The effect of different types of AOPs supported by hydrogen peroxide on the
decolorization of methylene blue and viscose fibers dyeing wastewater

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ABSTRACT

Wastewater from the textile industry containing a high concentration of organic and inorganic chemicals have strong color and residual chemical oxygen demand (COD). Therefore, advanced oxidation processes (AOPs) are very good candidates to treat textile industry wastewater. In this study, we investigated the effect of different types of AOPs supported with hydrogen peroxide (H2O2) on the treatment of viscose fibers dyeing wastewater. Fenton, photo-Fenton, and Fenton supported subcritical water oxidation (FSWO) processes were chosen as AOPs to compare the treatment efficiency of viscose fibers dyeing wastewater. The effects of solution pH, Fe2+ concentration, and H2O2 concentration on the treatment of viscose fibers dyeing wastewater were tested. The maximum color and COD removal efficiency was obtained corresponding to pH 2.5 for all oxidation methods when MB dye solution was used. However, the maximum efficiencies were obtained at pH 3.0 for real textile wastewater decolorization. The MB dye removal efficiency was increased to 97.22, 100, and 100% for Fenton, photo-Fenton, and FSWO processes, respectively, when the addition of H2O2 concentration was adjusted to 125 mg/L. However, the maximum color removal efficiencies of viscose fibers dyeing wastewater were obtained 56.94, 61.26, 64.11% for Fenton, photo-Fenton, FSWO processes, respectively. As a result, the FSWO showed maximum color removal efficiencies.

Key words: advanced oxidation process, fenton process, fenton supported subcritical water oxidation, methylene blue dye, Photo-Fenton process, viscose fibers dyeing wastewater

HIGHLIGHTS

- Fenton, photo-Fenton, and Fenton supported SWO processes were compared.
- Methylene blue dye was treated at pH 2.5 for all oxidation methods.
- MB dye removal was 97.22 and 100% for Fenton and photo-Fenton/FSWO processes.
- The highest color removal to treat real textile wastewater was 64.11% for FSWO.
1. INTRODUCTION

In the textile industry, every year up to 200,000 tons of dyes are discharged to receiving environment, due to the inefficiency of the dyeing and finishing process (Ogugbue & Sawidis 2011). Unfortunately, most of the dye chemicals are recalcitrant and resistant to conventional wastewater treatment processes and retain in the environment as a result of their high stability to light, temperature, water, detergents, chemicals, soap and other parameters such as bleach and ordinary chemical oxidation (Rodríguez Couto 2009). Environmental legislation sets a series of obligations to related industries to eliminate color from their dye-containing effluents before disposal into water bodies (Pereira & Alves 2012). However, wastewater from textile effluents causes possible risks of sunlight absorbing by color and ecologic breakdown in rivers and thereon causing breaks in the food chain.

Color removal by chemical oxidation method is based on the principle of inducing (partial) oxidation by breaking down the chromophore of dyes, conjugate bond systems in groups. All dyes contain many conjugated or aromatic bonds, and the oxidant chosen for oxidation initially reacts with unsaturated bonds, reducing it to compounds with smaller molecules (Drumond Chequer et al. 2013; Parisi et al. 2015).

Over the past 20 years, ecological risks and human stricter rules have been adopted in environmental regulations due to increased sensitivity to health. These constraints have developed much more advanced treatment technologies to meet these needs at a lower cost (Madhav et al. 2018). One of these technologies is called Advanced Oxidation Processes (AOP). These processes are generally strong even at ambient temperature and pressure, and initiates the hydroxyl radical (·OH) production, which is a selective, short electrophilic oxidant (OP = 2.8 eV) (Wang & Zhuan 2020). Hydroxyl radicals are unusual reactive species and attack organic molecules easily (Liu et al. 2014). AOPs are categorized by the production of the ·OH radicals which gives better conformity to particular treatment demands (Deng & Zhao 2015; Dewil et al. 2017). In general, there are four common processes for the production of ·OH radicals without light energy in which ozone or Fe^{2+} ions are used to generate ·OH radicals. These are composed of O_{3}/OH^{-}, O_{3}/H_{2}O_{2}, O_{3}/catalyst, and Fe^{2+}/H_{2}O_{2} (Fenton’s reaction). UV light can also be used to enhance the process efficiency which are O_{3}/UVC, H_{2}O_{2}/UVC, O_{3}/H_{2}O_{2}/UVC, TiO_{2}/UVA (Photocatalytic), Fe^{2+}/H_{2}O_{2}/UVA (Photo-Fenton) (Swaminathan et al. 2013; Hayat et al. 2015; Jorfi et al. 2016).

The Fenton process is the combination of ferrous ions (Fe^{2+}) and H_{2}O_{2} in an acid medium in which the formed ·OH radicals
attack the target pollutants by the oxidation of Fe$^{2+}$ to ferric ions (Fe$^{3+}$) (Equation (1)). At the same time, Fe$^{2+}$ is reproduced by the reaction between Fe$^{3+}$ and H$_2$O$_2$ (Equation (2)) (Bokare & Choi 2014).

$$\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \cdot \text{OH} + \text{OH}^{-} \quad (k_1 = 63 - 76 \text{M}^{-1}\text{s}^{-1}) \quad (1)$$

$$\text{Fe}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{2+} + \text{HO}_2^* + \text{H}^+ \quad (k_2 = 0.001 - 0.01 \text{M}^{-1}\text{s}^{-1}) \quad (2)$$

In Photo-Fenton, UV or visible light irradiation are used to drive the process that generates the oxidative `OH radicals from Fe$^{3+}$/H$_2$O$_2$. The reaction between H$_2$O$_2$ and UV light is not either significant because of the use of sub-milimolar (mM) H$_2$O$_2$ concentration (Equations (3) and (4)) (Ameta et al. 2018).

$$\text{Fe}^{3+}/\text{Fe(III)}(\text{OH})^{2+} + \text{hv} \rightarrow \text{Fe}^{2+}/\text{Fe(II)} + \cdot \text{OH} \quad (3)$$

$$\text{H}_2\text{O}_2 + \text{hv} \rightarrow 2 \cdot \text{OH} \quad (4)$$

Besides, the Fenton supported subcritical water oxidation (FSWO) method is an effective process for the oxidation of the contaminants in which wastewater is heated between 373 and 647 K with an adequate pressure to keep wastewater in liquid form (Yabalak 2018a). The subcritical state increases the H$^+$ and OH$^-$ concentrations by the ionization of water molecules. Also, the use of oxidizing chemicals such as hydrogen peroxide, permanganate, etc. improves the oxidizing efficiency of FSWO processes for the persistent contaminants (Yabalak et al. 2021). Table 1 shows the reactions for Fenton, photo-Fenton, FSWO processes.

Cosmetic wastewater was treated by applying of advanced photo-oxidation technique (photo-Fenton oxidation process) for removal of the residuals organic pollutants. The experimental results showed that Fenton’s oxidation process supplied 95.5% COD removal efficiency at pH 3, the dose of 1 mL/L H$_2$O$_2$ and 0.75 g/L for Fe(II) and Fe(III), and irradiation time 40 min (Ebrahiem et al. 2017). Fenton process was used for the treatment of textile wastewater and the process supplied 98% colour removal efficiency at pH 3 at FeSO$_4$ of 1.2 g/L and H$_2$O$_2$ of 0.1 mL/L (Patil & Raut 2014). Moreover, 85% COD removal efficiency was obtained at pH 3 at FeSO$_4$ of 1.2 g/L and dose of H$_2$O$_2$ of 0.6 mL/L. Treatment of textile wastewater was carried out by using the photo-Fenton oxidation process ( Sahuni et al. 2006). The results showed that 52 and 90% of COD and color were removed at pH = 3, 80 mg Fe$^{2+}$/L, 200 mg H$_2$O$_2$/L, 60 W UV power, and 5–10 min operating time. The treatment of the effluent from the textile industry was carried out by advanced oxidative processes of photo-Fenton assisted by different sources (natural sunlight, UV-A or visible LED lamps) ( de Souza et al. 2021). 88.7% COD and 100% color removal efficiencies were achieved by the use of the LED lamp. Combined chemical oxidation processes using potassium ferrate (VI) (K$_2$FeO$_4$) and Fenton (Fe(III)/H$_2$O$_2$) process was applied for the treatment of real wastewater from the textile industry characterized by an increased content of organic substances (COD = 1,920 mg/L) ( Thomas & Zdebik 2019). The use of both processes under optimal conditions supplied 75.4% COD removal efficiency with 472 mg/L final COD. In another study, 59.45% TOC and 97.92% of color removal efficiencies were achieved in the treatment of the real wastewater (initial TOC value of 4,200 ppm) of an industrial agrochemicals production plant using SWO method ( Yabalak & Gizir 2020).

In this study, the effect of different types of AOPs supported with hydrogen peroxide (H2O2) was investigated on the treatment of methylene blue (MB) dye and viscose fibers dyeing wastewater. The differences between Fenton, photo-Fenton, and

| Table 1 | The reactions carried out in Fenton, photo-Fenton, FSWO processes |
|-----------------|-----------------|-----------------|
| **Fenton** (Neyens & Baeyens 2003; Bautista et al. 2008) | **Photo-Fenton** (Rahim Pouran et al. 2015) | **FSWO** (Yabalak 2018a) |
| 2Fe$^{2+}$ + H$_2$O$_2$ + 2H$^-$ → 2Fe$^{3+}$ + 2H$_2$O | Fe(OH)$_2$ $^{hv}$ Fe$^{2+}$ + *OH $<$ 580 nm | H$_2$O$_2$ $^{heat}$ 2·OH |
| Fe$^{2+}$ + H$_2$O → Fe$^{3+}$ + *OH + OH$^-$ | H$_2$O$_2$ $^{2·OH}$ $<$ 310 nm | H$_2$O$_2$ + *OH → H$_2$O + *OH |
| Fe$^{3+}$ + H$_2$O → Fe$^{2+}$ + HO$_2^*$ + H$^+$ | Fe$^{2+}$ + HO$_2^*$ → Fe$^{3+}$ + OH$_2$ | H$_2$O$_2$ + *OH → O$_2^-$ + H$^+$ + H$_2$O |
| FeOOH$^{2-}$ → HO$_2^*$ + Fe$^{2+}$ | Fe$^{3+}$ + HO$_2^*$ → Fe$^{2+}$ + O$_2$ + H$^+$ | *OH + *OH → H$_2$O$_2$ |
| *OH + H$_2$O$_2$ → H$_2$O + HO$_2^*$ | *OH + *OH → H$_2$O$_2$ | *OH + HO$_2^*$ → H$_2$O + O$_2$ |
Fenton-supported subcritical water oxidation (FSWO) were explored to select the best method in treating dyed wastewater. The effects of solution pH, iron(II) (Fe$^{2+}$) concentration, initial dye concentration, and hydrogen peroxide (H$_2$O$_2$) concentration on color and chemical oxygen demand (COD) removal was systematically investigated.

2. MATERIALS AND METHODS

2.1. Materials and apparatus

Ferrous sulfate heptahydrate (FeSO$_4$$\cdot$7H$_2$O) and hydrogen peroxide (H$_2$O$_2$) were supplied from Merck (Darmstadt, Germany). FSWO experiments were performed in a home-made stainless-steel reactor described in our previous study (Yabalak 2018b). Nitrogen was used to keep in-reactor pressure at a required level. Methylene blue (MB) was provided from DyStar. The chemical structures and fundamental properties of the MB are shown in Table 2.

Viscose fibers dyeing wastewater was kindly provided from a local textile firm (Melike Textile) located in Gaziantep, Turkey. The characterization of the viscose fibers dyeing wastewater is shown in Table 3.

2.2. Methods for wastewater treatment

2.2.1. Fenton method

The Fenton oxidation experiments of MB dye and viscose fibers dyeing wastewater were carried out in a 500-mL beaker containing 150 mL of dye solution. The schematic illustration of the Fenton system is shown in Figure 1(a). The effects of solution pH, Fe$^{2+}$ concentration, initial dye concentration, and H$_2$O$_2$ concentration on MB oxidation and viscose fibers dyeing wastewater treatment were selected for Fenton experiments. All the experiments were carried out under constant stirring (250 rpm) for 60 min at 25 ± 1 °C. At the end of the reaction, Fe$^{3+}$ ions were removed from the reaction medium by increasing of solution pH up to 8.0 and precipitated iron hydroxides were separated by centrifugation (6,000 rpm, 10 min) and analyzed versus time to determine residual dye concentration. All samples were tested in duplicate and average values were presented.

2.2.2. Photo-Fenton method

Photo-Fenton oxidations were carried out in the multi-lamp laboratory-scale column reactor made-up of Pyrex glass with a capacity of 500 mL containing 150 mL of wastewater. The reactor design is similar to the one described previously (Kardes et al. 2020). The overall experimental setup is illustrated in Figure 1(b).

Table 2 | Chemical structures and essential properties of the MB dye

| Chemical formula | C$_{16}$H$_{18}$ClN$_3$S |
|------------------|------------------------|
| Molecular weight (g/mol) | 319.85 |
| Wavelength (nm) | 664 |
| Chemical structure (2D) |  |
| Chemical structure (3D) |  |
2.2.3. Fenton supported by Subcritical Water Oxidation (FSWO) method

FSWO experiments were carried out in a home-made stainless-steel reactor and it was performed according to previous work (Yabalak et al. 2019). Viscose fibers dyeing wastewater (150 mL) was placed into the reactor with a certain amount of H₂O₂ addition. The reactor was pressurized using N₂ gas (initial pressure of 30 bar) after closing it and the temperature was increased to a desired value.

2.2.4. Analysis

pH was measured by pH-meter (Thermo Scientific Orion 3-star). The closed reflux titrimetric method was used for COD analysis of the samples following Standard Method No.5220. Fenton and photo-Fenton reactions cannot proceed at pH > 10 (Ebrahiem et al. 2017). Therefore, the reaction was arrested instantly by adding NaOH to the reaction samples before COD analysis. Dye was analyzed using a UV-vis spectrophotometer (T90+ UV/VIS Spectrometer, PG Instruments Ltd). Color of the samples was measured at λ_{max} value (664 nm) for the MB dye. Color of the real textile wastewater samples was measured by 630 nm, which was λ_{max} value of the wastewater. The percentage of COD and color removal efficiency was calculated using the following Equation (1):

Removal efficiency (%) = \frac{C_i - C_f}{C_i} \times 100

where C_i and C_f were the initial and final COD or dye concentration (mg/L), respectively.
3. RESULTS AND DISCUSSION

3.1. The effect of pH on color removal efficiency

To determine the optimal pH, the experiments were conducted at different pH values varying from 2 to 6 with an initial MB dye concentration of 50 mg/L, \( \text{H}_2\text{O}_2 \) concentration of 50 mg/L, and \( \text{Fe}^{2+} \) concentration of 50 mg/L. In the present study, the maximum color removal from MB dye solution was obtained corresponding to pH 2.5 for all oxidation methods (Figure 2(a)).

The maximum color removal efficiencies of MB dye were obtained 96.28%, 96.45%, 97.56% for Fenton, photo-Fenton, FSWO processes, respectively. Therefore, subsequent experiments of Fenton, photo-Fenton, and FSWO were set for pH 2.5. The color removal efficiency decreased at over pH of 3.5. This may be because at higher pH (above 3.5), ferrous ions get easily converted to ferric ions, which tend to produce ferric-hydroxo complexes with \( \text{H}_2\text{O}_2 \). The low degradation at pH 2 may be due to the hydroxyl radical scavenging by \( \text{H}^+ \) ions and also there may be inhibition for the radical forming activity of iron (Shemer et al. 2006; Karale et al. 2014). Kakavandi et al. (2019) produced nanoscale zerovalent iron supported on kaolinite to oxidize acid black dye. In their research, 98% degradation was obtained at an optimum pH value of 2 (Kakavandi et al. 2019).

Unal & colleagues (2019) treated basic red 18 (BR18) and acidic red 88 (AR88) dyes using Fenton process with magnetite nanoparticles deposited on a glass substrate. For BR18, the maximum removal efficiency was 76% at pH value of 3.5. Totally AR88 degradation was noticed at pH 6 (Unal et al. 2019). Photo-Fenton supplied the maximum color removal efficiency compared to other oxidation processes. Saleh et al. (2021) compared the oxidation capabilities for the basalt as a heterogeneous catalyst for cationic dyes via Fenton and Photo-Fenton methods. The oxidation efficiency for the photo-Fenton was higher than the Fenton process (Saleh et al. 2021a). Khataee & colleagues (2016) reached a reactive orange 29 degradation efficiency of 94% at pH value of 2 (Khataee et al. 2016).

The efficiencies of the processes were also tested using the real textile wastewater obtained from viscose fibers dyeing bath. The maximum color removal was obtained corresponding to pH 3.0 for all oxidation methods (Figure 2(b)). The maximum color removal efficiencies of viscose fibers dyeing wastewater were obtained 52.78%, 54.79%, 59.12% for Fenton, photo-Fenton, FSWO processes, respectively. Therefore, subsequent experiments of Fenton, photo-Fenton, and FSWO were set for pH = 3.0. Differences in the removal efficiency were quite significant between synthetic MB dye solution and real textile wastewater. This can be explained by the fact that real textile wastewater contains different types of dyes and each dye can decompose at different pH values. Based on this result, one can state that the decomposition of pollutants presents in viscose fibers dyeing wastewater depends on the initial pH of the solution. Kos et al. studied the efficiency of the decomposition of pollutants present in textile wastewater in the Fenton process and maximum COD reduction in dyeing wastewater was found at pH = 3.5 (Kos et al. 2010).

**Figure 2** | (a) Color removal efficiency from MB dye solution \( (C_0 = 50 \text{ mg/L}, \text{H}_2\text{O}_2 = 50 \text{ mg/L}, \text{and Fe}^{2+} = 50 \text{ mg/L}) \) and (b) Color removal efficiency from viscose fibers dyeing wastewater \( (\lambda_{630} = 0.072 \text{ abs}, \text{H}_2\text{O}_2 = 50 \text{ mg/L}, \text{and Fe}^{2+} = 50 \text{ mg/L}) \).
3.2. The effect of Fe$^{2+}$ concentration on color removal efficiency

The effect of Fe$^{2+}$ concentration on color removal from MB dye solution can be seen in Figure 3(a) for Fenton, photo-Fenton, and FSWO processes. The highest color removal efficiency from MB dye solution was achieved for 50 mg/L Fe$^{2+}$ concentration which was 97.04%, 97.84%, and 98.76% for Fenton, FSWO, and photo-Fenton, respectively (Figure 3(a)). However, the maximum color removal efficiencies of viscose fibers dyeing wastewater were obtained 52.78%, 54.79%, 59.12% for Fenton, photo-Fenton, FSWO processes, respectively (Figure 3(b)). For the addition of 50 mg/L Fe$^{2+}$ concentration, Fe$^{2+}$ catalyzed H$_2$O$_2$ decomposition more efficiently which helped the generation of more ‘OH radicals that increased the MB dye removal efficiency (Javaid & Qazi 2019). Xu et al. (2015) noticed that the uses of overdose of Fe$^{2+}$ decreased the removal efficiency because of scavenging effects (Xu et al. 2015). The MB dye removal efficiency decreased for overdose Fe$^{2+}$ ion loads due to the ‘OH scavenging effect that means the conversion of ‘OH radicals into the hydroxyl ions during the oxidation of Fe$^{2+}$ in Equation (2) (Governo et al. 2017; Sohrabi et al. 2017). Figure 3(a) reveals that the MB dye removal efficiency decreases noticeably with the dose of catalyst higher than 50 mg/L Fe$^{2+}$ concentration. Thus, the optimum Fe$^{2+}$ concentration was accepted 50 mg Fe$^{2+}$/L or all AOPs methods. Saleh et al. (2021) have noticed similar results for the Fenton oxidation of textile wastewater (Saleh et al. 2021b). Dagher & colleagues (2018) degraded the methylene blue by Fenton process using Fe$_3$O$_4$ as a catalyst. The maximum degradation was 89% for the first cycle and sharply decreased to reach 62% at the fourth cycle (Dagher et al. 2018).

\[
\text{OH}^- + \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{OH}^-
\]  

3.3. The effect of H$_2$O$_2$ concentration on color removal efficiency

Hydrogen peroxide is a crucial parameter in determining the total removal efficiency of the AOPs. The addition of H$_2$O$_2$ concentration in different AOPs processes was varied from 0 to 125 mg/L. The MB dye removal efficiency was increased to 97.22, 100, and 100% for Fenton, photo-Fenton, and FSWO processes, respectively when the addition of H$_2$O$_2$ concentration was adjusted to 125 mg/L. It was seen that the MB dye removal efficiency remained almost constant for H$_2$O$_2$ concentrations higher than 50 mg/L (Figure 4(a)). However, the maximum color removal efficiencies of viscose fibers dyeing wastewater were obtained 56.94%, 61.26%, 64.11% for Fenton, photo-Fenton, FSWO processes, respectively (Figure 3(b)). The enhancement in MB dye removal efficiency was attributed to the increment in the ‘OH radicals with the addition of H$_2$O$_2$ concentration in Equation (3) (Sivagami et al. 2018; Sivagami et al. 2019). In general, the increases in the H$_2$O$_2$ concentration increases the removal efficiency until the optimum point. Beyond that point, the addition of excess amounts of H$_2$O$_2$ concentrations will has a negative effect due to the reactions in Equations (4) and (5) in which the oxidation mechanism is inhibited.

Figure 3 | (a) Color removal efficiency from MB dye solution (C$_0$ = 50 mg/L, H$_2$O$_2$ = 50 mg/L, and pH = 2.5) and (b) Color removal efficiency from viscose fibers dyeing wastewater ($\lambda_{430} = 0.072$ abs, H$_2$O$_2$ = 50 mg/L, and pH = 3.0).
because of the ·OH and HO2 radicals are consumed that are necessary for the degradation of MB dyes (Sennaoui et al. 2018). In previous study, the excessive H2O2 acts as hydroxyl radical scavenger and lowers the degradation efficiency for the textile wastewater (Saleh et al. 2021b). Therefore, the amount of H2O2 concentration should be adjusted to the optimum dosage which was 50 mg/L in our study.

\[
\begin{align*}
H_2O_2 + e^- & \rightarrow \cdot OH + OH^- \\
H_2O_2 + \cdot OH & \rightarrow H_2O + HO_2 \cdot \\
HO_2 \cdot + OH & \rightarrow H_2O + O_2
\end{align*}
\]

Yabalak et al. reported the 72.86% of TOC removal of Procion Crimson H-EXL dye solution with 100 ppm using 50 mM of H2O2 in SWO method (Kardes et al. 2020). They mentioned that subcritical water medium provides about 8% of TOC removal without using any oxidizing agent. Furthermore, H2O2 effectively transformed into OH radicals by this eco-friendly method. However, they also pointed that continuously increasing H2O2 concentration in the reaction medium do not increase the efficiency and over a specific concentration of H2O2 a series of chain reactions may be initiated which may lead thus depletion of OH radicals, thus decrease the efficiency (Kardeş et al. 2020). Chinh et al. (2021) have utilized the TiO2 and TiO2–SiO2 by coupling with graphene–gold nanocomposites for methylene blue and rhodamine B removal from the aqueous solutions. The photodegradation efficiency of the prepared catalyst was 88 and 28% for MB and RhB, respectively (Chinh et al. 2021).

In the Fenton process, the effects of pH, H2O2 concentration and Fe²⁺ concentration on individual MB dye removal were also investigated. It was seen that these three parameters alone were not effective in MB dye removal and all removal was due to Fenton reaction (Figure 5(a)). The effect of photolysis, Fe²⁺/UV, and H2O2/UV were also tested on MB dye removal efficiency for the photo-Fenton process (Figure 5(b)). H2O2 degraded the dye over 80% under UV light. The effect of temperature, Fe²⁺/temperature, and H2O2/temperature was investigated on the FSWO process. H2O2 and Fe²⁺ under temperature also degraded the dye over 80% (Figure 5(c)).

### 3.4. The effect of initial dye concentration on MB oxidation

Concerning decolorization data, a kinetic study was carried out using the non-linear data fitting for the pseudo-order kinetic model, which is shown in Equation (6) (Chinh et al. 2019).

\[
C^{(n-1)} = \frac{C_0^{(n-1)}}{1 + (n - 1)C_0^{(n-1)}kt}
\]
where; C and Co are the concentration at time t and the initial concentration (mg/L), respectively, k is is the pseudo-n order kinetic constant rate, n is the reaction order and t is the contact time (min). Origin software was used to facilitate the fitting issue for the decolorization of MB dye through Fenton, photo-Fenton, FSWO processes. The oxidation of MB dye by the three methods was found to occur in two steps; the first one is fast, which attributed to Fe$^{2+}$ and H$_2$O$_2$ reaction. The second step is slower than the first step and occurs due to the Fe$^{3+}$ accumulation and also because of the Fe$^{2+}$ recovery by H$_2$O$_2$ (Malik & Saha 2003; Barreto et al. 2016). Similar behavior was noticed in the degradation of methyl orange, phenol red and safranin T (Santana & Aguiar 2015). The nonlinear fittings for the zero and the first order models were not applicable, but the second order model had high regression coefficient as shown in Figure 6.

To have more precise view, it is very necessary to analyze data based on different models, thus, the linear forms for zero-, first-, and second-order models were used as shown in Equations (7)–(9).

\[
C_t = C_0 - k_0 t \quad (7)
\]
\[
\ln C_t = \ln C_0 - k_1 t \quad (8)
\]
\[
\frac{1}{C_t} = \frac{1}{C_0} + k_2 t
\] (9)

Linear regression analyses based on zero-, first-, and second-order reaction kinetics for the decolorization of MB dye through Fenton, photo-Fenton, FSWO processes were conducted to obtain the values of \(k_0\), \(k_1\), and \(k_2\), for which the results are shown in Table 4.

COD removal efficiencies were also investigated for MB dye and real textile wastewater treatment (Figure 7). The results depicted that COD removal efficiencies were 95.5\%, 100\%, 98.5\% for Fenton, photo-Fenton, FSWO processes, respectively. However, COD removal efficiencies for real textile wastewater were lower than MB dye. COD removal efficiencies were 50.9\%, 64.0\%, 61.1\% for Fenton, photo-Fenton, FSWO processes, respectively. The lower COD efficiency can be attributed to the hardly degradable material in textile wastewater such as additive materials and dyes. In previous study, the COD removal reached 72\% after 24 h (Vilardi et al. 2020).

Figure 6 | Second-order – model fitting for (a) Fenton process, (b) photo-Fenton process, (c) FSWO process.
Table 4 | MB dye decolorization percentages after 60 min through Fenton, photo-Fenton, FSWO processes, apparent kinetic rate constants of the zero- \( k_0 \), first- \( k_1 \), and second-order \( k_2 \)

| Reaction Systems | Dye concentration (mg/L) | Decolorization (%) | Zero Order | First Order | Second Order |
|------------------|-------------------------|--------------------|------------|-------------|--------------|
|                  |                         |                    | \( k_0 \) (mg/L.min) | \( k_1 \) (1/min) | \( k_2 \) (L/mg.min) |
| Fenton           | 50                      | 97.04              | 0.094      | 0.026       | 0.009        |
|                  | 100                     | 93.76              | 0.213      | 0.018       | 0.002        |
|                  | 250                     | 86.80              | 0.758      | 0.015       | 0.001        |
| Photo-Fenton     | 50                      | 98.76              | 0.009      | 0.011       | 0.001        |
|                  | 100                     | 98.82              | 0.132      | 0.035       | 0.013        |
|                  | 250                     | 96.00              | 1.028      | 0.034       | 0.013        |
| FSWO             | 50                      | 100                | 0.015      | 0.336       | 13.197       |
|                  | 100                     | 100                | 0.018      | 0.188       | 5.309        |
|                  | 250                     | 96.08              | 0.303      | 0.771       | 0.001        |

Figure 7 | COD removal efficiencies for MB dye and real textile wastewater (Experimental conditions for MB dye: Initial COD concentration: 125 mg/L, \( \text{Fe}^{2+} \) concentration = 50 mg/L, \( \text{H}_2\text{O}_2 \) concentration = 50 mg/L, pH = 2.5. (Experimental conditions for real textile wastewater: Initial COD concentration: 1,240 mg/L, \( \text{Fe}^{2+} \) concentration = 50 mg/L, \( \text{H}_2\text{O}_2 \) concentration = 125 mg/L, pH = 3.0).

4. CONCLUSION

In this study, the effects of different types of AOPs supported with hydrogen peroxide (H2O2) on the decolorization of Methylene Blue (MB) dye and viscose fibers dyeing wastewater were investigated. The degradation efficiencies for MB dye and textile wastewater via Fenton, photo-Fenton, and Fenton-supported subcritical water oxidation were compared. The effects of pH, \( \text{Fe}^{2+} \) concentration, \( \text{H}_2\text{O}_2 \) concentration, and initial dye concentration were explored. The MB dye removal efficiency increased to 97.22, 100, and 100% for Fenton, photo-Fenton, and FSWO processes, respectively, at pH 2.5, 50 mg/L \( \text{Fe}^{2+} \) concentration, and 125 mg/L \( \text{H}_2\text{O}_2 \) concentration. The maximum color removal efficiencies of viscose fibers dyeing wastewater were obtained 56.94%, 61.26%, 64.11% for Fenton, photo-Fenton, FSWO processes, respectively. The degradation of MB dye was fitted to the second-order kinetic model. All the oxidation processes supplied high dye removal, but the FSWO was the best.

DECLARATION OF INTERESTS

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.
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