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Treatment of wastewater containing Reactive Red 239 using Fenton oxidation processes with photo-assisted regeneration of Fe^{2+} catalyst

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ABSTRACT

The decolorization of Reactive Red 239 (RR239) dye using the Fenton method and photo-assisted Fenton oxidation (photo-Fenton) was investigated. The effects of experimental parameters including concentrations of Fenton's reagents, pH, and light intensity on the decolorization efficiency and initial rate constant of RR239 were evaluated. As the concentration of Fenton's reagents increased, the decolorization efficiency increased because of quick oxidation and Fe^{2+}-consumption. At pH 3, complete decolorization of RR239 was attained in 10 min using Fe^{2+} and H_2O_2 concentrations of 0.075 and 5 mM, respectively. Decolorization efficiency improved when using photo-assistance to regenerate Fe^{2+} catalyst. At 2 min, both Fenton oxidation and photo-Fenton oxidation using 9 W of UV light decolorized RR239 by 65%, but the initial rate constant was higher using 9 W photo-assistance. Moreover, 18 W of UV yielded the highest RR239 decolorization of 72% at 2 min with an initial rate of 28.01 mM^{-1} min^{-1}. A further increase in UV light intensity from 18 to 27 W depressed the initial rate constant. Chemical oxygen demand (COD) and total organic carbon (TOC) removals were 60% and 30%, respectively, under 18 W-assisted oxidation on Fe^{2+} catalyst. The energy cost of photo assistance was used to calculate the most efficient method for COD and TOC removal.

Keywords: Decolorization; Dye wastewater; Fe^{2+} consumption; Fenton oxidation; photo assistance; Reactive Red 239

1. Introduction

Currently, colored substances are extensively discharged by various industries, including the dye, textile, cosmetics, printing, paper, food, and plastics industries [1,2]. Dyes can be defined as a type of coloring particles that differ from other particles in their chemical composition and are used for coloring fabrics. Wastewater from dyeing and finishing factories is a significant source of environmental pollution [3]. Dye discharged to aquatic systems can cause negative effects such as (1) reduced light penetration, (2) decreased photosynthesis rate by aquatic plants, (3) reduced dissolved oxygen, (4) carcinogenic effects, and (5) the generation of toxic compounds in aquatic environments due to the release of harmful chemical compounds [2,4]. Dye contaminants released into water bodies consume the dissolved oxygen

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that is needed for aquatic life. Finally, dyes are directly toxic to the ecosystem and are resistant to treatment [2,5]. Azo dyes, which account for more than 50% of total dyes used, are very difficult to degrade due to their stable molecular structure with at least one azo bond (–N=N–) linked to an aromatic ring. The mono-azo dye Reactive Red 239 (RR239) is well-known and has been intensively used in the textile industry for dyeing cotton and polyester fabrics [6,7]. The chemical structure and properties of RR239 are reported in Table 1. The identified adverse effects of RR239 include reduced embryonic survival and hatching rates of zebrafish and high rates of morphological deformities [8]. Therefore, the treatment of dye wastewater containing RR239 is required before releasing it into an aquatic environment.

Previous studies have shown that several azo dyes can be successfully treated using Fenton oxidation, which is an Advanced Oxidation Process (AOP) technology used to degrade a wide range of dye pollutants [9,10]. Several azo dyes can be effectively degraded through Fenton oxidation via the reaction between hydrogen peroxide (H_2O_2) and ferrous ions (Fe^{2+}) in acidic condition to produce highly reactive hydroxyl radicals ($^{\bullet}OH$), which are a highly reactive ($E° = 2.8$ V) and non-selective oxidant, leading to the degradation of organic compounds. Advantages of the Fenton process include fast reaction time, low cost, non-toxicity, ease of controlling the reaction, and a high degradation rate with effective removal [11,12]. The $^{\bullet}OH$ produced in Fenton oxidation preferentially attacks the –N=N– bond of an azo dye molecule by cleaving the substituted and main groups and producing small aromatic rings and inorganic products. When treating dye wastewater containing an –N=N– group, the objective is to decolorize the azo dye by destroying the –N=N– group to increase the biodegradability and reduce the COD. The degradation of aromatic organic compounds by Fenton oxidation leads to the formation of simpler products such as maletic acid, oxalic acid, acetic acid, and finally CO_2 as the mineralization process progresses [13–15]. Stupar et al. [14] reported that the aromatic ring of Acid Blue 111 was opened by the cleavage of C(1)-N and C(4)-N bonds followed by the formation of phthalic acid and 1,4 dihydroxybenzene, which led to the formation of carboxylic acids, for example, formic, acetic, and oxalic acids, and finally to CO_2 and water [14]. Acid Blue 80 degradation by Fenton/ozonation was also found to decompose the ring-opening intermediate products through oxidation to products with lower molecular weight, finally resulting in oxalic acid, CO_2, and water [15]. Nevertheless, a large amount of sludge (ferric hydroxide) was produced during the process, and the high concentration of Fenton reagents may have caused a side effect that consumed $^{\bullet}OH$ [16]. The optimum treatment for wastewater by Fenton oxidation therefore requires investigation because the ferrous ions generated during the process need to be reduced for an efficient reaction. To avoid those problems, photo assistance of Fenton oxidation, namely photo-Fenton oxidation, has been identified as having great potential to improve Fenton oxidation and decrease its adverse effects. Photo-Fenton oxidation contributes to the regeneration of the Fe^{2+} catalyst and the production of $^{\bullet}OH$ by photodegradation of H_2O_2 under UV light [17–19]. For the aforementioned phenomenon, these mechanisms could facilitate the formation of $^{\bullet}OH$ and promote the degradation of organic compounds and the degradation rate. In spite of its potential, however, photo-Fenton oxidation is still seriously limited by its high cost and energy requirement. To our knowledge, there is little previous work on RR239 treatment via Fenton oxidation, but there are reports of RR239 treatment by ozonation, a kind of AOPs. The results of that treatment indicated that 50 mg L^{-1} RR239 was decolorized more than 95% in 4 min and COD removal was 62% after 25 min of the ozonation process, but it consumed almost 40 mg L^{-1} ozone [6].

In this study, we attempted to obtain the optimum decolorization efficiency of RR239 using Fenton oxidation and photo-assistance of Fe^{2+} catalyst. The decolorization of RR239 by oxidation via Fenton and photo-Fenton processes have rarely been reported. The main motivation for this work is the application of the Fenton oxidation process with the assistance of UV light and with Fe^{2+} as the catalyst for decolorization of RR239 in wastewater. The effects of operating parameters such as Fenton reagents, pH, and UV light intensity on RR239 decolorization and kinetics were also investigated. We report the change in Fe^{2+} concentration overtime during the reaction and the energy consumption of the treatment of RR239 for Fenton and photo-assisted Fenton oxidation on Fe^{2+} catalyst.

2. Materials and methods

2.1. Chemicals and materials

Reactive Red 239 (RR239) was supplied by DyStar Thai Ltd., Co., (Samutprakarn, Thailand). The properties of RR239 are shown in Table 1. Hydrogen peroxide (H_2O_2, 30% w/w, Merck, Germany), and ferrous sulfate heptahydrate ($FeSO_4{\cdot}7H_2O$, Qrec, New Zealand) were used for the Fenton experiment. The pH was adjusted using either sulfuric acid (H_2SO_4, Qrec, New Zealand) or sodium hydroxide (NaOH, Carlo Erba, France). All chemicals used were analytical grade with no further purification. Deionized water was used throughout the study.

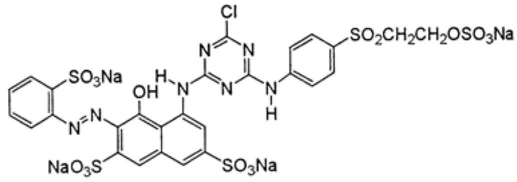
2.2. Fenton experiment

The experiments were conducted in a 1 L batch reactor with a magnetic stirrer (Stuart, CB162, England). The reactor was filled with 100 mg L^{-1} of synthetic RR239 wastewater. The initial pH of the solution was measured using a pH meter (Denver Instrument, UltraBasic, USA) and adjusted to the desired value using either H_2SO_4 or NaOH. After pH adjustment, a predetermined amount of $FeSO_4$ was added as the source of Fe^{2+}. The Fenton reaction was then started by adding H_2O_2 into the reactor. At time points of 0, 1, 2, 5, 10, 20, and 30 min, 1 mL of sample was taken from the reactor and immediately injected into a tube containing 4 mL of 0.01N NaOH to stop the Fenton reaction.

2.3. Photo-Fenton experiment

During the photo-Fenton process, the initial concentration of RR239 was again 100 mg L^{-1} for all experiments. The pH and $FeSO_4$ concentration obtained from the Fenton experiment were also applied here. The H_2O_2 was added and UV-C lights were turned on at the same time to activate the Fenton reactions. The synthetic wastewater containing

Table 1
Reactive Red 239 property

Dye	Reactive Red 239
Code	RR239
Commercial name	Reactive Brilliant Red 3BS
Chemical formula	$C_{31}H_{19}ClN_7Na_5O_{19}S_6$
Chemical structure	
Molecular weight (g mol^{-1})	1,136
λ_{max} (nm)	540

RR239 was irradiated by UV-C lights (9 Watts) that were installed outside of the reactor. Samples of 1 mL were taken at the predetermined time intervals following the same process as for the Fenton experiment.

2.4. Analytical method

The dye concentration was determined based on the absorbance of the sample (λ_{max} = 540 nm) measured by a spectrophotometer. The standard curve of RR239 was used to determine the concentration. The decolorization efficiency (DE) was then defined by the following expression:

$$\mathrm{DE}(\%) = \left(1-\frac{C_t}{C_0}\right)\times 100 \tag{1}$$

where C_0 and C_t are the concentrations at times 0 and t, respectively.

The data concerning the first 5 min were used to estimate the initial rate of RR239 decolorization (r):

$$r = \frac{\Delta[\mathrm{RR239}]}{\Delta t} = \left(\frac{[\mathrm{RR239}]_0-[\mathrm{RR239}]_5}{t_0-t_5}\right) = k_{\mathrm{obs}}[\mathrm{RR239}] \tag{2}$$

where $[\mathrm{RR239}]_0$ and $[\mathrm{RR239}]_5$ are the concentrations of RR239 in the solution at times 0 and 5 min, respectively, k_{obs} is the degradation rate constant, and t_0 and t_5 are the reaction times at 0 and 5 min, respectively.

The Fe^{2+} concentration was determined using the phenanthroline method [20]. The 1 mL sample was filtrated using 0.45 µm of cellulose acetate membrane (Verticlean) to remove the precipitates formed. The permeate sample was added to 1,10-phenenthroline agent. Then, DI water was added to obtain a volume of 50 mL before analyzing the sample with a Genesis 20UV-VIS spectrophotometer (λ_{max} = 510 nm). DI water mixed with sample without phenanthroline was used as a blank for every sample. The concentration was interpolated from a standard curve.

The COD of treated dye wastewater was determined by the closed-reflux titrimetric method based on the standard methods [20]. Analysis of total organic carbon (TOC) was performed using a multi N/CÒ 3100 TOC/TN analyzer (Analytik Jena AG, Jena, Germany) with catalytic oxidation on cerium oxide at 850°C. The carrier gas was air zero with a flow rate of 200 mL min^{-1}. Calibration of the analyzer was achieved with potassium hydrogen phthalate (99.5%, Merck) as the standard for total carbon.

3. Results and discussion

3.1. Effect of pH

The initial pH of the reaction is an important factor for RR239 decolorization. It is well-known that Fenton reactions have the highest efficiency when the pH is around 2–4 due to the solubility of Fe^{2+}. For this experiment, the pH of RR239 synthetic dye wastewater was adjusted to 2, 3, 5, and 6.25 (initial pH of RR239 solution), as shown in Fig. 1a. At 0–5 min, the RR239 was decolorized and Fe^{2+} was degraded very rapidly because of the Fenton reaction in which Fe^{2+} reacts with H_2O_2 very quickly to generate hydroxyl radicals ($^{\bullet}OH$) [21]. Then, RR239 molecules could be oxidized by $^{\bullet}OH$, as shown in reactions (3) and (4) [17,19,22].

$$\mathrm{Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^-}\ \left(k = 40-80\ \mathrm{M^{-1}\ s^{-1}}\right) \tag{3}$$

$$\mathrm{{}^{\bullet}OH + organic \rightarrow products} \tag{4}$$

The results showed that the RR239 was completely decolorized at pH 3 after 10 min, while the RR239 was decolorized only 10%–25% at pH 2, 5, and 6.25. At pH < 3, the proton (H^+) acts as a scavenger of $^{\bullet}OH$ in solution to react with hydrogen peroxide (H_2O_2) and form an oxonium ion ($H_3O_2^+$), making the H_2O_2 electrophilic and reducing its reactivity with Fe^{2+} [23]. At lower pH, the decolorization efficiency is decreased because $^{\bullet}OH$ is scavenged by hydronium ions, causing decomposition of H_2O_2 into O_2 and H_2O [24] as shown in reactions (5) and (6).

$$\mathrm{H_2O_2 + H^+ \rightarrow H_3O_2^+} \tag{5}$$

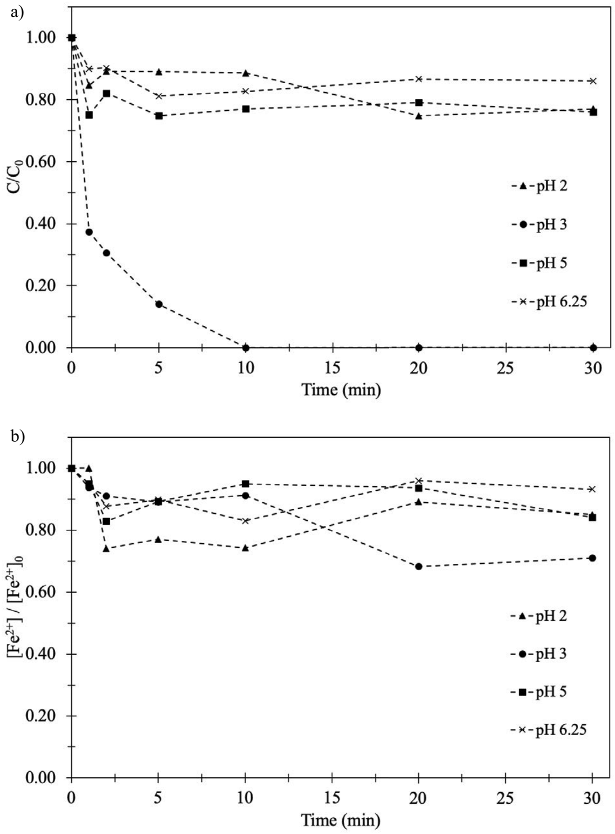


Fig. 1. Effect of pH on decolorization of RR239 under initial concentration of RR239 = 100 mg L^{-1}, Fe^{2+} concentration = 0.15 mM, and H_2O_2 concentration = 5 mM: (a) removal of RR239, and (b) remaining of Fe^{2+} during Fenton oxidation.

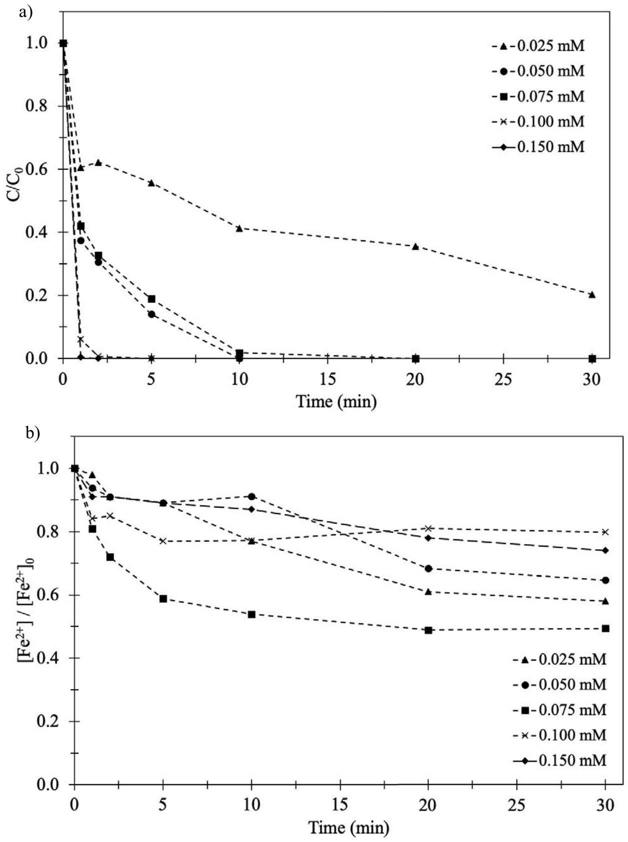


Fig. 2. Effect of Fe^{2+} concentration on decolorization of RR239 under initial concentration of RR239 = 100 mg L^{-1}, initial pH 3.0, and H_2O_2 concentration = 5 mM: (a) removal of RR239, and (b) remaining of Fe^{2+} during Fenton oxidation.

$$^{\bullet}OH + H^+ \rightarrow H_2O \tag{6}$$

The above results suggest that the Fenton's reaction was feasible at the unchanged pH; nevertheless, the RR239 decolorization efficiency decreased significantly when the initial pH increased from 3 to 6.25, as presented in Fig. 1a. The RR239 decolorization was only 24% at pH 6.25. This was because Fe^{2+}, which is the substrate for the Fenton process, is not stable at pH 5 [25] and forms into $Fe(OH)^{2+}$, $Fe(OH)_3$, and $Fe(OH)_4^-$ [26]. Moreover, the generated hydroxide could decompose and finally became oxygen, leading to decreased production of $^{\bullet}OH$ at higher pH values [27,28]. When the pH was increased to a near-neutral condition, the $^{\bullet}OH$ was not strong compared to acidic conditions [29]. This precipitation can also lead to an increase in the turbidity of the RR239 solution, resulting in less Fenton oxidation. It was concluded that the RR239 cannot be treated effectively by the conventional Fenton process at either low or high pH. The residual of Fe^{2+} was measured over time, and the results found that the remaining Fe^{2+} after 20 min was constant, as illustrated in Fig. 1b, related to the RR239 decolorization. It was observed that almost all Fe^{2+} was consumed or degraded to Fe^{3+} within 2 min after the Fenton oxidation started. During the Fenton reaction for all pHs, the Fe^{2+} consumption rates were 0.03–0.11 mM min^{-1} in the first 2 min, which decreased to 0.002 to 0.009 mM min^{-1} for the remaining reaction period, leading to increased $^{\bullet}OH$ generation to oxidize the RR239. The Fe^{2+} consumption at the final step was highest at pH 3 (0.009 mM min^{-1}), which accordingly supported the maximum RR239 decolorization. In contrast, at pH values 2, 5 and 6.25, the RR239 decolorization dropped later in the reaction period, possibly because the generation of $^{\bullet}OH$ was low and the Fe^{2+} unstable in the RR239 solution. A study by Matira et al. [30] also reported that Fe^{2+} decreased sharply within 3 min leading to quick removal of dimethyl sulfoxide (DMSO) by ordinary Fenton and fluidized-bed Fenton processes due to the transformation of Fe^{2+} to Fe^{3+}, then the remaining Fe^{2+} in the system was negligible.

3.2. Effect of initial Fe^{2+} concentration

The initial Fe^{2+} concentration is one of the main important parameters that influence the RR239 decolorization, as shown in Fig. 2a. Keeping the other parameters constant, the RR239 was completely decolorized with Fe^{2+} concentrations of 0.05, 0.075, 0.100, and 0.150 mM after 10, 20, 2, and 1 min, respectively. RR239 wastewater was decolorized by the $^{\bullet}OH$ radicals produced by Fenton process Eqs. (3) and (4), resulting in the color change from red to yellowish. This enhancement was due to the acceleration in H_2O_2 consumption caused by the reaction with the Fe^{2+} catalyst. In contrast, incomplete decolorization (80%) of RR239 took place in 30 min under 0.025 mM H_2O_2 due to the limitation of $^{\bullet}OH$ generation. The consumption of Fe^{2+} was constant after 20 min because the RR239 degradation was complete and the remaining H_2O_2 would removal due to the addition of H_2O_2 at once at the beginning, while the highest Fe^{2+} consumption to stimulate the Fenton oxidation was 0.075 mM. It can be seen from Figs. 2a and b that the RR239 decolorization and the decomposition of Fe^{2+} during the Fenton oxidation could be divided into two steps. After H_2O_2 was added to the RR239 solution, the color of RR239, and the concentration of Fe^{2+} decreased immediately (Step 1) for approximately 2 min. Subsequently, RR239 and Fe^{2+} gradually decreased (Step 2). This result was similar to a previous finding that the decolorization of Reactive Black 5 by the Fenton process increased with increased Fe^{2+} concentration [31].

The residual Fe^{2+} over time was observed after the addition of H_2O_2. It was observed that Fe^{2+} was consumed quickly, within 2 min after the start of the Fenton reaction. During the Fenton reaction, the Fe^{2+} consumption rates were 0.034–0.13 mM min^{-1} in the first 2 min and decreased to 0.01–0.03 mM min^{-1} after 30 min. It was also observed that at 0.75 mM of Fe^{2+}, the RR239 decolorization was complete in 20 min but the consumption of Fe^{2+} was highest compared to other concentrations, indicating an effective Fe^{2+} reaction with H_2O_2 resulting in quick decolorization due to the effective $^{\bullet}OH$ reaction. This result was similar to the decrease of Fe^{2+} over time observed for the treatment of *o*-toluidine by Fenton oxidation in that the Fe^{2+} consumption rate at an initial step was faster than that of the final step [32]. According to the results, the addition of excess Fe^{2+} not only increases the operational costs and the accumulation of sludge but also facilitates the scavenging effect of $^{\bullet}OH$ by Fe^{2+} in reaction (7), which has a negative effect on Fenton oxidation [19,33]. Thus, it was necessary to establish the optimum loading of Fe^{2+} to oxidize RR239.

$$Fe^{2+} + {}^{\bullet}OH \rightarrow Fe^{3+} + OH^{-} \left(k = 2.5 - 5 \times 10^{8} M^{-1}s^{-1}\right) \tag{7}$$

The Fe^{2+} concentration of 0.075 mM was selected as the optimum condition for further studies due to the complete RR239 decolorization and the lowest amount of residual Fe^{2+} after Fenton oxidation.

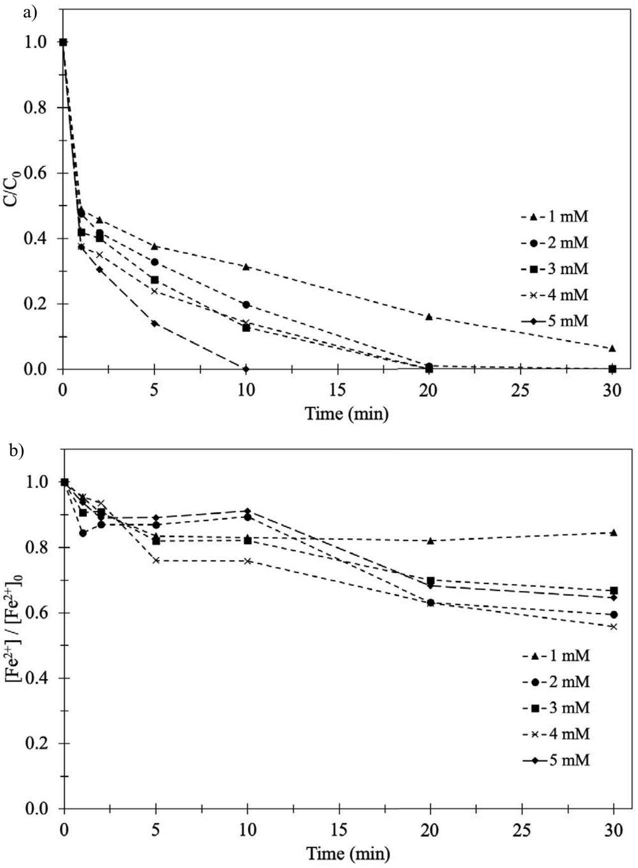


Fig. 3. Effect of H_2O_2 concentration on decolorization of RR239 under initial concentration of RR239 = 100 mg L^{-1}, initial pH 3.0, and Fe^{2+} concentration = 0.15 mM: (a) removal of RR239, and (b) remaining of Fe^{2+} during Fenton oxidation.

3.3. *Effect of initial H_2O_2 concentration*

Optimization of H_2O_2 is another critical factor in decolorization of RR239 that is important to investigate. In this study, the effect of initial H_2O_2 concentration on the decolorization of RR239 by the Fenton process was examined over the range of 1–5 mM, and the results are given in Fig. 3. The results showed that an increased H_2O_2 concentration could promote RR239 decolorization and that the RR239 was completely decolorized after 30 min. The decolorization of RR239 was accomplished rapidly given a high initial H_2O_2 concentration. The RR239 was rapidly decolorized in the first 10 min under an H_2O_2 concentration of 5 mM; in contrast, the complete decolorization of RR239 under 2–4 mM of H_2O_2 occurred after 20 min, as shown in Fig. 3a. At an initial H_2O_2 concentration of 1 mM, the RR239 was decolorized only 84% after 20 min of Fenton oxidation, which was slower than that at 2–4 mM. The efficiency of RR239 decolorization also fell to 94% at 1 mM. This significant difference was due to the abundance of $^{\bullet}OH$ generated by the Fenton reaction in the presence of a higher H_2O_2 concentration, in accordance with Eqs. (2) and (3). It can be explained by the fact that as the concentration of H_2O_2 increased, more molecules of H_2O_2 were available to react with Fe^{2+}, which increased the number of $^{\bullet}OH$, leading to oxidation of RR239. As with Fe^{2+}, an excessive concentration of H_2O_2 also presented a negative effect by competing with $^{\bullet}OH$ to oxidize organic compounds in reaction (8) [19].

$$H_2O_2 + {}^{\bullet}OH \rightarrow H_2O + {}^{\bullet}O_2H \left(k = 1.7 - 2.5 \times 10^{8} M^{-1}s^{-1}\right) \tag{8}$$

Fig. 5b shows the consumption of Fe^{2+} during the decolorization of RR239 by Fenton oxidation. The H_2O_2 concentrations higher than 3 mM were highly consumed within the first 5 min. It was observed that almost all of the Fe^{2+} was consumed or degraded very quickly within 2 min after the reaction started. The Fe^{2+} consumption rates in

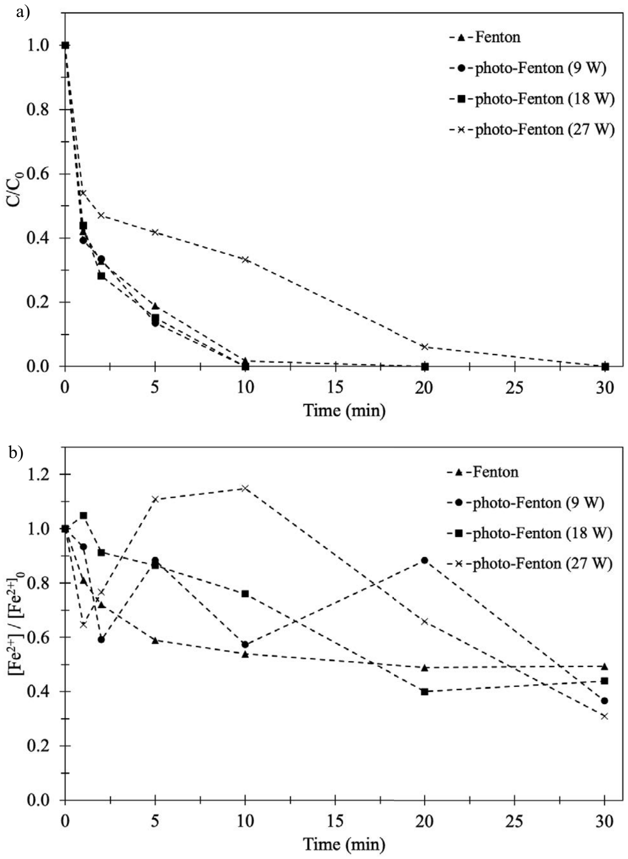


Fig. 4. Effect of UV light intensity on decolorization of RR239 under initial concentration of RR239 = 100 mg L^{-1}, pH 3.0, Fe^{2+} concentration = 0.075 mM, and H_2O_2 concentration = 5 mM: (a) removal of RR239, and (b) remaining of Fe^{2+} during Fenton and photo-Fenton oxidation.

the first 2 min were 0.04–0.07 mM min^{-1}, compared with 0.007–0.02 mM min^{-1} after 60 min. This observation was supported by the rapid RR239 decolorization in step 1 of the Fenton reaction. This occurs because H_2O_2 reacts readily with Fe^{2+} to generate $^{\bullet}OH$, followed by the oxidized RR239. This result is similar to the removal of aniline from wastewater using the electro-Fenton process, where the remaining Fe^{2+} increased with excess H_2O_2 after 10 min due to the reduction of Fe^{3+} from Fe^{2+} regeneration on the cathode side [13]. An optimum dosage of H_2O_2, therefore, is necessary for RR239 decolorization via Fenton oxidation, as excess H_2O_2 is not encouraged.

3.4. Effect of UV lights

The light intensity is also an important factor that affects the performance of photo-assisted Fe^{2+} catalyst oxidation. The experimental conditions of initial Fe^{2+} and H_2O_2 concentrations of 0.075 and 5 mM, respectively, at pH 3 obtained from the Fenton experiment were selected to study the effect of light intensity on RR239 decolorization. Light intensities of 9–27 W were supplied. Fig. 4a reveals that the decolorization efficiency of RR239 under a light intensity of 9 W was as high as Fenton oxidation for the first 5 min of the reaction, followed by complete decolorization after 30 min. However, the decolorization efficiency of RR239 in the first 5 min was increased to 72% with an increase in light intensity to 18 W. This was because the UV irradiation could regenerate the Fe^{2+} and produce $^{\bullet}OH$ by photoreduction of $Fe(OH)^{2+}$, according to Eq. (9) [17–19]. In addition, UV illumination could also increase the production of $^{\bullet}OH$, as shown in Eq. (10) [17,18,29], and the photolysis of a complex of Fe^{3+} with some oxidation product could lead to the regeneration of Fe^{2+}, as in Eq. (11) [34,35]. Thus, RR239 decolorization increased when exposed to UV. This could significantly reduce the amount of sludge produced due to the lower dose of iron required for Fenton oxidation.

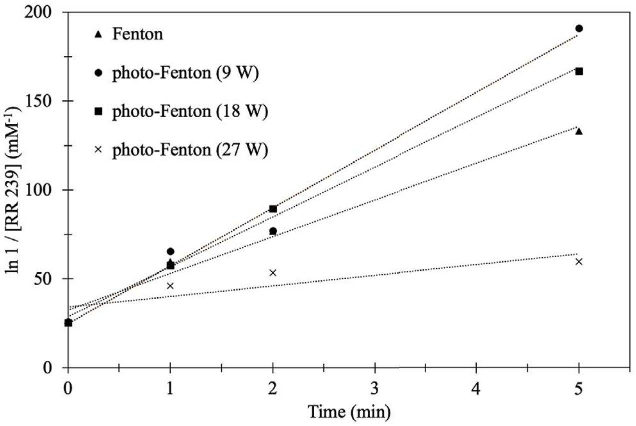


Fig. 5. Effect of UV light intensity on rate constant (k_{obs}) under initial concentration of RR239 = 100 mg L^{-1}, initial pH 3.0, Fe^{2+} concentration = 0.075 mM, and H_2O_2 concentration = 5 mM.

$$Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + {}^{\bullet}OH\left(k = 0.0012\ s^{-1}\right) \tag{9}$$

$$H_2O_2 + h\nu \rightarrow 2{}^{\bullet}OH\left(k = 0.5\ s^{-1}\right) \tag{10}$$

$$Fe\left(RCO_2\right)^{3+} + h\nu \rightarrow Fe^{2+} + CO_2 + R^{\bullet} \tag{11}$$

Fig. 4b shows the profile of Fe^{2+} remaining during the Fenton and photo-Fenton processes. The results found that Fe^{2+} was quickly consumed by the reaction with H_2O_2 to generate $^{\bullet}OH$ during the first 2 min, as presented in Eq. (3). Then, under UV irradiation for photo-Fenton, after 2 min Fe^{2+} fluctuated due to the regeneration and the instability of Fe^{2+}. Moreover, the amount of remaining Fe^{2+} did not differ depending on the completeness of RR239 decolorization. It was observed that the Fe^{2+} remaining in the Fenton oxidation gradually decreased, whereas, for the Fenton oxidation assisted by a 9 W light intensity, the Fe^{2+} remaining at 5 min (0.99 mM) was higher than that at 2 min (0.664). During the first 5 min of the reaction, Fe^{2+} consumption rates were 0.49, 0.131, 0.157, and 0.096 mM min^{-1} for the ordinary Fenton and the 9, 18, and 27 W photo-Fenton oxidations, respectively, which decreased to only 0.020–0.024 mM min^{-1}. This observation is also related to the RR239 decolorization in step 1 of the oxidation. The amount of Fe^{2+} was highest for

27 W, which was higher than the initial concentration due to the high supporting light intensity.

It was noted that the light intensity had a negative effect on the RR239 decolorization by the photo-Fenton reaction. This phenomenon was attributed to the scavenging effect, as explained in Eqs. (9) and (11). The increase of light intensity from 18 to 27 W could result in faster regeneration of Fe^{2+}, and Fig. 4b illustrates that a higher Fe^{2+} concentration was observed under higher light intensity, thereby enhancing Fe^{2+} abundance for $^{\bullet}OH$ production. As a result, the RR239 decolorization was decreased from 100% to 67% when light intensity increased from 18 to 27 W after 10 min. Additionally, the complete decolorization of RR239 under 27 W took 30 min compared to 10 min in other reactions.

A more detailed analysis of the individual COD and TOC profiles during the treatments highlights the different performances of the Fenton process and the photo-assisted Fenton process with different light intensities. It can be seen in Table 2 that all of the Fenton oxidations completely decolorized RR239 and decreased COD. The COD was reduced by more than 50%, being slightly higher for the photo-Fenton process with 9 W. This result indicates that the photo-assisted oxidation on Fe^{2+} catalyst is more efficient at decolorizing RR239 compared to the ordinary Fenton oxidation. This was due to the increased Fe^{2+} regeneration under photo-assistance, which can increase the amount of $^{\bullet}OH$ produced as in Eq. (9). Moreover, the removal efficiencies for TOC in the photo-Fenton reactions with 9 and 18 W were 39% and 36%, respectively. These phenomena show that the organic compounds (by-products) were efficiently mineralized with the assistance of UV light. The presence of UV radiation contributed to the reduction of Fe^{3+} to Fe^{2+}, resulting in a cycle of Fenton oxidation and strongly increasing COD and TOC removals. However, the TOC removal by the photo-Fenton oxidation with 27 W was only as high as the traditional Fenton (30%) due to the scavenging effect of Fe^{2+}. As a consequence, the amount of residual Fe^{2+} and the rate of Fe^{2+} consumption under 27 W were higher than under 9 and 18 W, leading to an insufficient amount of H_2O_2 to utilize the Fe^{2+}. This means that the Fe^{2+} was consumed slower than it was produced. This was the same result previously seen for the use of electro-Fenton for the regeneration of Fe^{2+} for aniline wastewater treatment. The results of that work found that the amount of Fe^{2+} remaining in the solution was increased after electricity was applied, after which the aniline, COD, and TOC removal rates increased [36]. The COD and TOC removals were possibly due to both photolysis and $^{\bullet}OH$ oxidation during photo-Fenton oxidations. In addition, $^{\bullet}OH$ preferentially attacks the azo-bond (–N=N–), and the optimal molar ratio of $[H_2O_2]/[Fe^{2+}]$ for RR239 decolorization was 67:1 but the theoretical molar ratio should be 11. However, the optimal molar ratio is different for decolorization of different azo dyes. For instance, the optimal molar ratio of $[H_2O_2]/[Fe^{2+}]$ was 50:1 with pH 3 for 50 mg L^{-1} Reactive Black 5 [31] and 11:1 at pH 3 for 300 mg L^{-1} Drimaren Orange HF 2GL [37]. This was possibly due to the fact that RR239 contains not only an azo group but also several sites such as hydroxylate biphenyl and benzene rings that might take part in competing $^{\bullet}OH$ reactions. Nevertheless, it was important to note that the $[H_2O_2]/[Fe^{2+}]$ molar ratio did not interfere with the RR239 degradation, as the $^{\bullet}OH$ was consumed to degrade the target compound at all times. It can be concluded that Fenton oxidation alone is not sufficient to oxidize both COD and TOC from RR239-contaminated wastewater. In summary, photo-assisted oxidation is expected to play an important role in enhancing RR239 degradation in Fenton oxidation owing to the acceleration of Fe^{3+} to Fe^{2+} by the energy provided, resulting in increased $^{\bullet}OH$ generation and decreased Fe^{2+} input.

3.5. Degradation kinetics

Rapid, almost complete decolorization of RR239 was observed in the first 2 min; therefore, the data collected in the first 2 min of the Fenton reaction were used to calculate the degradation rate. Three different kinetic models, including zero-order, first-order, and second-order, were used to fit the experimental data obtained from the decolorization by Fenton oxidation. The results indicated that a second-order reaction exhibited the highest correlation coefficients, while the fits of the zero-order and first-order models were not good due to low R^2. Therefore, the second-order model was used to describe the kinetics. Eq. (2) can be simplified to Eq. (12) and the relationship of ln1/[RR239] vs. time plotted to generate a straight line, as presented in Fig. 5, and the value of the initial second-order reaction rate constant can be obtained from the slope.

$$\ln\left(\frac{1}{\left[\text{RR239}\right]}\right) = k_{\text{obs}}t \qquad (12)$$

Table 2
RR239 decolorization and rate constant of RR239 in Fenton and photo-Fenton oxidations

Process	RR239 decolorization efficiency[a] (%)	COD removal efficiency[b] (%)	TOC removal efficiency[b] (%)	Initial rate[a] (mM^{-1} min^{-1})	R^2	Energy cost (kW h kg^{-1} COD)
Fenton	67	51.8	30.5	20.68	0.9812	7,257
Photo-assisted on Fe^{2+} catalyst						
9 W	67	60.2	39.3	32.53	0.9964	6,346
18 W	72	56.2	36.6	28.01	0.9964	6,915
27 W	53	52.6	29.8	5.95	0.7189	7,532

[a] 2 min of Fenton oxidation.

[b] 30 min of Fenton oxidation.

The initial rate constant and RR239 decolorization were calculated for the first 2 min and are summarized in Table 2 with the correlation coefficient (R^2). The results indicated that the RR239 decolorization efficiency in the first 2 min was highest (72%) for photo-Fenton at 18 W; in contrast, the lowest efficiency was obtained for the photo-Fenton at 27 W at 53%. Moreover, ordinary Fenton oxidation had an initial rate of 20.68 mM min^{-1}. Photo assistance at light intensities of 9 and 18 W was able to increase the initial rate constant by 1.57 and 1.35 times that of ordinary Fenton oxidation, respectively. This was mainly due to the fact that the light intensity could promote the decolorization efficiency during the photo assistance by enhancing the regeneration of Fe^{2+} followed by reaction with H_2O_2 to generate $^{\bullet}OH$. In contrast, the initial rate constant of photo-Fenton at 27 W was lowest at 5.95 mM min^{-1}. This means that the RR239 decolorization was slower compared to the other reactions and that complete decolorization took a longer time. As mentioned before, the scavenging effect of high loading of Fe^{2+} competed with H_2O_2 for the generation of $^{\bullet}OH$ to decolorize RR239.

From the overall study of Fenton oxidation and photo assistance, it can be seen that initial pH, initial concentrations of Fenton's reagents, and UV light intensity were important parameters for achieving the highest RR239 decolorization and COD and TOC removals. It was obvious that the assistance of UV light could reduce both the needed input of Fe^{2+} and the oxidation time substantially. In addition, photo-assistance could reduce the amount of sludge produced in the form of Fe^{3+}, providing an additional benefit of photo-Fenton over ordinary Fenton oxidation.

Hence, the initial degradation rate constant decreased and H_2O_2 was not efficiently used. The energy costs for the Fenton and photo-Fenton oxidations were discussed and are reported in Table 2. The operating costs of Fenton oxidation include chemicals and materials, energy consumption, and disposal costs, but the energy consumption is the main cost. The equation applied to calculate the energy cost is presented in Eq. (13):

$$\text{Energy cost}\left(\text{kW h/kg COD}\right) = \frac{\left(P \times t \times 1{,}000\right)_{\text{FO}} + \left(P \times t \times 1{,}000\right)_{\text{UV}}}{V \times \Delta\text{COD}} \tag{13}$$

where P is the rated power (kW), V is the volume (L) of wastewater, t is the reaction time (h), ΔCOD is the difference between the initial COD of RR239 and the final COD after treatment, FO is the electrical power used in the Fenton oxidation to operate the magnetic stirrer (500 W), and UV is the light energy used in each photo-assisted oxidation on Fe^{2+} catalyst.

According to Eq. (11), the energy cost increases when the light intensity applied increases. The energy cost should be considered when applying photo-Fenton oxidation. The results found that photo-assistance could reduce the energy required to remove 1 kg of COD. The energy consumption of the photo-Fenton reaction with 9 W was more efficient than that with 18, 27 W, and ordinary Fenton. Consequently, the energy cost should be one factor to consider when applying photo-assisted oxidation on Fe^{2+} catalyst to reduce the operational cost.

4. Conclusions

In this work, high efficiencies of ordinary Fenton and photo-assisted Fenton oxidation on Fe^{2+} catalyst for decolorization of RR239 were obtained. In the case of the ordinary Fenton process for decolorization of RR239, the parameters that affected the reaction performance include the initial concentrations of Fe^{2+} and H_2O_2 and pH. Fe^{2+} catalyst contributed with H_2O_2 was very effective for decolorizing 100 mg L^{-1} RR239 dye solution. Complete decolorization of RR239 was achieved within 30 min, but Fe^{2+} still remained in the system. The initial concentrations of the Fenton's reagents were the main important factors for the Fenton oxidation. The RR239 decolorization efficiency increased with the concentrations of Fenton reagents, while pH 3 was the best condition for oxidation. In the case of photo-Fenton, RR239 decolorization efficiency was increased and faster than ordinary Fenton oxidation due to the facilitation of Fe^{2+} regeneration. RR239 was quickly decolorized at the initial step of the reaction together with the consumption of Fe^{2+}. The initial rate constants for RR239 decolorization by photo-Fenton (9–18 W) were 1.35–1.57 times higher than the rate for ordinary Fenton oxidation. At the light intensity 27 W, the complete decolorization of RR239 slowed to 30 min and the initial rate constant decreased to less than 0.29 times the rate for ordinary Fenton. The highest COD and TOC removals achieved with Fenton oxidation were 60% and 39%, respectively, in the presence of 0.075 mM Fe^{2+} and 5 mM H_2O_2 at pH 3 with 18 W UV light assistance. Under these conditions, energy consumption was highly efficient.

Author contributions

All authors proposed the study and participated in this research and in manuscript preparation. PS and KS carried out and processed the experiment. SS designed the experiment and analyzed the results, including the effects of parameters on RR239 decolorization and kinetic studies. AK analyzed the photo-assisted Fenton oxidation experiments. This research was advised by PP. The manuscript was written with contributions from all authors. All authors read and approved the final manuscript.

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