# Experimental Study on the Treatment of HMX Explosive Wastewater by Fenton Process

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**Abstract**. HMX has bactericidal properties. It is difficult to eliminate it by classic treatment methods. In this experiment Fenton reagent were employed to treat HMX wastewater. The effect of reaction time, $H_2O_2$ dosage, $FeSO_4 \cdot 7H_2O$ dosage, pH were investigated, and the optimum condition was determined via the single factor experiments. The results show that the treatment efficiency of HMX wastewater obviously by Fenton reagent. The optimum conditions with 25°C; $H_2O_2$ Concentration at 1% and dosage at 0.2mL; $FeSO_4 \cdot 7H_2O$ concentration at 0.01% and dosage at 8.3mL; pH at 3; reaction time at 80min;initial HMX concentration at 4mg/L and CODcr concentration at 214mg/L can reach the best removal efficiency of HMX as 81.4%and CODcr concentration at 155mg/L after the reaction.

## 1. Introduction

Oktoheim(HMX), highly toxic, has a very strong stimulant effect on human eyes. When injected intravenously, Oaktor will lead to a breakdown of the circulatory system and disturbance of the central nervous system in the animals [1].The immediate symptoms of HMX can cause cardiovascular depression or atrophy, resulting in hyperactivity and convulsions. And HMX increaseds sensitivity to light, stimulation and vibration [2].When the treatment is not proper, it may cause serious pollution to the environment, and the pollutants are difficult degradated [3~5]. Because of its difficult degradability, many countries have suffered from varying degrees of hazard from industrial explosives owing to vast area, the harm resulted from scattered explosive industry in China to the environment and human is not obvious at first. Many toxic substances enter into human body and other living things, causing short-term and potential long-term harm [6~9]. Therefore, the treatment of explosive wastewater is of great significance. Fenton reagent process has certain effect on organic wastewater treatment according to reported data. In this paper, Fenton reagent was used to degrade HMX wastewater. The effects of pH value, $H_2O_2$ dosage, $Fe^{2+}$ dosage and time on the treatment efficiency of

HMX wastewater and COD were studied. The optimal conditions for the degradation of HMX wastewater by Fenton reagent were studied.

## 2. Experimental materials and methods

### 2.1. Preparation of simulated wastewater for laboratory use
The wastewater used in this experiment is simulated wastewater. 300ml acetone and 10ml dimethyl sulfoxide are dissolved in water and stirred fully. 5gHMX is added into the wastewater accurately. The mixture is diluted to 15L with water and stirred for 24 hours. Filter with cotton and gauze and put it in a closed container. The HMX concentration of simulated wastewater is 4mg/L, CODcr=214mg/L. Determination of HMX in waste Water by Spectrophotometry with naphthalene ethylenediamine Hydrochloride and potassium dichromate method. Determination of $Fe^{2+}$ by spectrophotometric method [10].

### 2.2. Experimental design
The effects of five operation parameters on the removal rate of HMX and CODcr in HMX wastewater were studied respectively. The pH value of wastewater, amount of $H_2O_2$, dosage of $Fe^{2+}$, time and the operation parameters of only adding $Fe^{2+}$ were taken as the main target factors of the experiment. The change trend of $Fe^{2+}$ was determined with time as a single factor. Experimental conditions: The initial content of HMX wastewater was 4mg/L, the initial content of CODcr was 214mg/L, the volume was 100mL; The concentration of $H_2O_2$ is 0.01%, and the concentration of $FeSO_4 7H_2O$ is 0.01%.

## 3. Results and analysis

### 3.1. Effects of single factors on removal efficiency

*3.1.1. Effect of pH on removal efficiency of HMX and CODcr.* Five 250mL conical bottles were added to 100mL HMX water samples, respectively. Adding $H_2O_2$ solution of 2Qth and 0.01% $Fe^{2+}$ solution of 8.3ml; adjust pH to 1, 2, 3, 5, 7 respectively; each conical bottle was packed with tinfoil paper and reacted at 25°C for 120 minutes in constant thermostatic oscillator. The absorbance of the sample and the blank control sample was determined by using the operating conditions of the standard tube determined by the ethylenediamine hydrochloride spectrophotometry. The absorbance value of the water sample after the reaction was subtracted from the absorbance value of the blank pair. According to the standard curve that has been drawn, the content of HMX is obtained. Finally, the removal rate of HMX and the content of CODcr were calculated. Based on data, see Figure 1.

It can be observed from Figure 1, when pH was 3:00, the removal rate of HMX was the highest. When the pH value was less than 3 or more than 3:00, the removal rate of HMX was obviously decreased. It can also be observed according to the diagram; The change of CODcr content is similar to that of HMX removal rate, and the content of CODcr is the lowest when pH is 3:00.When the pH value was less than 3 or more than 3:00, the content of CODcr increased compared with the pH value of 3:00, the reason of which is that the concentration of H + in water is too high when pH is too low. This will inhibit the reaction of $Fe^{3+}+H_2O_2 \longrightarrow Fe^{2+}+HO_2+H$ [11~13]. And $Fe^{3+}$ could not be reduced to $Fe^{2+}$, which affected the oxidation ability of Fenton reagent. But when pH is too high, more $HO_2$ base is produced [14~17]. $HO_2$ radical has no activity for organic matter. To sum up the above, the optimal pH value in Fenton experiment was 3.0.
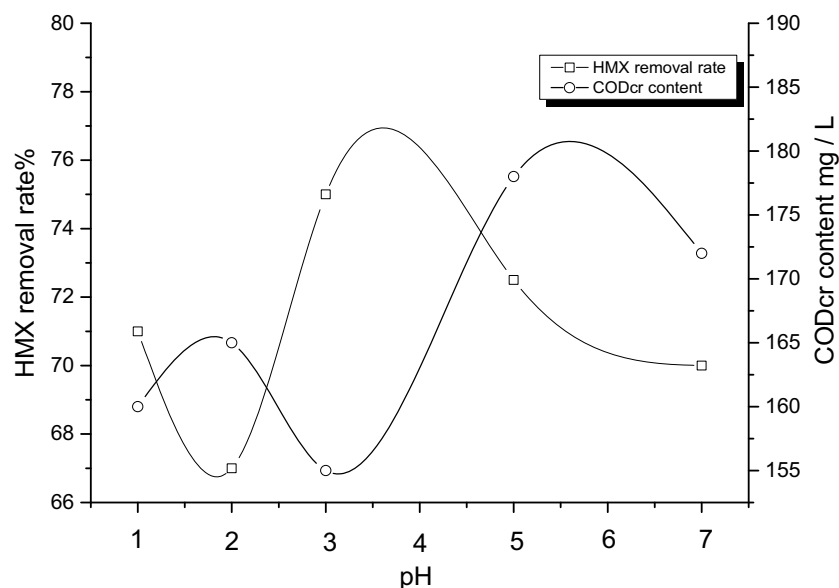
**Figure 1.** Effects of pH on removal of HMX and COD.

*3.1.2. Effect of $Fe^{2+}$ content on removal efficiency of HMX and CODcr.* Five 250mL conical bottles were added to 100mL HMX water samples, respectively. Adding 2Qth $H_2O_2$ solution; 0.01% $Fe^{2+}$ of 0mL, 41.7mL, 16.7mL, 8.3mL and 5.6mL were added in the conical bottles, respectively. The content of $Fe^{2+}$ solution was calculated according to the content of $n(Fe^{2+}):n(H_2O_2)$. It is equal to 0, 1:2, 1:5, 1:10 and 1:15, respectively. Adjust pH to 3; each conical bottle was packed with tinfoil paper and reacted at 25°C for 120 minutes in a constant temperature oscillator. The absorbance of the sample and the blank control sample was determined by using the operating conditions of the standard tube determined by the ethylenediamine hydrochloride spectrophotometry. The absorbance value of the water sample after the reaction was subtracted from the absorbance value of the blank pair. The content of HMX is derived from the standard curve that has been drawn [18]. Finally, the removal rate of HMX and the content of CODcr were calculated. See Figure 2 based on experimental data and results.
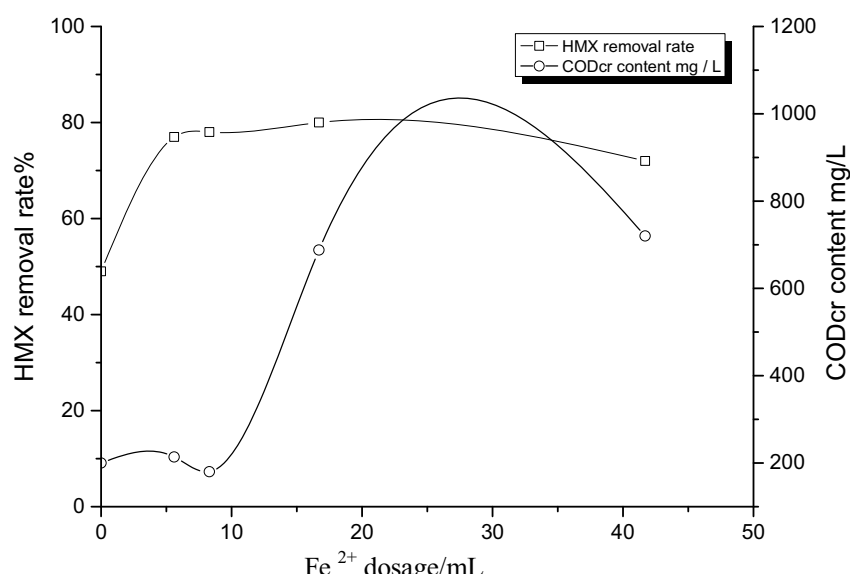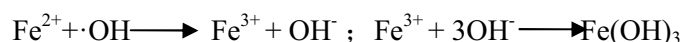


**Figure 2.** Effect of $Fe^{2+}$ dosage on removal efficiency of HMX and COD.

As can be seen from Figure 2, When $Fe^{2+}$ dosage is less than 8.3mL ($n(Fe^{2+})$:$n(H_2O_2)$ < 1: 10), the removal rate of HMX increased with the increase of $Fe^{2+}$ dosage. But when $Fe^{2+}$ dosage is greater than 8.3mL ($n(Fe^{2+})$:$n(H_2O_2)$ > 1:10), the removal of HMX was the first to stabilize and then decreased. The reasons are: $Fe^{2+}$ is a necessary condition for the formation of OH radical. In the absence of $Fe^{2+}$, it is mainly $H_2O_2$ hydrolysis to produce free radicals, so the amount of free radicals and the rate of formation are very small [19]. With the increase of $Fe^{2+}$ dosage, the·OH free radical produced by decomposition increases gradually, and the removal rate of HMX increases gradually, but when $Fe^{2+}$ is added too much, $Fe^{2+}$ will cause side effects [20];

$$Fe^{2+}+\cdot OH \longrightarrow Fe^{3+} + OH^- \; ; \; Fe^{3+} + 3OH^- \longrightarrow Fe(OH)_3$$

Because it consumes a lot of ·OH to form $Fe(OH)_3$ flocculation and sedimentation. Therefore, only the appropriate amount of $Fe^{2+}$ can keep the reaction going smoothly [21].

The trend line of COD can be seen: When $Fe^{2+}$ dosage was equal to 8.3ml, the content of CODcr was the lowest, and the content of CODcr increased gradually with the increase of $Fe^{2+}$ dosage. The reason is that the presence of $Fe^{2+}$ interferes with the determination of CODcr. In this experiment, $Fe^{2+}$ was fully oxidized to $Fe^{3+}$ by aeration method to produce CODcr after filtration and treatment of flocculants, but the effect was not good. To sum up the above: The optimum value of $Fe^{2+}$ dosage is 8.3mL, which satisfies $n(Fe^{2+})$:$n(H_2O_2)$=1: 10.

*3.1.3. Effect of $H_2O_2$ dosage on removal efficiency of HMX and CODcr.* Five 250mL conical bottles were added to 100mL HMX water samples, respectively. 0Qth, Qth, 2Qth, 3Qth, 4Qth $H_2O_2$ and 8.3ml 0.01% $Fe^{2+}$ solution were added. Adjust pH to 3; each conical bottle was packed with tinfoil paper and reacted at 25°C for 120 minutes in a constant temperature oscillator. The absorbance of the sample and the blank control sample was determined by using the operating conditions of the standard tube determined by the ethylenediamine hydrochloride spectrophotometry. The absorbance value of the water sample after the reaction was subtracted from the absorbance value of the blank pair. According to the standard curve that has been drawn, the content of HMX is obtained. Finally, the removal rate of HMX and the content of CODcr were calculated. Based on experimental data and results, see Figure 3.
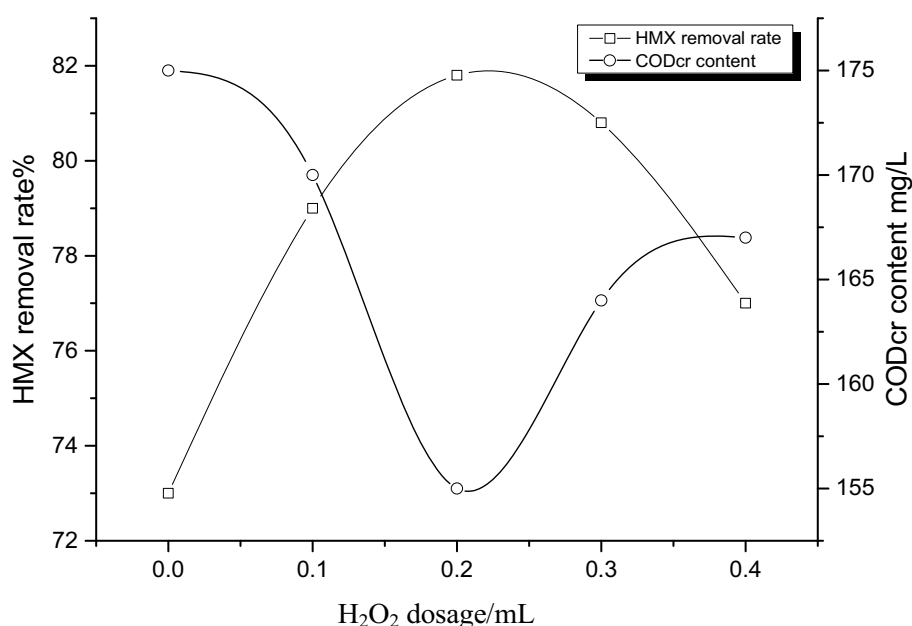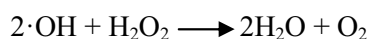


**Figure 3.** Effect of $H_2O_2$ dosage on removal efficiency of HMX and COD.

As can be seen from Figure 3, when the dosage of $H_2O_2$ is less than 2Qth, the removal rate of HMX and CODcr increases with the increase of the dosage of $H_2O_2$. However, when the dosage of $H_2O_2$ solution is more than 2Qth, the removal rate of HMX decreases with the increase of the dosage of $H_2O_2$ solution. The content of CODcr was also increased when the dosage of $H_2O_2$ was equal to 2Qth. The reasons may be: The amount of ·OH free radical produced by $Fe^{2+}$ decomposition increased as the dosage of $H_2O_2$ solution increased. However, when the amount of $H_2O_2$ solution is too much, there is an optimum ratio of $Fe^{2+}$ and $H_2O_2$, because the amount of $Fe^{2+}$ is higher than the optimal amount of $H_2O_2$, which will inhibit the reaction. When the amount of $H_2O_2$ is high, hydrogen peroxide can quench the hydroxyl radical and make it ineffective to decompose itself [22]. The following reactions occurred;

$$2 \cdot OH + H_2O_2 \longrightarrow 2H_2O + O_2$$

In addition, excessive $H_2O_2$ could not decompose to produce more hydroxyl radicals, but instead oxidized $Fe^{2+}$ to $Fe^{3+}$ at first, thus consuming $H_2O_2$ and inhibiting the production of hydroxyl radical [23]. Therefore, the removal rate of HMX decreased when the dosage of $H_2O_2$ was more than 2Qth. To sum up, the dosage of $H_2O_2$ solution is 0.2mL. (2Qth to meet the amount of $H_2O_2$).

*3.1.4. Effect of reaction time on removal efficiency of HMX and CODcr.* Seven 250mL conical bottles were added to 100mL HMX water samples, respectively. Adding $H_2O_2$ solution of 2Qth and 0.01% $Fe^{2+}$ solution of 8.3ml;Adjust pH to 3; The conical bottles were packed with tinfoil and reacted at 25°C for 20, 40, 60, 80, 100, 120 and 140 minutes, respectively, in constant temperature oscillator. The absorbance of the sample and the blank control sample was determined by using the operating conditions of the standard tube determined by the ethylenediamine hydrochloride spectrophotometry. The absorbance value of the water sample after the reaction was subtracted from the absorbance value of the blank pair. According to the standard curve that has been drawn, the content of HMX is obtained. Finally, the removal rate of HMX and the content of CODcr were calculated. See Figure 4 based on experimental data and results.
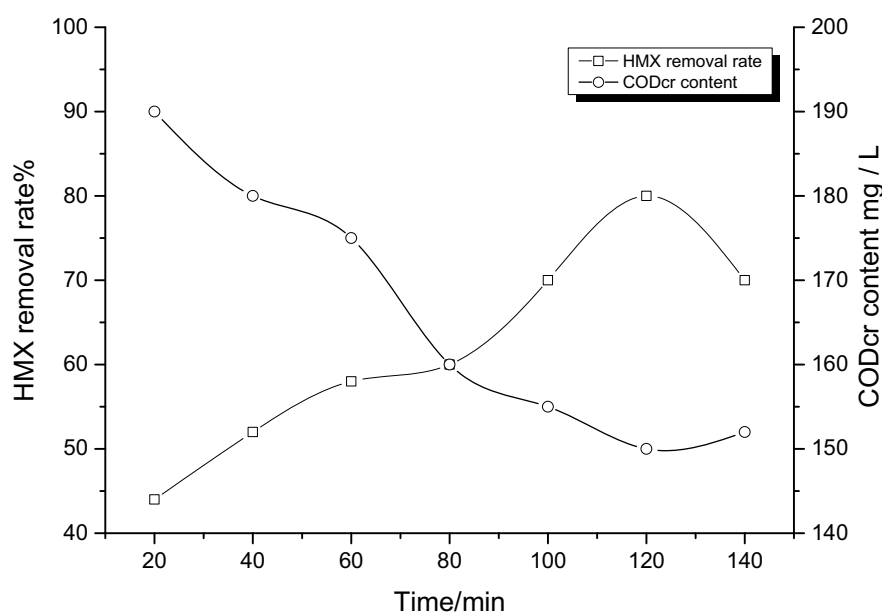


**Figure 4.** Effect of reaction time on removal efficiency of HMX and COD.

According to Figure 4, it can be seen that the removal rate of HMX wastewater by Fenton process increases with time, and the content of CODcr decreases slowly with the prolongation of time. After

the reaction of 120min, the removal rate of HMX was 81% while the removal rate of CODcr was small. In addition to the effect of $Fe^{2+}$ ion, the degradation of HMX by Fenton reagent is relatively fast, but the mineralization of HMX is a relatively slow process [24].To sum up the above; the optimum reaction time was 120min.

*3.1.5. Treatment effect under optimal experimental conditions.* The experimental scheme determined by single factor is the best scheme of theory, and this experiment is verified by the best scheme of theory.

Five 250mL conical bottles were added to 100mL HMX water samples, respectively. Adding $H_2O_2$ solution of 2Qth and 0.01% $Fe^{2+}$ solution of 8.3ml; Adjust pH to 3; each conical bottle was packed with tinfoil paper and reacted at 25°C for 120 minutes in a constant temperature oscillator. The absorbance of the sample and the blank control sample was determined by using the operating conditions of the standard tube determined by the ethylenediamine hydrochloride spectrophotometry. The absorbance value of the water sample after the reaction was subtracted from the absorbance value of the blank pair. According to the standard curve that has been drawn, the content of HMX is obtained. Finally, the removal rate of HMX and the content of CODcr were calculated. The experimental conditions and results are shown in Table 1.

**Table 1.** Removal efficiency of HMX and CODcr under optimal conditions.

| HMX content mg/L | pH value | $Fe^{2+}$ dosage /mL | $H_2O_2$ dosage/mL | Reaction time /min | HMX removal rate % | CODcr content mg/L |
|---|---|---|---|---|---|---|
| 4 | 3 | 8.3 | 0.2 | 120 | 81.0 | 155 |

*3.2. Effect of only adding $Fe^{2+}$ on HMX removal efficiency*

Five 250mL conical bottles were added to 100mL HMX water samples, respectively. And 0.01% $Fe^{2+}$ solution of 83.3mL, 41.7mL, 16.7mL, 8.3mL and 5.6mL was added into the conical bottles, respectively. (The content of $Fe^{2+}$ was calculated by adding of $Fe^{2+}$). $(Fe^{2+}):n(H_2O_2)$ Equal to 1:1:2, 1:5, 1:10, 1:15, respectively; Adjust pH to 3; Each conical bottle was packed with tinfoil paper and reacted at 25°C for 120 minutes in a constant temperature oscillator. The absorbance of the sample and the blank control sample was determined by using the operating conditions of the standard tube determined by the ethylenediamine hydrochloride spectrophotometry. The absorbance value of the water sample after the reaction was subtracted from the absorbance value of the blank pair. According to the standard curve that has been drawn, the content of HMX is obtained. Finally, the removal rate of HMX was calculated. Based on experimental data and results, see Figure 5.

The removal rate of HMX by only adding $Fe^{2+}$ was compared with the removal rate of HMX by the amount of $Fe^{2+}$ in Fenton reaction system. The results are shown in Figure 6.

According to Figure 6, it is observed that HMX can be removed by adding divalent iron ions alone. However, it was found that the removal rate of HMX by single factor $Fe^{2+}$ in Fenton system was significantly higher than that by adding divalent iron alone. Therefore, it can be concluded that the oxidation of organic compounds by Fenton reagent is due to the reaction of $Fe^{2+}$ and $H_2O_2$, which is catalyzed by $Fe^{2+}$ ion to produce hydroxyl radical. (·OH) and direct action of hydroxyl radical on various organic compounds lead mineralization, so as to achieve the purpose of reducing wastewater content and COD[25]. Therefore, the most significant factor in the Fenton system is the dosage of $H_2O_2$.
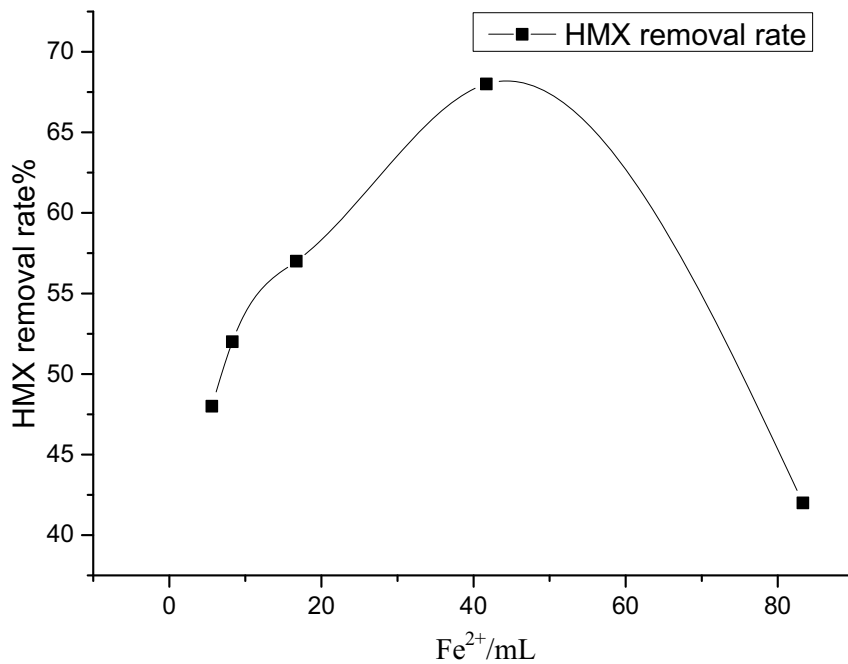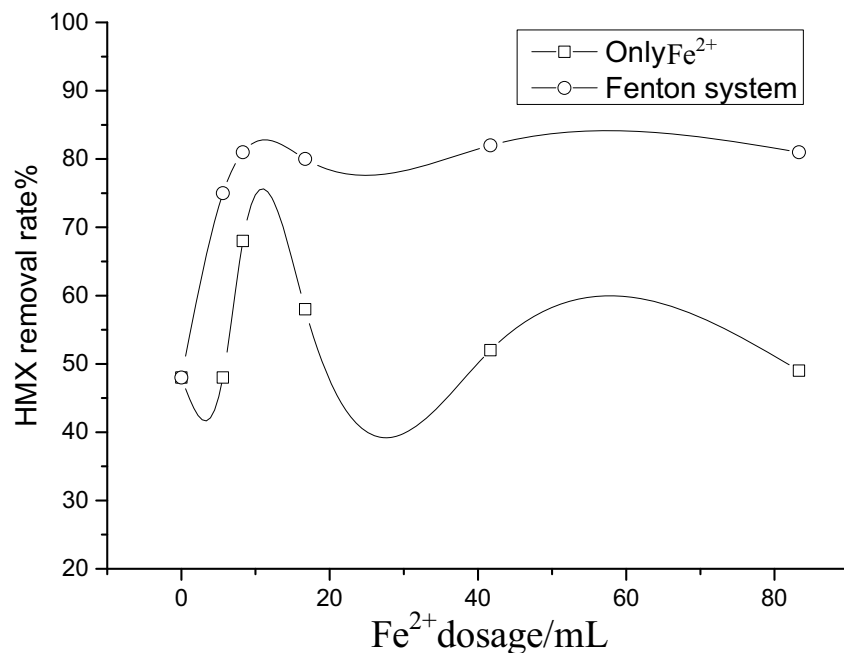
**Figure 5.** Effect of $Fe^{2+}$ only on HMX removal.



**Figure 6.** Comparison of removal rate of HMX by adding $Fe^{2+}$ and single factor $Fe^{2+}$ in Fenton system.

### 3.3. Change of $Fe^{2+}$ ion and removal rate of HMX in reaction system

Seven 250mL conical bottles were added to 100mL HMX water samples, respectively. Adding $H_2O_2$ solution of 2Qth and 0.01% $Fe^{2+}$ solution of 8.3ml;Adjust pH to 3;The conical bottles were packed with tin foil and reacted at 25°C for 20, 40, 60, 80, 100, 120 and 140 minutes respectively. The absorbance of the sample and the blank control sample was determined by using the operating conditions of the standard tube determined by the ethylenediamine hydrochloride spectrophotometry. The absorbance value of the water sample after the reaction was subtracted from the absorbance value

of the blank pair. According to the standard curve that has been drawn, the content of HMX is obtained. Finally, the removal rate of HMX was calculated. The absorbance of water sample after reaction was determined by o-phenanthroline spectrophotometry. After subtracting the absorbance value of blank pair, the content of $Fe^{2+}$ was obtained according to the standard curve that had been drawn. Based on the experimental data, see Figure 7.
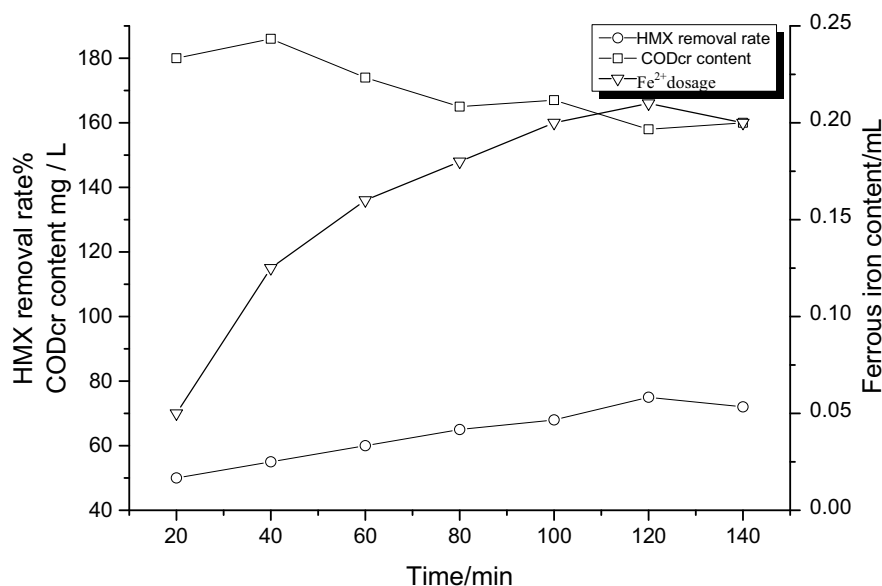


**Figure 7.** Effect of reaction time on removal efficiency of HMX and COD and change of $Fe^{2+}$.

According to figure 3.7, it can be seen that the removal rate of HMX wastewater by Fenton process increases with time, and the content of CODcr decreases slowly with the prolongation of time. The removal rate of HMX was 81% while the removal rate of CODcr was less than that of HMX. In addition to the effect of $Fe^{2+}$ ions, the degradation of HMX by Fenton reagent is relatively fast, but the mineralization of HMX is a relatively slow process. The concentration of $Fe^{2+}$ ion in the solution is on the rise, which may be due to the increase of $Fe^{2+}$ ion concentration. $Fe^{2+}$ catalyzes the decomposition of $H_2O_2$ to produce hydroxyl radical in Fenton reaction and then releases divalent iron. The initial addition of quantitative $Fe^{2+}$ ion was also used by Fenton reaction, so $Fe^{2+}$ ion was oxidized with water to produce $Fe^{3+}(OH)_3$. The amount of flocculant decreases. Therefore, the content of $Fe^{2+}$ ion in solution increases with time.

## 4. Conclusion

In this paper, the treatment of explosive wastewater by Fenton method was studied, and the effects of five experimental parameters on the removal rate of HMX and CODcr in HMX wastewater were studied respectively. The main target factors of this experiment were pH value, $H_2O_2$ dosage, $Fe^{2+}$ dosage, time and only adding $Fe^{2+}$. The change trend of $Fe^{2+}$ was determined with time as a single factor. Through the analysis of the experimental results, the conclusions are as follows:

a) The concentration of divalent iron in Fenton system increases with time. The reason is that $Fe^{2+}$ catalyzes the decomposition of $H_2O_2$ to produce hydroxyl radical in Fenton reaction. With the persistence of Fenton reaction, the initial addition of quantitative $Fe^{2+}$ ions was also more utilized by Fenton reaction, so $Fe^{2+}$ ion was oxidized to produce $Fe^{3+}(OH)_3$ in aquatic products. The amount of flocculant decreases. Therefore, the content of $Fe^{2+}$ ion in solution increases with time; b)In the experiment of treating HMX explosive wastewater by Fenton process, the effect of the reaction depends on the optimum ratio of $Fe^{2+}$ and $H_2O_2$, that is, n.($Fe^{2+}$):n($H_2O_2$) 1:10. Adding too much $H_2O_2$ or $Fe^{2+}$ to HMX was not significant; c) The experimental results of the treatment of HMX explosive

wastewater by Fenton process show that the most significant factor of the treatment effect is the dosage of $H_2O_2$.

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