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Treatment of explosive-contaminated wastewater through the Fenton process

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ABSTRACT

Owing to the extremely high chemical oxygen demand (COD), toxicity, and acidity of the explosive-contaminated wastewater, biological processes cannot be directly applied for its treatment. Therefore, Fenton's reagent was employed to treat the explosive wastewater before discharge. The Fenton process is also the easiest and most reliable method of advanced oxidation. The treatment of this wastewater with pH, COD, acetate, nitrate, and sulfate contents of 2.32, 200 $g\,L^{-1}$, 160 $g\,L^{-1}$, 40 $g\,L^{-1}$, and 35 $g\,L^{-1}$, respectively, was investigated in this study. The effects of the hydrogen peroxide feeding rate, ferrous ion dosage, and hydrogen peroxide dosage on the efficiency of the Fenton process were investigated. The optimal conditions obtained in this study for the treatment of explosive wastewater were 358 mM of Fe^{2+} and continuous feeding of hydrogen peroxide (0.33 $mL\,min^{-1}$), without pH adjustment or temperature control. The highest COD removal efficiency was 70% with an oxidation efficiency (OE) of 75% in 3 h. The addition of hydrogen peroxide had no impact on the observed COD conversion.

Keywords: Advanced oxidation processes; Explosive wastewater; COD; Fenton; Oxidation efficiency

1. Introduction

Explosives can be classified as either low or high explosives, depending on their rate of decomposition. Low explosives burn rapidly, whereas high explosives undergo detonation. High explosives are normally used in mining, demolition, and military warheads. Nitro aromatics, such as TNT (2,4,6-trinitrotoluene) and tetryl (2,4,6-trinitrophenyl-*n*-methylnitramine), and nitramines, such as RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine) and HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine), are classified as high explosives. HMX is synthesized by nitrating hexamine in the presence of nitric acid, acetic acid, acetic anhydride, paraformaldehyde, and ammonium nitrate. An explo-

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sive may either be a chemically pure compound or a mixture of other explosives. Most of explosives were mixture upon the application. Explosives are known to be toxic to aquatic and terrestrial organisms [1–3].

Explosives can enter the environment from the sites where they are manufactured, stored, disposed of, or used in military training [4]. In the past, the methods of production and storage of explosives led to their wide dispersion in the environment [5], especially in soil and groundwater. Traditional treatment procedures for the removal of explosives from wastewater are adsorption, advanced oxidation processes (AOPs) [3], chemical reduction, and bioremediation [6]. Chemical reduction by iron metal may promote transformation and detoxification [7,8], but it is not a stand-alone and complete remediation method. The potential advantages of bioremediation include low cost, ease of operation and public acceptance. However, explosives may require a long time to be mineralized, which are the major problems for this biological treatment approach. The AOPs generate a significant quantity of hydroxyl radicals ($^{\bullet}OH$, $E^0 = +2.8\,V$ vs. NHE) to oxidize recalcitrant organic contaminants and finally, mineralize them to CO_2 and H_2O. Several procedures can be used to generate hydroxyl radicals, such as O_3/H_2O_2, UV/H_2O_2, UV/O_3, $UV/O_3/H_2O_2$, UV/TiO_2, and Fenton [9,10]. Recently, the Fenton's oxidation combined with biological process on advanced treatment of the wastewater has been studied [11,12]. Fenton's reagent has been efficiently used as a chemical pretreatment process for wastewater treatment because it is fast, effective, reliable, and easy to use. Fenton reactions are very complicated, as shown below [13,14].

$$\begin{aligned} &Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^- \\ &\quad k = 40\text{–}80\ M^{-1}\ s^{-1} \end{aligned} \tag{1}$$

$$\begin{aligned} &RH + {}^{\bullet}OH \rightarrow {}^{\bullet}R + H_2O \\ &\quad k = 5.1\text{–}7.6 \times 10^9\ M^{-1}\ s^{-1} \end{aligned} \tag{2}$$

$$\begin{aligned} &Fe^{2+} + {}^{\bullet}OH \rightarrow Fe^{3+} + OH^- \\ &\quad k = 3.0 \times 10^8\ M^{-1}\ s^{-1} \end{aligned} \tag{3}$$

$$\begin{aligned} &H_2O_2 + {}^{\bullet}OH \rightarrow HO_2^{\bullet} + H_2O \\ &\quad k = 2.7 \times 10^7\ M^{-1}\ s^{-1} \end{aligned} \tag{4}$$

H_2O_2 reacts with Fe^{2+} to produce $^{\bullet}OH$ (Eq. (1)), which can oxidize the organic contaminants in the wastewater (Eq. (2)). However, if the concentration of Fenton's reagent is too high, it quenches the $^{\bullet}OH$, as shown in Eqs. (3) and (4).

Fenton's reagent is widely used as a simple combined oxidant to treat various types of organic contaminants such as chlorobenzene [15], nitrobenzene [16], aromatic amines [17,18], and nitro aromatics [3,13,19]. Other applications include the treatment of textile wastewater [20], pharmaceutical wastewater [21], and paper pulp manufacturing effluents [22]. Fenton process is most effective in treatment of wastewater contaminated with organic pollutants. Explosive wastewater compounds generally contain nitro aromatics, such as TNT, RDX, and HMX (Fig. 1). According to the previous study [17,19,23], Fenton process has been effectively used to degrade nitro-aromatic and aromatic amines. Hence, Fenton process could be expected to degrade the explosive wastewater from explosive manufacturing plant.

In this study, the effects of the hydrogen peroxide feeding rate, ferrous ion dosage, and hydrogen peroxide dosage on the efficiency of the Fenton process were investigated. Fenton's reagent was used to remove the chemical oxygen demand (COD) from a very acidic explosive wastewater that contained toxic compounds and high organic content which impeded its biological treatment. The optimal condition for explosive wastewater degradation by Fenton reaction was also determined.

2. Materials and methods

2.1. Wastewater characteristics

The product yield of HMX is about 55–60% with RDX as an impurity. The explosive wastewater was obtained from an explosive manufacturing plant in Taiwan. Table 1 displays the characteristics of the explosive wastewater.

2.2. Chemicals

H_2O_2 (35%) was obtained from Chang Chun Petrochemical Co., Ltd. (Taiwan). Ferrous sulfate and sodium hydroxide were purchased from Merck and Company, Inc. All chemicals were of reagent grade

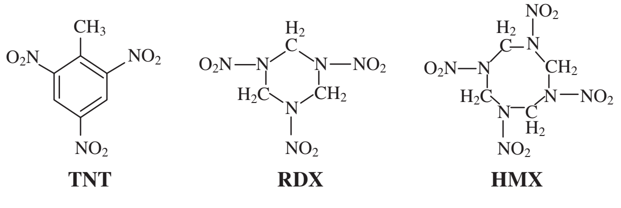

Fig. 1. Structures of explosive compounds.

Table 1
Main characteristics of the explosives wastewater studied with the Fenton's reagent

Parameter	Value
pH	2.32
COD ($g\,L^{-1}$)	200
Acetate ($g\,L^{-1}$)	160
Nitrate ($g\,L^{-1}$)	40
Sulfate ($g\,L^{-1}$)	35
TNT ($mg\,L^{-1}$)	<1
RDX ($mg\,L^{-1}$)	174
HMX ($mg\,L^{-1}$)	42

and were used as received without further purification. All aqueous solutions were prepared using water purified by a Millipore Simplicity system ($R = 18.2\,M\Omega\,cm$). Glassware was acid-washed and rinsed before use.

2.3. Procedure and analysis

Batch experiments were performed in a 1000-mL reactor with a magnetic stirrer. Five hundred milliliters of wastewater was treated at room conditions without temperature or pH control. The temperature was not controlled because Fenton reactions with high organic concentration cause a violent reaction with the sample, resulting in rapid boiling of the sample. After ferrous sulfate was added to the wastewater, H_2O_2 was continuously fed through a peristaltic pump (Cole-Parmer Instrument Co., Masterflex C/L Model 77120-70) at a rate that depended on the desired dosage. The withdrawn samples were diluted 500 times with deionized water, and 1 M NaOH was added to stop the oxidation reaction ($pH > 10$) [13]. To eliminate the excess H_2O_2, the diluted solution was kept in the dark at room temperature for 24 h. The COD was determined using the closed reflux titrimetric method, according to the Standard Methods [24]. The pH was measured using a SUNTEX TS-1 portable pH/mV meter, and the temperature was measured using a thermometer.

3. Results and discussion

3.1. Effect of hydrogen peroxide feeding rate

The theoretical dosage of H_2O_2 was calculated on the basis of the disproportion of H_2O_2 by a catalyst to provide 0.5 mole of O_2 for each mole of H_2O_2 [25]. Because an excess amount of H_2O_2 can react with hydroxyl radicals, as shown in Eq. (4), H_2O_2 was continuously fed to diminish the scavenging effect. The effect of the H_2O_2 feeding rate was determined by keeping the total H_2O_2 mass constant but varying the feeding rate from $0.33\,mL\,min^{-1}$ to $0.25\,mL\,min^{-1}$ and then, to $0.11\,mL\,min^{-1}$; the feeding times corresponding to these feeding rates are 150, 200, and 440 min, respectively. It was found that the highest COD removal rate occurred at the highest H_2O_2 feeding rate, i.e. the removal at a feeding rate of $0.33\,mL\,min^{-1}$ was better than that at 0.25 and $0.11\,mL\,min^{-1}$, as shown in Fig. 2. However, the overall removal efficiency at 480 min was around 70% for all cases.

Compared to the prolonged addition of H_2O_2, the intensive addition of H_2O_2 in a shorter period produced higher $^{\bullet}OH$ intensity. This implies that the organic pollutants in wastewater are more susceptible to $^{\bullet}OH$ than other scavenging species such as Fe^{2+} and H_2O_2. Therefore, competitive reactions from other inorganic scavengers became minimal and did not interfere with the oxidation of the organic pollutants. With regard to the COD removal, it can be concluded that the H_2O_2 feeding rate did not have any impact on the oxidation rate. After 480 min, the remaining organic pollutants were found to be resisting $^{\bullet}OH$ oxidation. This is because the final COD in all cases was steady at around $30\,g\,L^{-1}$. Therefore, a faster H_2O_2 feeding rate or a shorter reaction time would be preferred because the oxidation efficiency (OE) was almost the same even at a higher feeding rate. Hence, the feeding rate of $0.33\,mL\,min^{-1}$ was used in all the subsequent experiments.

3.2. Effect of ferrous ion dosage

As shown in Eq. (3), Fe^{2+} also competes with organic pollutants for $^{\bullet}OH$. Hence, an appropriate amount of Fe^{2+} is required for process optimization. The smaller the amount of iron, the slower is the oxidation rate. However, the maximum iron content is

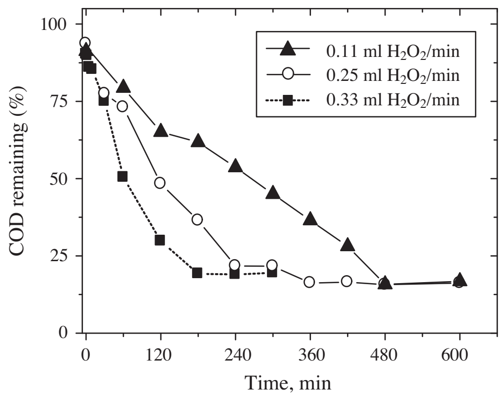

Fig. 2. Effect of H_2O_2 feeding rate on the COD removal. Experimental conditions: 358 mM Fe^{2+}, $pH_{initial}$ 2.65.

limited by the solubility of Fe^{2+}. The typical peroxide-to-iron molar ratio employed in wastewater treatment is 1–1000 [14]. The Fe^{2+} concentrations were set at 0, 14, 36 and 358 mM. The results shown in Fig. 3 indicate that the COD removal rate and efficiency increase with an increase in Fe^{2+} concentration. The highest removal efficiency of 70% was obtained at 180 min, with 358 mM of Fe^{2+}. This implies that under the studied conditions, Fe^{2+} was the limiting chemical. Hence, increasing the Fe^{2+} concentration could potentially catalyze the decomposition of H_2O_2, thereby generating $^{\bullet}OH$.

Fig. 4 shows the changes in the COD and temperature with the continuous feeding of H_2O_2. Experimental results indicate that during the first 5 min, the temperature rapidly increased to 47°C due to the effect of the Fenton reaction (Eq. (1)) and oxidation reactions (Eq. (2)), which are exothermic reactions [26]. After the initial Fe^{2+} was exhausted (Eq. (1)), the temperature was maintained for 5–9 min and then, rapidly increased to 80°C at the 16th minute by the Fenton-like reaction, as shown in the following equations [20,26]:

$$Fe^{3+} + H_2O_2 \leftrightarrow Fe\text{–}OOH^{2+} + H^+ \quad K_{eq} = 0.0036 \tag{5}$$

$$Fe\text{–}OOH^{2+} \rightarrow Fe^{2+} + HO_2^{\bullet} \quad k = 2.7 \times 10^{-3}\ s^{-1} \tag{6}$$

$$Fe^{3+} + HO_2^{\bullet} \rightarrow Fe^{2+} + O_2 + H^+\, k < 2 \times 10^3\ M^{-1}\ s^{-1} \tag{7}$$

As shown in Eqs. (5)–(7), Fe^{3+} is converted to Fe^{2+}, which reacts with the remaining H_2O_2 (Eq. (1)) to produce hydroxyl radicals that can enhance the degradation of organic content in explosive wastewater. However, Eq. (5) is very slow as compared to Eq. (1).

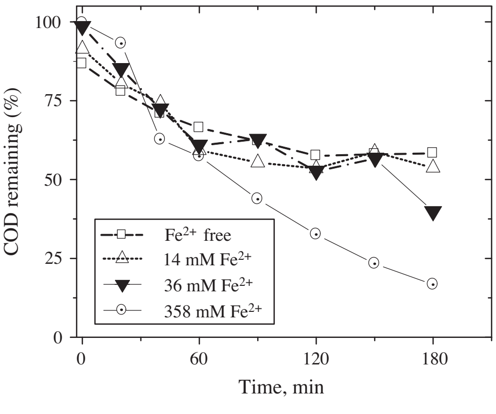

Fig. 3. Effect of Fe^{2+} on the COD removal. Experimental conditions: H_2O_2 feed rate 0.33 mL min^{-1}, $pH_{initial}$ 2.65.

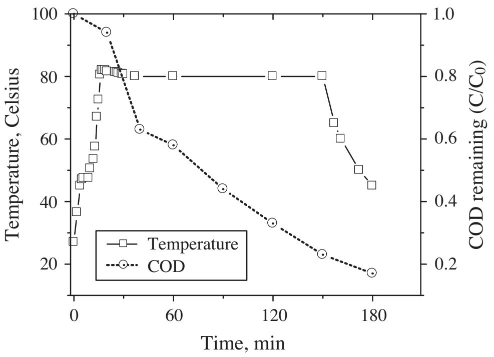

Fig. 4. Changes in the COD and temperature during treatment with Fenton's reagent. Experimental conditions: 358 mM Fe^{2+}, $pH_{initial}$ 2.65 and H_2O_2 feed rate 0.33 mL min^{-1}.

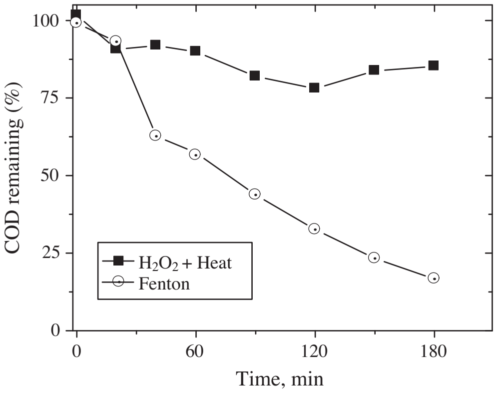

Fig. 5. Changes in the COD during treatment with Fenton's reagent with control experiment. Experimental conditions: $pH_{initial}$ 2.65, H_2O_2 feed rate 0.33 mL min^{-1} and 358 mM Fe^{2+}.

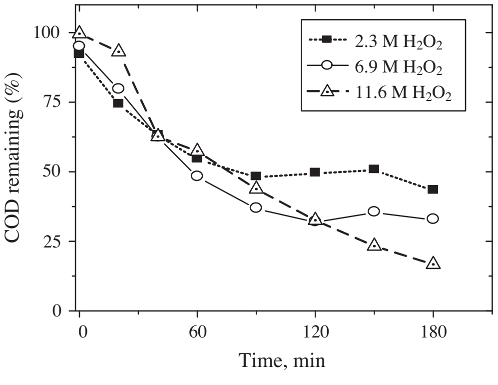

Fig. 6. Effect of H_2O_2 on the COD removal. Experimental conditions: 358 mM Fe^{2+}, $pH_{initial}$ 2.65 and H_2O_2 feed rate 0.33 mL min^{-1}.

Table 2
First-order constants for the COD removal

H_2O_2 (M)	Fe^{2+} (mM)	k_{obs} (min^{-1})	$t_{1/2}$ (min)
11.6	1440	0.0086	81
11.6	360	0.0095	73
11.6	36	0.0050	139
11.6	14	0.0047	147

Therefore, the limiting factor in these reactions is the presence of Fe^{2+} in the system. After 16 min, the temperature was almost constant until the end of the H_2O_2 feeding at 150 min, after which, the temperature slowly reduced, as shown in Fig. 4.

The control conditions for treating explosive wastewater with Fenton's reagent are shown in Fig. 5. The results show that the effects of evaporation and H_2O_2 oxidation can be ignored.

3.3. Effect of hydrogen peroxide dosage

Similar to Fe^{2+}, H_2O_2 also significantly scavenges $^{\bullet}OH$, if it is present in an excess amount (Eq. (4)). Therefore, an appropriate amount of H_2O_2 is also required for process optimization. The amount of H_2O_2 was varied from 2.3 M to 6.9 M and then, to 11.6 M as shown in Fig. 6. It was found that 11.6 M of H_2O_2 provided the best COD removal. From Eq. (1), 1 mole of H_2O_2 generates 1 mole of hydroxyl radicals, which subsequently reacts with the organic pollutants in the wastewater to generate CO_2. The OE of H_2O_2 for oxidation process is defined as [27]

$$\mathrm{OE} = \frac{\Delta\mathrm{COD}\ (\mathrm{mgL^{-1}})}{\mathrm{available\ O_2}\ (\mathrm{mgL^{-1}})} \times 100 \tag{8}$$

where, the available O_2 denotes the theoretical amount of reactive oxygen in the charged H_2O_2 in terms of two oxygen equivalents per mole of peroxide. Thus, OE is the ratio of the amount of oxidation of the wastewater substrate, as measured by the COD variation, to the maximum amount of oxidation possible using H_2O_2. As the H_2O_2 dosage applied here can attain a maximum oxidation of 75%, H_2O_2 decomposition may also occur because of heat or the recalcitrant oxidation of by-products.

3.4. Transformation of COD

To model the COD reduction as per the Fenton process, the data were fitted to zero-order, first-order, and second-order kinetic models, and the best fit was found to be the first-order rate equation. In simpler terms, increasing the initial Fe^{2+} dosage was beneficial for increasing the rate constant (k_{obs}). However, on increasing the molar concentration of Fe^{2+} to 1440 mM, the observed rate constant decreased because of the scavenging effect of Fe^{2+}, as shown in Eq. (3). The results are summarized in Table 2. The highest rate constant obtained in this study was 0.0095 min^{-1}, which was equivalent to a half-life ($t_{1/2}$) of 73 min.

4. Conclusions

The Fenton process was successfully employed to treat wastewater contaminated by explosives. The optimal conditions for wastewater treatment are an initial Fe^{2+} concentration of 358 mM and continuous feeding of (11.6 M) H_2O_2 at 0.33 mL min^{-1}. The COD removal efficiency and OE achieved under these conditions were 70% and 75%, respectively. Increasing the Fe^{2+} concentration accelerated the oxidation rate, but changes to the H_2O_2 feed rate did not have any impact on the COD conversion. Increase in both the concentration of Fe^{2+} and the dosage of H_2O_2 enhanced the removal efficiency with Fe^{2+} showing a greater impact under the conditions used in this study.

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