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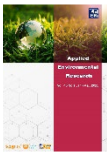

Research Article

Fenton and Photo-Fenton for Treatment of Red Water Containing Trinitrotoluene: A Comparative Study

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Abstract

Wastewater originating from the production of TNT explosives (red water) contains special hazardous substances that must be treated before discharging into the water environment. In this study, we applied both conventional Fenton and photo-Fenton (UV-Fenton) processes to treat COD and color in red water. In the Fenton process, the COD and color removal efficiencies were 75.5 and 92.4%, respectively, under optimal operating conditions of pH = 3, $[Fe^{2+}]$ = 0.3 g L^{-1}, H_2O_2/Fe(II) ratio = 10:1, reaction time = 120 min. In the UV-Fenton process, the efficiencies were 76.1 and 94.2%, respectively, under optimal operating conditions of pH = 3, $[Fe^{2+}]$ = 0.21 g L^{-1}, H_2O_2/Fe(II) ratio = 7:1, reaction time = 90 min. These results indicate that the use of ultraviolet could reduce not only the reaction time but also the chemical use (i.e. H_2O_2 and Fe^{2+}), thus reducing the sludge production. Importantly, the UV-Fenton process significantly increased the BOD_5/COD ratio from 0.13 to 0.58, which greatly enhanced the biodegradability of the wastewater for biological treatment. Therefore, UV-Fenton can be applied as an effective pretreatment in the treatment of red water with high color and organic pollutants.

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Introduction

In recent years, the defense industry has been rapidly developed due to tense issues of disputes and conflicts of interest between countries. Every year, the production facilities of explosives and defense propellants emit a large amount of wastewater into the environment. Red water and acidic water are the main types of wastewater generated during the production process at the defense explosives factory. Most of the explosives used in military and civilian are 2,4,6-trinitrotoluene (TNT), cyclotrimethyl trinitramine (RDX), and cyclotetramethylene-tetranitramine (HMX), which are toxic. These are substances listed by the US Environmental Protection Agency (EPA) as the top pollutants. Red water is generated by washing raw TNT with sodium sulfite (Na_2SO_3) to remove asymmetric TNT molecules and other impurities [1-2]. This type of wastewater often contains highly toxic and explosive components such as TNT, DNT, nitroglycerin (NG), dinitrophenol (DNP), hexogen (RDX), and octogen (HMX). In addition, it contains strongly nitrosated compounds and nitro compounds with aromatic rings such as $Ar(NO_2)XSO_3Na$, trinitrobenzene (TNB), and dinitrobenzene (DNB) – the asymmetric isomers of TNT when dissolve in sulfide-containing wastewater will produce a red color. The toxicity of organic components in red water causes significant effects on humans and the natural environment if not treated thoroughly. All nitro compounds with aromatic rings are highly toxic, chemically stable, and resistant to biodegradation. They are dangerous to

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the nervous, skin, and circulatory systems and cause dermatitis, cancer, and blood diseases. Mineralization products of TNT, when degraded by a photochemical process, can be carcinogenic or genetically modified. Thus, red water with intense color, high refractory organic content, dissolved solids, and COD must be completely treated before being discharged into the environment [3].

In Vietnam, along with the development of the defense industry, the risk of pollution by toxic substances generated during the production, storage, and use of TNT is increasing day by day. In particular, waste from TNT explosives production facilities, including red water, contains a high concentration of TNT and their asymmetric isomers, which are highly toxic, causing soil pollution, and water resources, significantly affecting human life and living organisms. Currently, red water at the Z113 factory (Tuyen Quang, Vietnam) is treated by concentration method and then burned with diesel oil. This method is not thorough because the combustion process produces a lot of toxic gases and the products that formed slag are harmful to the environment. In addition, the cost is expensive. Several methods have been applied to treat the red water from TNT production, such as incineration [4], adsorption [5–11], coagulation [12], wet air oxidation [13], vacuum distillation [14–15], photocatalysis [16–19], electrochemical oxidation [20–21], persulfate activation [22], biodegradation [23–24], Fenton process [25], and combined advanced oxidation processes (AOPs) such as Fenton/TiO_2/O_3/UV [26]. The Fenton process is based on the reaction between iron ions and hydrogen peroxide under acidic conditions creating $HO^\bullet$ radical with high redox potential (2.8 V compared to conventional hydrogen electrode) that can decompose persistent organic pollutants into compounds with lower molecular weight and toxicity and even into carbon dioxide and water. Additionally, they can be performed at room temperature and atmospheric pressure. Fenton reagents are readily available and easy to handle, are simple to make, require no special equipment, and are easily integrated into existing water treatment processes, such as coagulation, filtration, and biological treatment [27]. For wastewater containing TNT, among the technology, Fenton methods have many advantages, achieving high efficiency in the treatment of TNT, and nitro-containing compounds in the wastewater of the defense industry [28-30]. The biggest disadvantages of the Fenton process are that it works only in the low pH region, the amount of H_2O_2 required is very large to produce hydroxyl radicals, the unstable operation of Fe(II) salts, and the mineralization of pollutants may take place incompletely [31]. It also increases operating costs in terms of chemical consumption and secondary waste disposal requirements. In recent years, Fenton-like processes have emerged and are beginning to show more promise in reducing operating costs and enhancing pollutant treatment efficiency. In particular, photo-Fenton is considered a simple solution that increases the treatment efficiency of the process, thus reducing the iron and H_2O_2 contents that are necessary for the complete mineralization of the pollutant.

In this study, we conducted the treatment of the red water from the Z113 Factory (Tuyen Quang, Vietnam) by the conventional Fenton and photo-Fenton (UV 254 nm) processes. The properties of the red water were analyzed. The experiment at the laboratory was carried out to determine the influence of operating factors on the COD removal efficiency and decoloration in the wastewater as well as to find out the optimal operating conditions for the highest pollution treatment efficiency. The research results are the basis for expanding the application of this process in practice to solve serious pollution problems caused by this type of wastewater in the actual conditions of Vietnam.

Materials and methods

1) Materials

Pure chemicals, most in analytical grade, are directly used in this study without any further purification. Some of the main chemicals include $FeSO_4{\cdot}7H_2O$, H_2O_2 (30%), NaOH, H_2SO_4 (98%), $K_2Cr_2O_7$, Ag_2SO_4, and $HgSO_4$. They were all bought from Shanghai Macklin Biochemical Co., Ltd, China.

2) Methods

Red water is collected at the concentrated wastewater tank right after the step of refining TNT and neutralizing it with H_2SO_4 at factory Z113 (Tuyen Quang, Vietnam) according to TCVN 6663-1: 2011 (ISO 5667-1:2006) and TCVN 5999: 1995 (ISO 5667-10:1992). Wastewater samples were preserved and transferred to the laboratory for further use according to TCVN 6663-3: 2008 (ISO 5667-3:2003). Wastewater samples at the laboratory were analyzed for initial pollution properties such as pH (TCVN 6492:2011 (ISO 10523:2008) - SMEWW 2550 B), color (TCVN 6185:2015), suspended solids (TCVN 6625:2000 (ISO 11923:1997) - SMEWW 2540), total nitrogen (TN) (SMEWW 4500-Norg B:2012), chemical oxygen demand (COD) (ISO 6060:1989 - SMEWW 5220), and 5-Day biochemical oxygen demand (BOD5) (SMEWW 5210 B). The raw wastewater before treatment was analyzed, and the values of the parameters were taken as the average value with standard deviation, as given in Table 1.

The Fenton experiment was conducted in a 250 mL beaker. Accordingly, 100 mL of red water was taken into a cup and added with Fe(II) and H_2O_2 at the required H_2O_2/Fe(II) ratio (e.g, for the ratio of 10:1, $[H_2O_2] = 3$ g L^{-1} and $[Fe^{2+}] = 0.3$ g L^{-1}). The solution pH was adjusted using NaOH 1M or H_2SO_4 1M solutions. The solution was then stirred for 2 h to facilitate the reaction, and the COD and color of the sample were determined during the reaction time. The process of removing excess H_2O_2 was done by adding 40 mg of MnO_2, then raising the temperature to 60 – 70 °C and pH = 8–9, and stirring for 60 min. The solution was filtered through a 0.45 µm filter and then sent for COD analysis [32]. The effect of operating factors on the red water treatment was conducted in the pH range of 2–7, H_2O_2/Fe(II) ratio range of 1:1 to 30:1, Fe(II) concentration range of 0.09 - 1.2. g L^{-1}, and reaction time from 30 to 180 min. For the UV-Fenton process, Figure 1 shows the experimental setup. A UV lamp (15W, TN5-425-40, Tepro, China) surrounded by a quartz tube was used as a UV radiation source and was placed in the middle of a 2-layer reactor with water circulation to maintain the temperature of 25 °C. On the model, there are also chemical filling positions and water sampling locations. Operating factors such as pH and the ratio of H_2O_2/Fe(II) were also investigated, which was similar to the conventional Fenton process. Typically, the UV-Fenton process requires a lower amount of chemicals than the conventional Fenton. Therefore, the ratio of H_2O_2/Fe(II) ranges from 1:1 to 20:1 corresponding to the Fe(II) content range of 0.03–0.45 g L^{-1}. All the experiments were in duplicate and the results were presented in average values with errors. The experiments using only UV (no Fenton reagent) and only H_2O_2 (no Fe^{2+}, no UV) were also performed under the same experimental conditions as the UV-Fenton process.

The COD treatment and decoloration efficiency are calculated by Eq. 1.

$$H\% = \left(1 - \frac{C_t}{C_o}\right) \times 100 \qquad \text{(Eq. 1)}$$

Where C_t is COD content (mg L^{-1}) or color (Pt-Co) after treatment and C_o is COD content (mg L^{-1}) or color (Pt-Co) before treatment.

Results and discussion

1) Red water properties

The parameters of the wastewater were analyzed, including pH, color, COD, total nitrogen (TN), and total suspended solids (TSS), as presented in Table 1. Accordingly, most of the parameters exceeded the limits of the standard (Vietnam National Technical Regulation on Industrial Wastewater, QCVN 40:2011/BTNMT). Specifically, the COD and color levels were 9 and 155 times higher than those in the standard (Colum B). Therefore, this wastewater must be treated before being released into the environment.

Table 1 Analysis results of some parameters of red water

Parameter	Value	QCVN 40:2011/BTNMT
pH	7.4 ± 0.2	5.5 - 9
COD (mg L^{-1})	**1,344 ± 54.65**	150
BOD_5 (mg L^{-1})	**182 ± 7.75**	50
Color (Pt-Co)	**20,637 ± 628.71**	150
TN (mg L^{-1})	170.2 ± 1.32	40
TSS (mg L^{-1})	752 ± 17.36	100

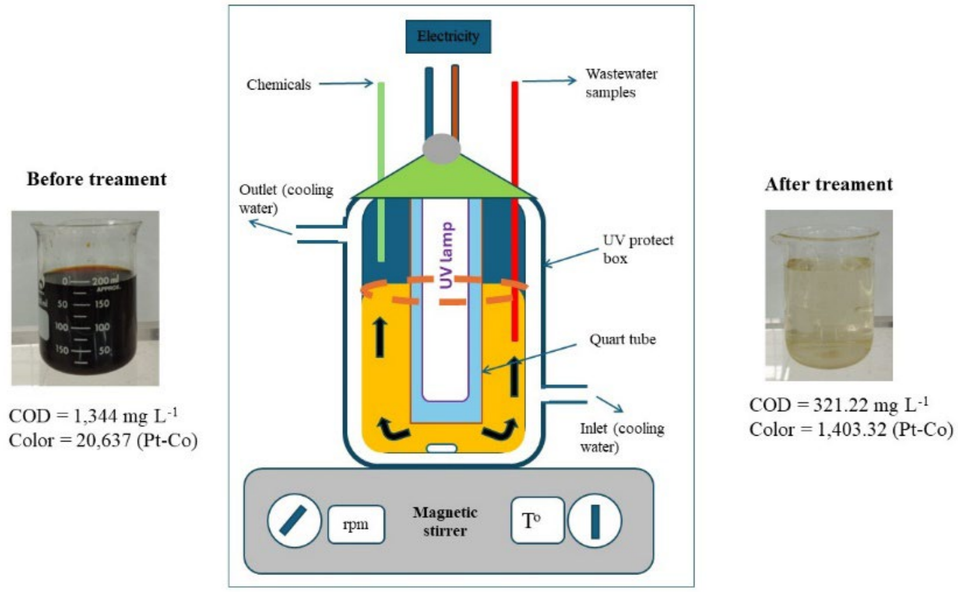

Figure 1 Experimental set-up for UV-Fenton process in red water treatment.

2) Effect of pH on red water treatment

The pH value would be the most important factor in the Fenton processes since the homogeneous Fenton processes only work well in acidic conditions. In this work, the solution pH range of 2–7 was applied to investigate the influence of pH on color and COD treatment efficiency of wastewater (Figure 2). One can clearly see that pH significantly affected the COD removal efficiency but did not significantly change the decoloration efficiency of the system. When pH ≤ 3, COD removal efficiency was more than 70%, and the color was more than 90%. When pH changed from 4 to 7, the COD removal efficiency decreased from 67.09 to 45.72% for conventional Fenton and from 66.86 to 50% for UV-Fenton. The acidic environment is a prerequisite for the generation of $HO^{\bullet}$ in the Fenton processes. When the pH increases, the concentration of HO^{-} in the solution increases, thus hindering the formation of the $HO^{\bullet}$ and promoting the precipitation of iron in $Fe(OH)_3$ form. This process occurs more rapidly than the reduction of Fe^{3+} to Fe^{2+}, resulting in reduced Fe^{2+} regeneration and decreased the Fenton reaction rate. Therefore, the COD removal efficiency significantly decreases and decoloration efficiency slightly decreases when the pH increases. At low pH of 2–3, under too high $[H^+]$, Fe^{2+} converts into $[Fe(H_2O)_6)]^{2+}$ complex form, which reacts with H_2O_2 slower than Fe^{2+} ions [33]. Besides, too high H^+ concentration condition initiates a reaction between H^+ and H_2O_2 to produce $H_3O_2^+$, which is less active with Fe^{2+} than H_2O_2. These reasons explain why the yield does not fluctuate much in the range of pH 2–3 [34]. Here, there is no significant difference in the effect of pH on COD removal and decoloration efficiencies of both conventional Fenton and UV-Fenton processes, and the treatment efficiency of these two processes was almost the same regardless of the different amounts of chemicals used. At pH < 4, the Fe^{3+} ions are in the form of $[Fe^{3+}(OH)^-]^{2+}$ complex, which has a fast ability to absorb UV light energy in the region of 180–400 nm and generates $HO^{\bullet}$ radical (Reactions 1–2) [27, 35]. The $HO^{\bullet}$ radical produced by this reaction explains that the chemical content in the UV-Fenton method is less than that of the conventional Fenton, but the yield is almost the same. From the above results and explanations, the optimal pH for the Fenton process of COD treatment and the decolorization of red water is chosen at pH 3.

3) Effect of H_2O_2/Fe^{2+} ratio on red water treatment

In the Fenton method, the H_2O_2/Fe^{2+} content plays an important role since it determines the ability to generate $HO^{\bullet}$ radicals to react with pollutants. When increasing the concentration of H_2O_2 (i.e., increasing the H_2O_2/Fe^{2+} ratio) in the reaction, the amount of $HO^{\bullet}$ radicals will generate more, leading to increased treatment efficiency. However, when the concentration of H_2O_2 is too high, it leads to an excess amount of H_2O_2 that reacts with $HO^{\bullet}$ radicals (Reaction 3).

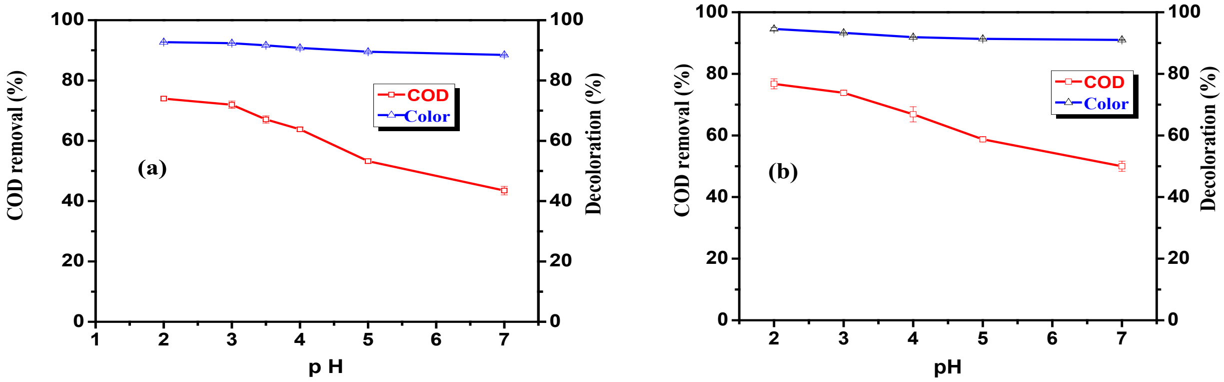

Figure 2 Effect of solution pH on red water treatment by (a) Fenton and (b) UV-Fenton (condition for Fenton: $[H_2O_2] = 3$ g L^{-1}, $[Fe^{2+}] = 0.3$ g L^{-1}; UV-Fenton: $[H_2O_2] = 1.47$ g L^{-1}, $[Fe^{2+}] = 0.21$ g L^{-1}; pH = 2 - 7, time = 120 min).

$$Fe^{3+} + H_2O \rightarrow [Fe^{3+}(OH)^-]^{2+} + H^+ \quad \text{(Reaction 1)}$$

$$[Fe(OH)]^{2+} + h\upsilon \rightarrow HO^{\bullet} + Fe^{2+} \quad \text{(Reaction 2)}$$

$$H_2O_2 + HO^{\bullet} \rightarrow HO_2^{\bullet} + H_2O \quad \text{(Reaction 3)}$$

This reaction occurs with a relatively large rate constant (3.3×10^{7} M^{-1} s^{-1}) [30, 36], so the treatment efficiency will not increase significantly even with increasing H_2O_2 content. Thus, it is not beneficial for the treatment process in both technical and economical aspects when using high H_2O_2 concentration. The influence of the H_2O_2/Fe^{2+} ratio on COD removal and decoloration efficiencies was investigated at the ratio from 1:1 to 30:1 (Figure 3). In the conventional Fenton, the treatment efficiency increased when keeping the $[Fe^{2+}] = 0.3$ g L^{-1} and increasing the H_2O_2 content from 0.3 to 3 g L^{-1}. The COD removal and decoloration efficiencies increased from 15.87 to 68.25% and from 10.76 to 90.72%, respectively. But if continuing to raise the concentration of H_2O_2 to 4.5–9.0 g L^{-1}, the COD removal and decoloration efficiencies did not change significantly compared to the $[H_2O_2]$ = 3 g L^{-1} (Figure 3(a)). The H_2O_2/Fe^{2+} ratio also greatly affects the treatment efficiency of the UV-Fenton process. As the H_2O_2 concentration increased, the treatment efficiency increased. The reaction of the $[Fe^{3+}(OH)^{-}]^{2+}$ complex by UV radiation produces the $HO^{\bullet}$ radical thus the amount of Fe^{2+} and H_2O_2 used in UV-Fenton is less than in the conventional Fenton. Specifically, when the content of $Fe^{2+} = 0.21$ g L^{-1} and the H_2O_2 concentration increased from 0.21 to 4.2 g L^{-1}, the COD removal and decoloration efficiencies increased from 34.66 to 86.93% and from 10.76 to 91.95%, respectively (Figure 3(b)). Moreover, when the ratio of H_2O_2/Fe^{2+} = 7:1, the COD removal and decoloration efficiencies were stable and almost equivalent to the Fenton process (H_2O_2/Fe^{2+} = 10:1). H_2O_2 has a major role in $HO^{\bullet}$ formation for Fenton processes. In UV-Fenton, the UV agent is capable of activating Fe^{3+} to form $HO^{\bullet}$ radicals and Fe^{2+} (Reaction 2). Therefore, the ratio of H_2O_2/Fe^{2+} can be reduced to 7:1 instead of 10:1 but still be able to treat the pollutants. Therefore, for red water, the H_2O_2/Fe^{2+} ratio of 10:1 is suitable for the conventional Fenton process and that of 7:1 is suitable for the UV-Fenton process.

4) Effect of Fenton reagent concentration on red water treatment

Based on the optimal ratio of H_2O_2/Fe^{2+}, the experiment was carried out to change the concentration of Fe^{2+} in the range of 0.09 - 1.2 g L^{-1} for conventional Fenton 0.03–0.45 g L^{-1} for UV-Fenton while the H_2O_2 content corresponds to the optimal ratio (i.e., at constant optimal $[H_2O_2]$:[Fe^{2+}] ratio). When the Fe^{2+} content increased, the COD removal efficiency and decolorization rose to 73.64 % and 92.08%, respectively (Figure 4(a)) and the treatment efficiency increased significantly in the Fe^{2+} concentration range of 0.09–0.3 g L^{-1}. Figure 4(b) shows that the COD removal and decolorization efficiency increases with increasing Fe^{2+} content in the UV-Fenton, where less Fe^{2+} content is used but still achieves high COD treatment and decolorization efficiency. First, Fe^{2+} acts as a catalyst to activate H_2O_2 to form $HO^{\bullet}$ radicals (Reaction 4). Initially, an increase in the concentration of Fe^{2+} causes more generation of $HO^{\bullet}$, thus enhancing the treatment efficiency. However, this increase can only be up to a certain level to reach an equilibrium point. When the concentration of Fe^{2+} is too high, the excess Fe^{2+} has not yet reacted with H_2O_2 ($k_{Fe(II)/H2O2}$ = 63 M^{-1} s^{-1}) then a reacts with the $HO^{\bullet}$ radical ($k_{Fe(II)/HO^{\cdot}}$ = 3×108 M^{-1} s^{-1}) [30, 36], thus reducing the amount of $HO^{\bullet}$ produced and thereby reducing the treatment efficiency. In addition, when the amount of Fe^{2+} is high, it will promote the formation of $Fe(OH)_3$ precipitate, thus increasing the amount of sludge and the cost of treatment. Therefore, the concentration of Fe^{2+} was chosen at 0.3 g L^{-1} for conventional Fenton and 0.21 g L^{-1} for UV-Fenton. For UV-Fenton, the UV agent has a role in enhancing the COD removal and decolorization treatment efficiency of red water. In the UV-Fenton system, besides the reaction that generates the $HO^{\bullet}$ of Fe^{2+}, there is another reaction that generates the $HO^{\bullet}$ caused by UV irradiation (Reaction 5). It increases the amount of $HO^{\bullet}$ in the solution and helps regenerate Fe^{2+} to form a consumption-regeneration cycle, thereby increasing the efficiency of the process. Due to the effective regeneration of Fe^{2+} in UV-Fenton, the initial Fe^{2+} concentration can be reduced while keeping the same level of pollutant removal efficiency. Therefore, UV-Fenton can outperform conventional Fenton in treating red water under the same operating conditions but with lower initial Fe^{2+} content and lower iron sludge production.

$$Fe^{2+} + 2H_2O_2 \rightarrow Fe^{3+} + HO^{-} + HO^{\bullet} \qquad \text{(Reaction 4)}$$

$$Fe^{3+} + H_2O + h\upsilon \rightarrow HO^{\bullet} + Fe^{2+} + H^{+} \qquad \text{(Reaction 5)}$$

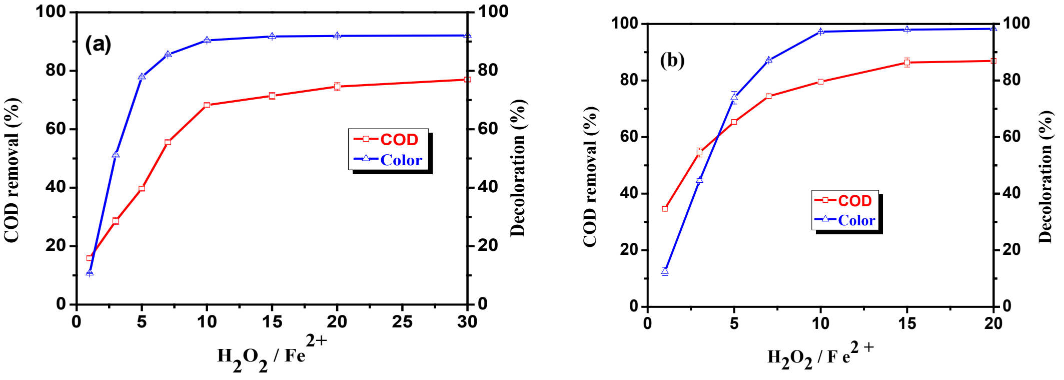

Figure 3 Effect of H_2O_2/Fe^{2+} ratio on red water treatment by (a) Fenton and (b) UV-Fenton (condition: Fenton: $[Fe^{2+}] = 0.3$ g L^{-1}, $H_2O_2/Fe^{2+} = 1:1 – 30:1$; UV-Fenton: $[Fe^{2+}] = 0.21$ g L^{-1}, $H_2O_2/Fe^{2+} = 1:1 - 20:1$; pH = 3, time = 120 min).

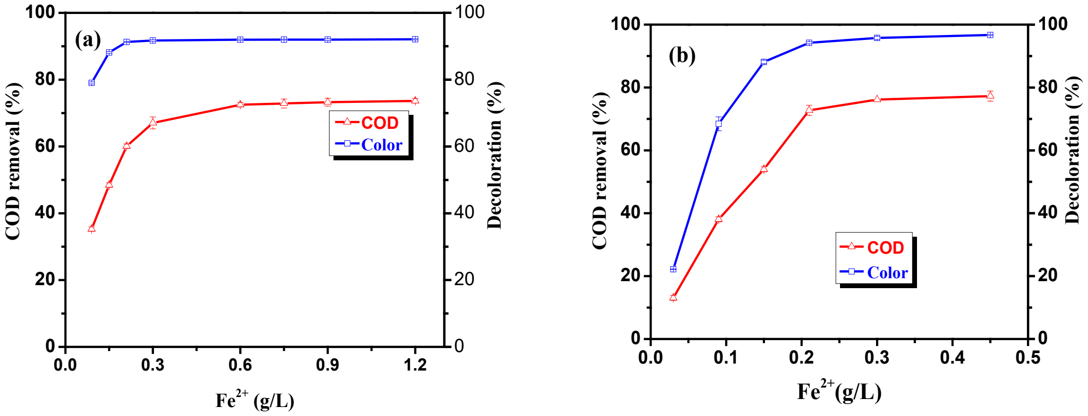

Figure 4 Effect of Fenton reagent concentration on COD treatment and decolorization efficiency of (a) Fenton and (b) UV-Fenton (condition: $[Fe^{2+}] = 0.09 – 1.2$ g L^{-1}; $H_2O_2/Fe^{2+} = 10$; UV-Fenton: $[Fe^{2+}] = 0.03 – 0.45$ g L^{-1}, $H_2O_2/Fe^{2+} = 7$; pH = 3, time = 120 min).

5) Effect of reaction time on red water treatment

Figure 5 shows the red water treatment efficiency during 180 min. From 30 to 120 min, the COD removal efficiency increased from 49.17 to 72.5% (Figure 5(a)). A negligible increase in treatment efficiency after 120 min of reaction, which is due to (i) most of the pollutants were removed, (ii) Fe^{2+} content decreased due to conversion to Fe^{3+}, and (iii) less amount of $HO^{\bullet}$ produced. Under the promotion of UV agents, the reaction in the UV-Fenton system occurs faster. After only 90 min, COD removal efficiency reached 76.1%, 30 min sooner than conventional Fenton (Figure 5(b)). The $HO^{\bullet}$ radical is generated more and faster in the UV-Fenton system. Furthermore, the absorption of UV excites the pollutants and promotes them to become a more reactive state, thereby increasing the reaction and giving a significantly faster treatment rate in the UV-Fenton process. In addition, the color removal efficiency increased slightly from 86.33% to 91.11% (from 30 to 120 min) and 78.57% to 93.61% (from 20 to 90 min) for Fenton and UV-Fenton processes, respectively. After 120 min for Fenton and 90 min for UV-Fenton, the removal efficiency changed insignificantly. Under UV irradiation but without adding Fe^{2+} and H_2O_2, the color removal efficiency reached only 7.8% after 90 min. The presence of UV and Fenton reagent strongly increased the color removal efficiency from 7.82% to 78.57%. This may be due to the generation of much more hydroxyl radicals in the presence of Fenton's reagent (Reactions 4–8) and the photochemical regeneration of Fe^{2+} (Reaction 2) [27]. Compared to COD treatment efficiency, the color decreases rapidly, especially in the first 90–120 min. The dark red color of the initial red water is determined by the presence of the compounds 2,6-dinitro toluene (2,6-DNT), 2,4-dinitro toluene (2,4-DNT), 2,4,6-trinitro toluene (TNT), 2,4-DNT-3-SO_3Na and 2,4-DNT-5-SO_3Na [26, 37]. The decomposition mechanism of red water by Fenton and UV-Fenton processes is based on the formation of hydroxyl radicals, that non-selectively attack the above pollutants to form intermediate products of 1,3,5-trinitrobenzene (1,3,5-TNB), 2,4-

DNT, 3-dinitrobenzene (1,3-DNB), and nitrobenzene (NB). These intermediates continue to be decomposed into small products of nitrobenzene and finally mineralized into CO_2, H_2O, and NO_3^- [26]. Therefore, the suitable red water treatment times in the Fenton and UV-Fenton systems were chosen at 120 and 90 min, respectively.

Figure 6 presents the COD removal of red water by four treatment methods at the optimal reagent doses and treatment times. The results showed that COD removal efficiency decreased in the order UV Fenton (76.1%) > Fenton (75.5%) > H_2O_2 (17.1) > UV (4.05%). When only UV irradiation without adding Fenton reagents, the COD removal efficiency reached only 4.05%, so this is not a suitable treatment method. This may be due to the low transmittance in the red water due to its dark black color [38]. When adding only H_2O_2, the COD removal efficiency was also low at 17.1%, this is due to the low ability of H_2O_2 to directly oxidize wastewater since the redox potential of H_2O_2 is 1.78 V [39]. However, the Fenton and UV-Fenton processes are effective in treating red water. In UV-Fenton processes, UV radiation enhances the pro-cess efficiency and kinetics. Specifically, UV radiation causes the reduction of Fe^{3+} to Fe^{2+} (Reaction 2), which allows the use of Fenton reagents at lower concentrations, which has the advantage of producing less sludge in neutralization and precipitation of soluble iron after treatment. In addition, UV radiation also contributes to converting H_2O_2 into hydroxyl radicals according to Reactions 6-8. These results corroborate the effectiveness of the UV-Fenton oxidation process using less chemicals, requiring shorter treatment times, and producing hydroxyl radicals more efficiently as compared to the Fenton, or UV and H_2O_2.

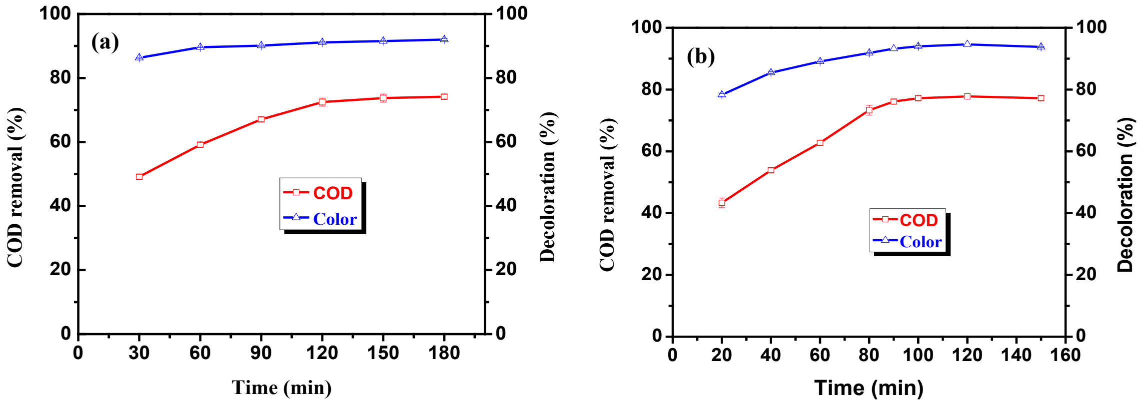

Figure 5 Effect of reaction time on COD treatment and decolorization efficiency (condition: $[Fe^{2+}] = 0.3$ g L^{-1}, $H_2O_2/Fe^{2+} = 10$; UV-Fenton: $[Fe^{2+}] = 0.21$ g L-1, $H_2O_2/Fe^{2+} = 7$; pH = 3, time 0 - 180 min).

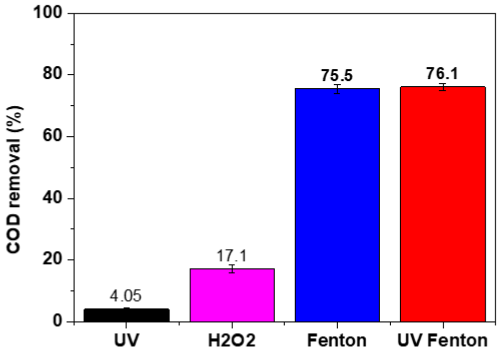

Figure 6 Comparisons of various processes for red water treatment.

$H_2O_2 + h\upsilon \rightarrow 2HO^{\bullet}$ (Reaction 6)

$H_2O_2 \rightarrow HO_2^- + H^+$ (Reaction 7)

$HO_2^- + h\upsilon \rightarrow HO^{\bullet} + O^-$ (Reaction 8)

6) Comparision with other works

Table 2 compares the UV-Fenton and Fenton processes for different types of industrial wastewater. The results showed that UV-Fenton gave higher treatment efficiency than conventional Fenton processes. Noticeably, the BOD_5/COD ratio significantly increased after the UV-Fenton process, proving that the process can effectively break down the complex structure of organic pollutants and transform recalcitrant wastewater to become more biodegradable ones. Using UV-Fenton increased the BOD_5/COD ratio from 0.13 (before treatment) to 0.58 (after treatment), proving that the treated red water is ready to be treated by biological methods. In addition, the BOD_5/COD ratio in the UV Fenton process (0.58) was much higher than that in the traditional Fenton (0.41), proving the high efficiency of the UV-Fenton process in breaking recalcitrant organic substances in the red water into biodegradable ones. The TN and TSS treatment efficiency was also recorded for Fenton (22.5% and 26.1%, respectively) and UV-Fenton (41.6% and 47.2%, respectively). Therefore, after being treated by UV-Fenton, biological treatment is needed to simultaneously remove BOD_5 and nutrients (e.g. nitrogen). Besides, our study has some advantages such as low H_2O_2/Fe^{2+} ratio with low H_2O_2 dosage, high removal efficiency of COD (76.1%) and color (93.2%), and short treatment time (90 min).

Table 2 Comparison of UV-Fenton and traditional Fenton for different industrial wastewater treatment

Wastewater	Characteristics of wastewater	Optimal conditions	Treatment efficiency (%)	Remark	References
Red water	COD: 1,344 mg L^{-1} Color: 20,637 Pt-Co BOD_5: 182 mg L^{-1} BOD_5/COD: 0.13 pH: 7.4	UV-Fenton: H_2O_2 =1,470 mg L^{-1} Fe^{2+} = 210 mg L^{-1} H_2O_2/Fe^{2+} = 7 pH = 3.0 Time = 90 min T = 25 °C Lamp: 15 W, UV light, 254 nm Fenton: H_2O_2 = 3,000 mg L^{-1} Fe^{2+} = 300 mg L^{-1} H_2O_2/Fe^{2+} = 10 pH = 3.0 Time = 120 min T = 25 °C	UV-Fenton: COD: 76.1% Color: 93.2% BOD_5/COD: 0.58 TN: 26.1% TSS: 47.2% Fenton: COD: 75.5% Color: 92.4% BOD_5/COD: 0.41 TN: 22.5% TSS: 41.6%	Low H_2O_2/Fe^{2+} ratio, low H_2O_2 dosage, short treatment time BOD_5/COD ratio =0.58 (UV-Fenton) > 0.41 (Fenton), proving the enhancement in biodegradability	This work
Red water	COD: 65,300 mg L^{-1} Color: 2,046 Pt-Co pH: 8.5	UV-Fenton: H_2O_2 =120,000 mg L^{-1} Fe^{2+} = 800 mg L^{-1} H_2O_2/Fe^{2+} = 150 pH = 4.0 Time = 30 hours T = 25 °C Lamp: 24 W, UV light, 254 nm	UV-Fenton: COD: 48.7% Color: 54.1%	High H_2O_2/Fe^{2+} ratio, high H_2O_2 dosage	[26]
Red water	COD: 1,600 mg L^{-1} pH: 8.5	UV-Fenton: H_2O_2 =1,632 mg L^{-1} Fe^{2+} = 55.84 mg L^{-1} H_2O_2/Fe^{2+} = 29.22 pH = 3.2 Time = 160 min T = 25 °C Lamp: 20 W, UV light, 254 nm	UV-Fenton: COD: 75%	High H_2O_2/Fe^{2+} ratio, high H_2O_2 dosage	[40]

Table 2 Comparison of UV-Fenton and traditional Fenton for different industrial wastewater treatment (*continued*)

Wastewater	Characteristics of wastewater	Optimal conditions	Treatment efficiency (%)	Remark	References
Explosive wastewater	COD: 220,000 mg L^{-1} pH: 2.32	Fenton: H_2O_2 = 394,400 mg L^{-1} Fe^{2+} = 19,990 mg L^{-1} H_2O_2/Fe^{2+} = 19.72 pH = 2.65 Time = 180 min T = 25 °C	COD: 75%	High H_2O_2/Fe^{2+} ratio, high Fe^{2+} and H_2O_2 dosage	[41]
Landfill leachate	COD: 7,700 mg L^{-1} BOD_5: 1,300 mg L^{-1} BOD_5/COD: 0.17 Color: 1,152 pH: 6.7 NH_4^+-N: 2,402 mg L^{-1}	UV-Fenton: H_2O_2 = 4000 mg L^{-1} Fe^{2+} = 30 mg L^{-1} H_2O_2/Fe^{2+} = 133 pH = 4.0 Time = 60 min T = 25 °C Lamp: 30 W, UV-C, 254 nm	UV-Fenton: COD: 56.30% BOD_5/COD: 0.67 Fenton: COD = 39.20% BOD_5/COD: 0.52	High H_2O_2/Fe^{2+} ratio, high H_2O_2 dosage UV-Fenton can convert complex and non-biodegradable organic pollutants into simple and biodegradable ones.	[42]
Landfill leachate	COD: 1,280 mg L^{-1} BOD_5: 121 mg L^{-1} BOD_5/COD: 0.0945 pH: 7.52	UV-Fenton: H_2O_2 =13,600 mg L^{-1} Fe^{2+} = 402.84 mg L^{-1} H_2O_2/Fe^{2+} = 34 pH = 3.0 Time = 180 min T = 25 °C Lamp: 80 W, UV light, 254 nm	COD: 87.9% BOD_5/COD: 0.44	High H_2O_2/Fe^{2+} ratio and H_2O_2 dosage BOD_5/COD ratio increased from 0.0945 to 0.44 UV-Fenton can effectively remove almost organic pollutants and enhance the BOD_5/COD ratio of the leachate	[43]
Textile Wastewater	COD: 47,000 mg L^{-1} BOD_5: 9,906 mg L^{-1} BOD_5/COD: 0.21 pH: 9	UV-Fenton: H_2O_2 = 20,740 mg L^{-1} Fe^{2+} = 224 mg L^{-1} H_2O_2/Fe^{2+} = 93 pH = 6.0 Time = 60 min T = 25 °C Lamp: 30 W, UV light, 254 nm	COD: 80% BOD_5/COD: 0.26	High H_2O_2/Fe^{2+} ratio and H_2O_2 dosage BOD_5/COD ratio insignificantly changed after treatment.	[44]
Palm oil refinery wastewater	COD: 2,088 mg L^{-1} BOD_5: 541 mg L^{-1} BOD_5/COD: 0.26 pH: 7.0	H_2O_2 = 4,437 mg L^{-1} Fe^{2+} = 60 mg L^{-1} H_2O_2/Fe^{2+} = 74 pH = 3.0 Time = 180 min T = 25 °C Lamp: UV light, 254 nm	COD: 80% BOD_5/COD: 0.44	High H_2O_2/Fe^{2+} ratio and H_2O_2 dosage Long treatment time UV-Fenton can effectively remove almost organic pollutants and enhance the BOD_5/COD ratio of the leachate	[45]
Produced water (PW) from natural gas fields	COD: 1,865 mg L^{-1} BOD_5: 800.6 mg L^{-1} BOD_5/COD: 0.43	UV-Fenton: H_2O_2 = 10,178 mg L^{-1} Fe^{2+} = 770 mg L^{-1} H_2O_2/Fe^{2+} = 13 pH = 3.0 Time = 120 min T = 25 °C Lamp: UV light, 254 nm	COD: 82% BOD_5/COD: 0.76	High H_2O_2/Fe^{2+} ratio and H_2O_2 dosage Treated wastewater was suitable for biological treatment	[46]

Conclusions

This work employed UV-Fenton as an effective method for removing recalcitrant pollutants in red water. Red water is a type of wastewater that contains dangerous toxic components and the Fenton process is a potential solution to remove its COD and color at pH = 3. In conventional homogeneous Fenton, COD removal and decoloration reached 75.5% and 92.4%, respectively, after 120 min with [Fe^{2+}] = 0.3 g L^{-1}, and H_2O_2/Fe^{2+} ratio = 10. In the UV-Fenton process, these efficiencies reached 76.1% and 94.2%, respectively, after 90 min, $[Fe^{2+}] = 0.21$ g L^{-1}, and H_2O_2/Fe^{2+} ratio = 7. The UV agent enhances the treatment efficiency, reducing the initial Fe^{2+} content and the amount of secondary sludge generated. The biodegradability of the wastewater after being treated by UV-Fenton was higher than that of conventional Fenton. The complex nature and composition of the red water from the TNT production process results in a limited treatment capacity of the Fenton process. Therefore, for highly polluting wastewater, Fenton-type processes such as UV-Fenton are a preferred solution for pre-treatment to increase the biodegradability of the wastewater and enhance the treatment efficiency of the following biological treatment steps.

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