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Comparative Evaluation of Fenton and Persulfate Processes with UV/H_2O_2 for Batik Wastewater Treatment: Optimizing Fe^{2+} and $S_2O_8^{2-}$ Ratio by H_2O_2 for Enhanced Pollutant Degradation

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ABSTRACT: Wastewater generated from industrial processes including the batik industry in Indonesia contains high organic pollutants and dyes. In this study, the advanced oxidation process that will produce hydroxyl radicals was used to degrade pollutants in this batik industry wastewater. This study aims to compare the Fenton and Persulfate processes with the influence of variations in the concentration of Fe^{2+} and $S_2O_8^{2-}$ added. This method is carried out by adding H_2O_2 as an oxidant which is added to each catalyst, namely Fe^{2+} and $S_2O_8^{2-}$ in the presence of a combination of UV light. Fenton process was carried out in 60 minutes and Persulfate process was carried out in 45 minutes. In this study, there was a tendency to increase the efficiency of COD and color removal along with the increasing concentration of each catalyst added. The highest COD and color removal efficiency occurred at a ratio of H_2O_2:Fe^{2+} and H_2O_2: $S_2O_8^{2-}$ of 1: 0.08.

KEYWORDS: advanced oxidation process, fenton, hydroxyl radical, persulfate, wastewater

I. INTRODUCTION

The batik industry in Indonesia is one of the industries that is still widely found today. Batik is one of Indonesia's cultural heritages. However, in the production process, this industry can produce wastewater that comes from the coloring process. The wastewater may contain biodegradable and non-biodegradable pollutants (Mangla et al., 2019; Rosa et al., 2020). One of the areas that is the center of the batik industry that is still developing today is Sidoarjo, where there are around 10-20 batik craftsmen (Puspitasari et al., 2023). In the batik industry, the production process includes sewing, dyeing, coloring, waxing, and adding tapioca. In the coloring process, Naphthol ($C_{10}H_8O$) dye is used, which is one type of azo dye. The dyes used usually contain synthetic materials. In using this dye, salt is added to strengthen the color (Larasati et al., 2021).

One of the technologies that can be used to treat batik wastewater is the Advanced Oxidation Process (AOPs). AOPs produce hydroxyl radicals that are able to degrade pollutants into more environmentally friendly compounds as seen in **Figure 1** (Shen et al., 2022). Some other oxidation processes used include oxidation with $KMnO_4$, $K_2Cr_2O_7$, and $Na_2S_2O_8$, which can partially oxidize pollutants, but these partially oxidized pollutants can become secondary pollution sources. Meanwhile, AOPs can perform complete mineralization by producing inorganic products (Kumari & Kumar, 2023). Frequently used advanced oxidation processes include the Fenton process that combines H_2O_2 with Fe^{2+}, UV-based AOPs, UV/O_3, UV/H_2O_2, UV/NaClO, and UV/peroxymonosulfate (UV/PMS) (Shen et al., 2022; Wang et al., 2023).

These advanced oxidation processes divided into four categories, including chemical processes that use chemical reagents and catalysts, photochemistry that uses solar energy or ultraviolet sources, electrochemistry that utilizes electrical sources, and sonochemistry that uses ultrasound. Chemical processes are one of the longest used to generate reactive oxygen species with the help of chemicals to degrade pollutants, such as in the Fenton process. Photochemical processes use a combination of ultraviolet light as one of the sources of hydroxyl radicals (OH•). Besides the Fenton process, the Persulfate process ($S_2O_8^{2-}$) is also used in wastewater treatment, which requires activation through several methods such as using UV, heat, electrons generated by light, and transition metals. This activation produces sulfate radicals ($SO4^{-}$•) (Kumari & Kumar, 2023).

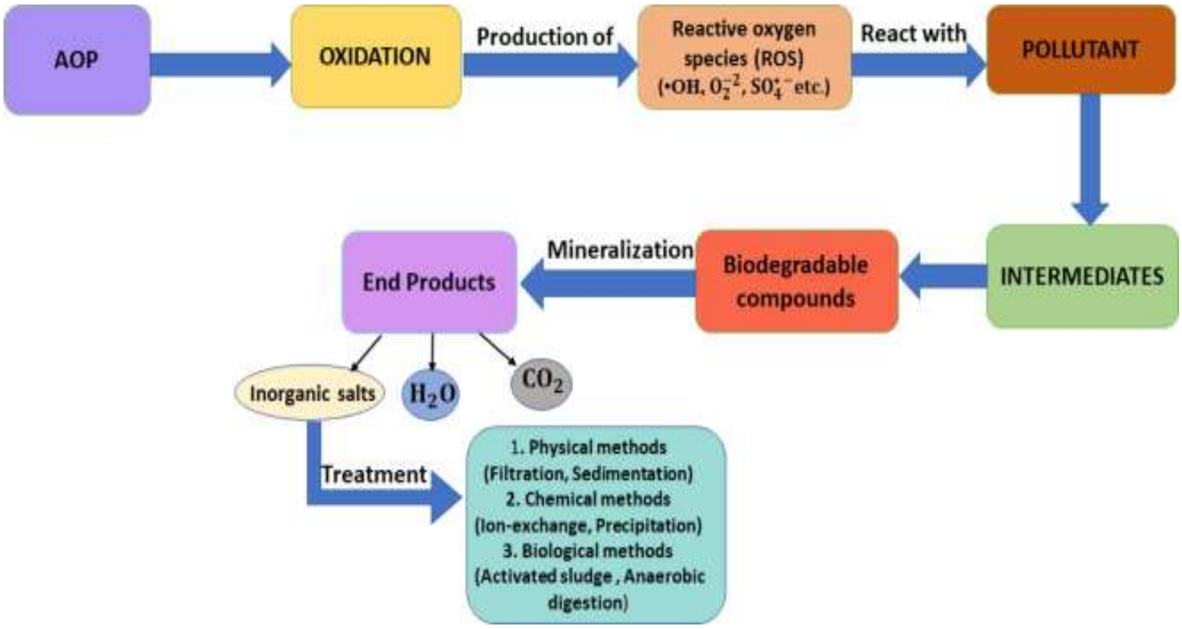

Figure 1. Advanced Oxidation Process (Kumari & Kumar, 2023)

The concentration of Fe^{2+} and $S_2O_8^{2-}$ added affects the results of wastewater treatment. Research by Cifci et al. (2020) used the Fe^{2+}/S_2O_8 and UV/S_2O_8 processes with variations in Fe^{2+} concentration. This research was conducted at pH 2 within oxidation time of 60 minutes. The result showed COD removal 57,2% at the 8th Fe^{2+} concentration variation, then decreased. The highest color removal was achieved at the 5th Fe^{2+} concentration variation. The optimal pH in this oxidation process is pH 3 with a reaction time of 1 hour. In the variation of Fe concentration with 200 ppm H_2O_2, reaction time of 2 hours, and temperature of 30°C, the Fenton process showed optimal results at Fe concentration of 250 ppm with color and COD removal of 74.23% and 46.2%. As for the photo-Fenton process, the optimal Fe concentration was 200 ppm with color and COD removal of 95.02% and 82.79%, respectively (Kaya & Asci, 2019).

Based on this issue, the aim of this research is to compare the use of fenton and persulfate processes in the presence of varying concentrations of Fe^{2+} and $S_2O_8^{2-}$ to degrade organic pollutants and dyes in batik industry wastewater.

II. MATERIALS AND METHOD

A. Characteristics of Batik Wastewater

Batik wastewater was collected from batik industry in Sidoarjo on 2024. This sample was taken at the dyeing basic process. Some parameters was analyzed as the characterization of this batik wastewater, they are pH, organic compound (COD), and color. This characterization can be seen in Error! Reference source not found..

Table 1. Batik wastewater characterization

Parameter	Result	Unit
pH	7-10	-
COD	2000-4500	mg/L
Color	930,75	mg/L

B. Chemical Reagents and UV Reactor

Hydrogen peroxide (H_2O_2) 30% was used in this process as oxidant. This material was added with 1 M iron (II) sulfate heptahydrate ($FeSO_4.7H_2O$) and 1 M sodium persulfate ($Na_2S_2O_8$) as catalyst. Batch experiments in this study were conducted in AOPs reactor (60×45×50 cm^3). This reactor was made from wood which was covered with aluminium foil. The sample was used in this experiment was 1 L which was stirred at 300 rpm with a magnetic stirrer. The operating pH used was pH 3 for Fenton process and pH 4 for Persulfate process. This pH was adjusted by adding 2 M sulfuric acid (H_2SO_4).

C. Fenton and Persulfate Oxidation Process

The oxidant:catalyst ratios used for both processes were H_2O_2:Fe^{2+} and H_2O_2:$S_2O_8^{2-}$ namely 1:0.04; 1:0.06; and 1:0.08, respectively. In this process, a combination with ultraviolet (UV) light was used as much as 1 lamp with a power of 6 W. The Fenton process was carried out for 60 minutes and the Persulfate process was carried out for 45 minutes. Samples were taken at the 30th and 60th minutes for the Fenton process. Samples were taken at the 30th and 45th minutes for the Persulfate process. 1 L of wastewater was put into a beaker glass and set at a predetermined pH. H_2O_2 and catalyst were added according to the predetermined ratio for each catalyst.

D. Analytical Measurement

The samples were analyzed for COD and color to measure the effectiveness of these both processes. COD was analyzed using spectrophotometric method at 420 nm after closed reflux. This measurement was used with HACH test tube. Color was analyzed with naphthol standard solution calibration using spectrophotometric method at 600 nm.

The calculation of COD and color removal was done using the formula as follows:

$$\text{Color Removal (\%)} = \frac{C_0 - C_e}{C_0} \times 100 \qquad (1)$$

$$\text{COD Removal (\%)} = \frac{COD_0 - COD_e}{COD_0} \times 100 \qquad (2)$$

where C_0 is the initial color (mg/L), C_e is the final color (mg/L), COD_0 is the initial COD (mg/L), and COD_e is the final COD (mg/L).

III. RESULTS AND DISCUSSION

A. The Fe^{2+} Concentration Effect on COD and Color Removal by H_2O_2/Fe^{2+}/UV

The Fenton process in this study was carried out by combining H_2O_2 and Fe^{2+} with UV light. The reaction that occurs in the Fenton process is seen in the reaction below. The Fenton method is carried out under acidic conditions. Some studies show that the pH used in the Fenton process is pH 3.

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

$OH\bullet + H_2O_2 \rightarrow HO_2\bullet + H_2O$ (4)

$Fe^{2+} + OH\bullet \rightarrow Fe^{3+} + OH^-$ (5)

$Fe^{3+} + O_2H \rightarrow Fe^{2+} + O_2 + H^+$ (6)

Organic pollutant + $OH\bullet \rightarrow$ Degraded product (7)

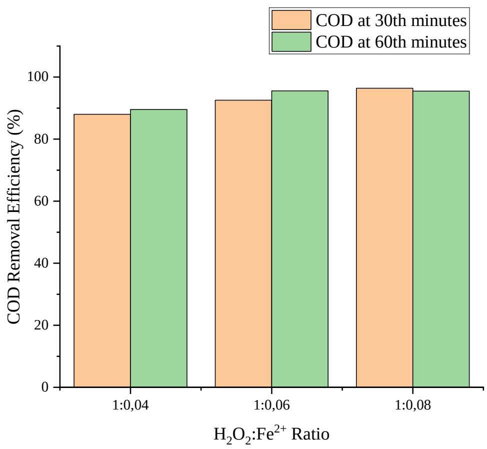

Figure 2. The Fe^{2+} concentration effect on COD removal by H_2O_2/Fe^{2+}/UV

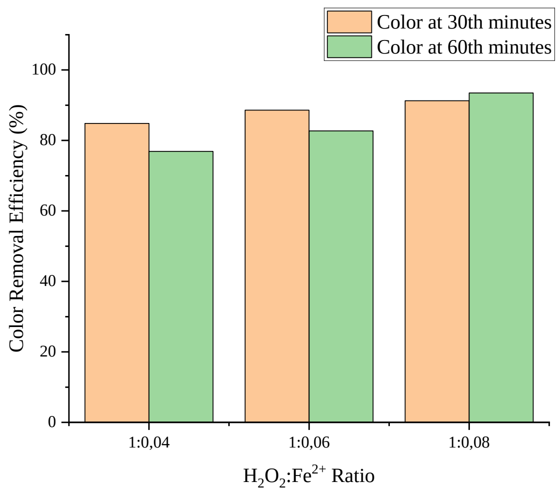

Figure 3. The Fe^{2+} concentration effect on color removal by $H_2O_2/Fe^{2+}/UV$

Figure 2 and **Figure 3** shows that increasing the addition of Fe^{2+} concentration in this treatment process tends to increase the removal efficiency of COD and color, whether sampling at 30 minutes or 60 minutes. The highest COD and color removal efficiency is at a ratio of H_2O_2:Fe^{2+} of 1: 0.08. Fe^{2+} concentration plays an important role in the treatment process. Fe^{2+} concentration can degrade organic pollutant until the certain concentration. Fe^{2+} ions react with H_2O_2 to produce other compounds and hydroxyl radicals (OH•), reactive species responsible for the degradation of pollutants as seen in reaction (3) until (7) (Tuncer & Sönmez, 2023). However, the decrease in COD and color removal efficiency was due to the presence of excess H_2O_2. Under excessive H_2O_2 conditions, Fe^{3+} can react with H_2O_2 to produce more hydroperoxyl radicals (HO_2•). These radicals contribute to the degradation process of pollutants, as in the following reaction (8) (Unal Yilmaz et al., 2023).

$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + O_2H\bullet + H^+$ (8)

The addition of Fe^{2+} can increase the color efficiency due to the formation of the hydroxyl radical. These radicals will degrade the dye molecules as seen in reaction (9) in a faster time. However, at excessive Fe^{2+} concentrations can cause the addition of color residues, thus reducing the removal efficiency (Benassi et al., 2021).

$\text{Dye} \xrightarrow[\text{OH}\bullet]{\text{UV}} \text{degraded product}$ (9)

Increasing the concentration of Fe^{2+} in this wastewater treatment will further reduce the color in the wastewater. This is because the formation of hydroxyl radicals from the reaction that occurs in the Fenton process will degrade these organic pollutants which cause the decomposition of the chemical structure in them with the presence of H-substraction and C-C unsaturated bonds (GilPavas et al., 2019).

B. The $S_2O_8^{2-}$ Concentration Effect on COD and Color Removal by $H_2O_2/S_2O_8^{2-}/UV$

The Persulfate process in this study used H_2O_2 and $S_2O_8^{2-}$ combined with UV light for the Persulfate activation process. This activation process will produce sulfate radicals (SO_4^-•) as seen in the reaction (10) (Kumari & Kumar, 2023; Nidheesh et al., 2022). Persulfate concentration is one of the factors that affect the wastewater treatment process. This concentration will affect the removal of pollutants in wastewater. The higher the concentration of persulfate used, the efficiency of pollutant removal will increase. This is due to the presence of sulfate radicals which will affect the oxidation potential in breaking down organic compounds. This oxidation potential will increase compared to persulfate anion. This reaction process can be seen in reaction (11) and (12) (Ahmadi et al., 2019).

$S_2O_8^{2-} + UV \rightarrow 2SO_4^-\bullet$ (10)

$S_2O_8^{2-} + SO_4^-\bullet \rightarrow S_2O_8^{2-} + SO_4^-\bullet$ (11)

$SO_4^-\bullet + SO_4^-\bullet \rightarrow S_2O_8^{2-}$ (12)

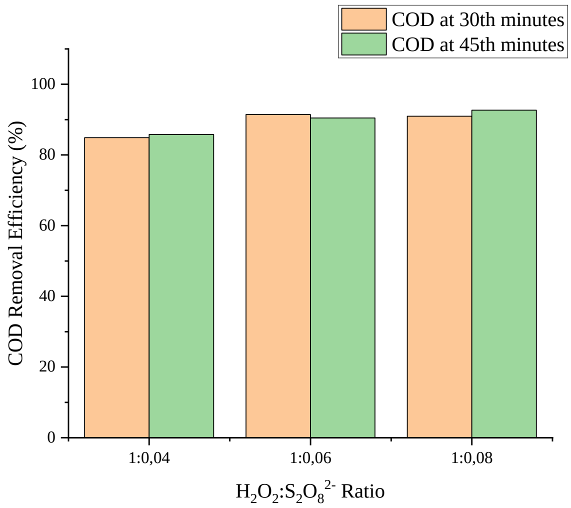

Figure 4. The $S_2O_8^{2-}$ concentration effect on COD removal by H_2O_2/ $S_2O_8^{2-}$/UV

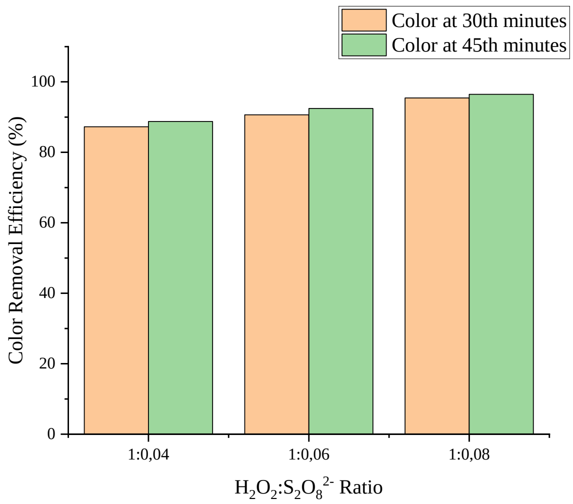

Figure 5. The $S_2O_8^{2-}$ concentration effect on color removal by H_2O_2/ $S_2O_8^{2-}$/UV

Figure 4 and **Figure 5** shows that the addition of increasing concentrations of $S_2O_8^{2-}$ tends to increase the removal efficiency of COD and color. The highest COD and color removal efficiency in this process is at the H_2O_2:$S_2O_8^{2-}$ ratio of 1:0.08. This is because the sulfate radicals formed will react to form hydroxyl radicals that can degrade pollutants. Sulfate radicals and hydroxyl radicals have a role in degrading pollutants, but hydroxyl radicals have a higher oxidation potential than sulfate radicals (Jorfi & Ghaedrahmat, 2021).

$SO_4^-\bullet + H_2O_2 \rightarrow OH\bullet + HSO_5^-$ (11)

$HSO_5^- + UV \rightarrow SO_4^-\bullet + OH\bullet$ (12)

$SO_4^-\bullet + OH^- \rightarrow SO_4^{2-} + OH\bullet$ (13)

An increase in removal efficiency due to an increase in persulfate was also carried out by Khatri et al. (2018) showing an increase in COD removal efficiency. This is due to the formation of sulfate radicals from the reaction that occurs.

IV. CONCLUSION

In this study, it can be concluded that the Fenton and Persulfate processes can be used to treat batik industry wastewater. The concentration of each catalyst used must be considered because it will affect the COD and color removal efficiency produced. Increasing the concentration of each catalyst added to this wastewater treatment tends to show an increase in COD and color removal efficiency. In this study, the highest COD and color removal efficiency was obtained in both processes, namely at the concentration ratio of H_2O_2: Fe^{2+} and H_2O_2:$S_2O_8^{2-}$, namely 1: 0.08. Furthermore, it can be done about other concentration variations of each catalyst and an increase in the UV power used.

Comparative Evaluation of Fenton and Persulfate Processes with UV/H_2O_2 for Batik Wastewater Treatment: Optimizing Fe^{2+} and $S_2O_8^{2-}$ Ratio by H_2O_2 for Enhanced Pollutant Degradation

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