Tifa Paramitha: Conceptualization, writing- review editing.

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