

Study on the exothermic characteristics of $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ homogeneous Fenton degradation of o-phenylenediamine wastewater

Yuntao Yan[†], Ke Zhang, Yanpeng Mao^{†,*}, Yong Dong^{*}

National Engineering Laboratory for Reducing Emissions from Coal Combustion, Engineering Research Center of Environmental Thermal Technology of Ministry of Education, Shandong Key Laboratory of Energy Carbon Reduction and Resource Utilization, School of Energy and Power Engineering, Shandong University, Jinan, Shandong 250061, China, Tel. +86 53188399372; Fax: +86 531 88395877; email: dongy@sdu.edu.cn (Y. Dong), Tel. +86 53188399012; email: yanyuntao@sdu.edu.cn (Y. Yan), Tel. +86 05186358579; emails: kezhang@sdu.edu.cn (K. Zhang), maoyanpeng@sdu.edu.cn (Y. Mao)

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ABSTRACT

This study examined the heat-releasing behavior of the homogeneous $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ Fenton system in the degradation of organic wastewater. The organic molecule o-phenylenediamine (OPD) in an aqueous solution was used as the target pollutant. The reaction path of O_3 and $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ homogeneous Fenton degradation of OPD was compared and analyzed, and the effects of H_2O_2 dosage, Fe^{2+} concentration, initial reaction temperature, and the solution pH, on the temperature rise (ΔT), chemical oxygen demand, degradation rate (η), and temperature rise time (T) were analyzed. It was found that O_3 and the homogeneous $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ Fenton system release a large amount of heat during the degradation of OPD wastewaters. Compared with O_3 , homogeneous $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ Fenton exhibits better degradation and exothermic characteristics. When 200 mL of 0.04 mol L^{-1} OPD was reacted with 0.2 mol L^{-1} of H_2O_2 and 10 mmol L^{-1} of Fe^{2+} at a pH of 7.9 and T_0 of 30°C, the resulting ΔT was 11.3°C and η was 93.75%. The superposition of multiple reactions of the Fe^{2+} catalyzes the cyclic reaction of H_2O_2 to generate free radicals, the reaction of radical degradation of OPD, and the self-quenching reaction of free radicals is the main reason for the obvious enhancement of homogeneous $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ Fenton exothermic performance.

Keywords: Fenton; Degradation; $\text{Fe}^{2+}/\text{H}_2\text{O}_2$; Exothermic reaction

1. Introduction

The combustion of fossil fuels such as coal, petroleum, and natural gas for energy production is the primary anthropogenic source of greenhouse gases like CO_2 . Global climate change, which is a consequence of excessive greenhouse gas emissions, has received a great deal of attention from governments worldwide. To reduce the emission of greenhouse gases, various clean energy technologies (e.g., wind and solar power) and comprehensive energy utilization technologies (e.g., heat pumps) have seen rapid development [1–3]. In particular, sewage water source heat

pumps (SWSHPs) can be used to enhance the low-grade heat of wastewaters into high-grade heat for heating in winter or industrial manufacturing processes, with the use of small amounts of electricity. Therefore, SWSHPs reduce the emission of greenhouse gases caused by the combustion of fossil fuels used to provide heat [4,5], and they also decrease the cost of producing high-grade heat sources. Hence, a wastewater source heat pump (WWSHP) is a comprehensive energy utilization technology that has excellent prospects for widespread application. Given a fixed set of conditions, the higher the temperature of the wastewater, the greater the amount of heat that can be collected

* Corresponding authors.

[†] These authors contributed equally to this work.

by a WWSHP. Therefore, research about technologies that increase wastewater temperature during wastewater processing is important for increasing the amount of heat that can be extracted by WWSHPs, as well as the comprehensive utilization of energy from wastewater sources.

The conventional homogeneous Fenton process is an advanced oxidation process (AOP) that produces strongly oxidizing hydroxyl radicals to degrade organic matter [6,7]. This process is strongly oxidizing and procedurally simple [8,9]; however, it can only be used in a narrow range of pH and has a tendency to generate large amounts of iron sludge [10–12]. Studies regarding the Fenton process have mainly focused on extending the applications of the process and overcoming the weaknesses of the conventional homogeneous Fenton process. For example, in studies to extend the applications of the Fenton process, Zeng et al. [13] and Jiang et al. [14] applied the Fenton oxidation process to the treatment of wastewaters that contain refractory organic pollutants like methylene blue and nitrobenzene. Yin et al. [15], Xing et al. [16], Fan et al. [17] used the Fenton process for sludge treatment, soil remediation, denitrification, and cancer treatment. In efforts to overcome the intrinsic weaknesses of the Fenton process, Deng et al. [18] prepared an iron vanadate catalyst via aqueous precipitation, which extended the pH range of the Fenton process to 3.0–8.0, thus creating a Fenton system capable of operating beyond a narrow range of pH values. Fang et al. [19] prepared a molecular sieve catalyst via hydrothermal synthesis, which eliminated the tendency of the Fenton process to produce iron sludges. Wang et al. [20] used the photo-Fenton process to improve on the low degradation rates of the conventional Fenton process. Nonetheless, no reports have been published about the heat produced by Fenton reagents during the degradation of organic wastewaters, or the mechanisms by which heat is released during these degradation processes.

In recent years, several studies have been published about the use of Fenton AOP systems in wastewater treatment, sludge treatment, and soil remediation. However, there are no reports about the heat-releasing behaviors of homogeneous $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ Fenton systems during wastewater treatment. This study examined the heat-releasing behavior of the homogeneous $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ Fenton system in the degradation of organic wastewater. The organic molecule *o*-phenylenediamine (OPD) in an aqueous solution was used as the target pollutant. The reaction path of O_3 and $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ homogeneous Fenton degradation of OPD was compared and analyzed, and the effects of H_2O_2 dosage, Fe^{2+} concentration, initial reaction temperature, and the solution pH, on the temperature rise (ΔT), chemical oxygen demand (COD) degradation rate (η), and temperature rise time (T) were analyzed. The degradation and exothermic characteristics of the homogeneous $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ Fenton system for OPD wastewater treatment were summarized, and the related mechanisms were discussed.

2. Experiments

2.1. Reagents and equipment

The reagents utilized included: 30% H_2O_2 , $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, H_2SO_4 , NaOH, Ag_2SO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$, $\text{C}_6\text{H}_8\text{N}_2$ (*o*-phenylenediamine),

and $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$. All reagents were purchased from Sinopharm Chemical Reagent Co., Ltd., (China).

This study used a laboratory stirrer (JJ-1, Changzhou Boyuan Instrument Plant, China), a digital display thermostatic water bath (HH-S, Tianjin Saidelisi Experimental Analyzer Factory, China), temperature and humidity recorder (TH22R-XX, Hua Han Wei Co., Ltd., China), pH meter (PHS-3C, Yoke Instrument Co., Ltd., China), and a COD analyzer (JHR-2, Genstar Electronic Technology Co., Ltd., China), O_3 generator (XT-200GC, Xi Shang Technology Co., Ltd., China).

2.2. Experimental setup

As shown in Fig. 1, the experimental apparatus was mainly composed of a 500 mL round bottom flask, an insulating layer, a temperature and humidity recorder, and a stirrer. The insulation layer was placed on the outer wall of the round bottom flask, and the outer surface of the round bottom flask was completely wrapped. The inside of the 500 mL round bottom flask was provided with a temperature measuring tube and a stirring rod. The temperature measuring tube was connected to the temperature and humidity recorder through a wire, and the stirring rod was connected to the mixer through the flask mouth.

2.3. Experiment process

2.3.1. Preparation and testing of simulated wastewater

A certain amount of OPD was weighed, and a certain concentration of OPD simulated wastewater was prepared in a 2,000 mL volumetric flask with deionized water. The pH of the simulated wastewater was adjusted with a 5% sulfuric acid solution and a 5% sodium hydroxide solution. The potassium dichromate method was used to determine the COD of the solution.

2.3.2. Warm-up preparation

The volumetric flask containing the OPD solution was placed in a constant temperature water bath. The constant temperature water bath was set to a value higher than the initial reaction temperature of 10°C . The heating was continued till the temperature of the OPD solution was close to that of the water bath temperature. Before the experiment, a measuring cylinder was used to accurately measure the heated OPD solution around the bottom flask, and the mixer was started at a rate of 600 r min^{-1} . The experimental system was naturally cooled. The heat of the OPD solution was transferred to the round bottom flask and then the insulating layer in turn. This ensured that the temperature between the inner layer of the round bottom flask and the insulating layer was increased to be close to the temperature of the OPD solution.

2.3.3. $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ Fenton degradation reaction experiment

When the temperature of the OPD solution is lowered to the initial reaction temperature, the H_2O_2 solution is first added to the OPD solution, and the $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ solid powder is added to the OPD solution at intervals of 2 min.

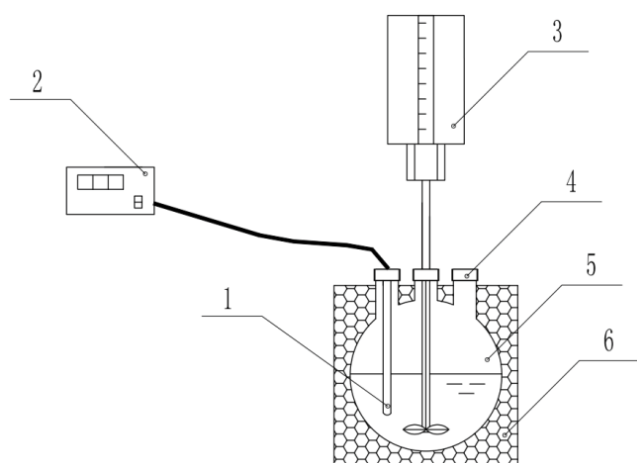


Fig. 1. Experimental device diagram. (1) Thermometer; (2) temperature and humidity recorder; (3) stirrer; (4) addition port; (5) 500 mL round-bottom flask; (6) insulation layer.

The temperature and humidity recorder was then started, and the reaction temperature and time of the solution were recorded. The frequency of data recording was conducted once every 5 min. The value of the solution temperature rise (ΔT) during the reaction was calculated by Eq. (1). The continuous temperature rise time T of the solution was calculated by the time period from the start of the reaction to the time when the solution temperature reached the highest value and the temperature drop inflection point occurred. After the reaction began, samples were collected at 10 min intervals and a moderate speed qualitative filter paper (102) was used to filter the sample. The COD of the filtrate was measured using potassium dichromate. The level of COD reduction in the solution, ΔC , was calculated using Eq. (2). The COD degradation rate of the solution was calculated using Eq. (3).

$$\Delta T = T - T_0 \quad (1)$$

$$\Delta C = C_0 - C \quad (2)$$

$$\eta = \frac{\Delta C}{C_0} \times 100\% \quad (3)$$

where ΔT is the temperature difference before and after the degradation of the OPD solution, T is the highest temperature reached after OPD solution reaction, T_0 is the temperature before the OPD solution reaction, and ΔC represents the amount of COD degradation based on measurements taken before and after the degradation of the OPD solution. The quantity C_0 is the initial COD value of the OPD solution and C is the COD value after degradation. The quantity η is the COD degradation rate of the OPD solution.

2.3.4. O_3 degradation reaction experiment

When the OPD solution temperature drops to the set initial reaction temperature, turn on the O_3 generator, pass O_3 into the OPD solution, and start the temperature and humidity recorder to record the reaction temperature and

reaction time of the solution. The frequency of data recording is once every 5 min. The recording or analysis method of ΔT , T , ΔC and η during the reaction is the same as the Fe^{2+}/H_2O_2 Fenton degradation reaction experiment.

3. Results and discussion

3.1. Analysis of reaction characteristics

In order to analyze the reaction path and degradation exothermic performance of Fe^{2+}/H_2O_2 homogeneous Fenton degrading OPD wastewater, O_3 and Fe^{2+}/H_2O_2 homogeneous Fenton reagents were used to degrade OPD wastewater respectively. The reaction conditions are: the concentration of OPD sewage is 0–0.04 mol L^{-1} , the volume is 200 mL, pH = 7.8, the initial reaction temperature is 30°C; the concentration of Fe^{2+} is 10 mmol L^{-1} , the concentration of H_2O_2 is 0.2 mol L^{-1} ; The dosage of O_3 is 0.1 $m^3 h^{-1}$, and the experimental results are shown in Figs. 2 and 3. From Figs. 2 and 3, it can be seen that O_3 and Fe^{2+}/H_2O_2 Fenton both increased the temperature of the solution during the degradation of OPD wastewater. The concentration of OPD wastewater rose from 0.01 to 0.04 mol L^{-1} the temperature rise values of the solution after O_3 degradation of OPD sewage are 2.5°C, 5.1°C, 7.3°C, 9.5°C, and the COD degradation values are 1,497.9; 2,827.4; 4,165.5; and 5,187.3 mg L^{-1} , respectively. The temperature rise values of the solution after Fe^{2+}/H_2O_2 homogeneous Fenton degraded OPD wastewater were 9.1°C, 10.3°C, 10.9°C, 11.3°C, and the COD degradation value was 1,795.7; 3,102.8; 5,100.2 and 7,541.8 mg L^{-1} . The COD degradation value of homogeneous Fe^{2+}/H_2O_2 Fenton reagent degrading OPD wastewater is slightly higher than that of O_3 degradation OPD wastewater, but the solution temperature rise is significantly higher than that of O_3 degradation OPD wastewater and the lower the OPD concentration, the greater the difference in solution temperature rise. Compared with the solution temperature rise value and COD degradation value of O_3 degrading OPD

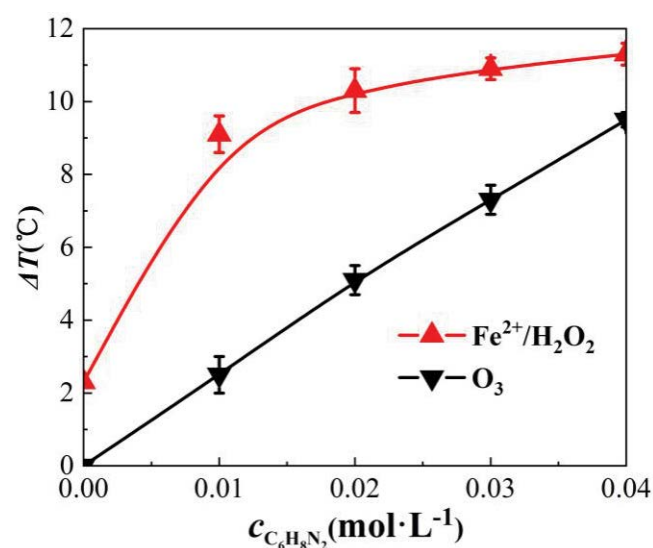


Fig. 2. Influence of OPD concentration on degradation exothermic performance.

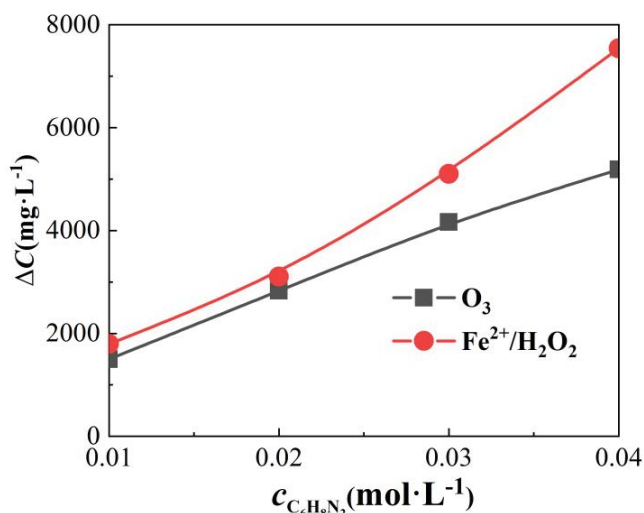
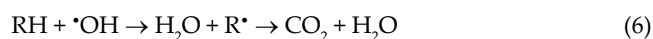
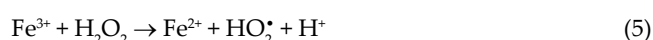


Fig. 3 Influence of OPD concentration on degradation exothermic performance.

wastewater, the homogeneous Fe²⁺/H₂O₂ Fenton reagent shows better degradation exothermic performance.

It can also be seen from Figs. 2 and 3 that the initial concentration of OPD sewage is 0 mg L⁻¹, that is, when O₃ is added to the same volume of deionized water, the temperature rise of deionized water is 0, indicating that O₃ has no exothermic reaction in deionized water occurs, and the Fe²⁺/H₂O₂ Fenton reagent chemically reacts in deionized water and releases heat. When the OPD solution concentration increases from 0 to 0.04 mol L⁻¹, in the process of O₃ degradation of OPD, every time the initial OPD concentration increases by 0.01 mol L⁻¹ unit, the temperature rise of the solution increases approximately by 2.4°C and COD degrades. The value increased approximately by 1,296.8 mg L⁻¹, and the solution temperature rise value and COD degradation value increased approximately in direct proportion to the initial concentration of OPD wastewater, indicating that the single oxidation exothermic process of O₃ oxidation OPD mainly occurred in the process of O₃ degradation OPD. The homogeneous Fe²⁺/H₂O₂ Fenton degrades OPD wastewater, when the initial concentration of OPD wastewater is 0, that is, when homogeneous Fe²⁺/H₂O₂ Fenton reagent is added to the same volume of deionized water, the temperature rise of deionized water is 2.1°C, indicating that Fe²⁺ catalytic reaction occurs with H₂O₂ in deionized water and releases heat. After OPD was added to deionized water, the sewage temperature increased rapidly. When the concentration of OPD sewage was 0.01 mol L⁻¹, the temperature rise of the solution was 9.1°C; continue to increase the initial concentration of OPD sewage, and the sewage temperature only increased gently, without the above during the process of O₃ degradation of OPD, the temperature rise of the solution is approximately proportional to the initial concentration of OPD wastewater. This may be due to various exothermic reactions in the process of homogeneous Fe²⁺/H₂O₂ Fenton degradation of OPD wastewater. According to the Fenton reaction mechanism [21], there are multiple reactions including Eqs. (4)–(8) in the process of homogeneous

Fe²⁺/H₂O₂ Fenton degradation of sewage. Fe²⁺, Fe³⁺ catalyze the cyclic reaction of H₂O₂ to produce •OH radicals [Eqs. (4) and (5)], the oxidation reaction of OPD oxidation by •OH radicals and the quenching reaction of H₂O₂ [Eq. (6)], the consumption of •OH and HO₂• radicals themselves [Eqs. (7) and (8)], may have generated heat. Compared with the single oxidative exothermic process of O₃ degradation OPD process, the superposition of multiple exothermic reaction processes may be the main reason for the effective increase of sewage temperature during the homogeneous Fe²⁺/H₂O₂ Fenton degradation OPD process.



3.2. Effects of the concentration of H₂O₂

In order to study the effect of the concentration of H₂O₂ on ΔT , η , and t , the reaction conditions were set as follows: the concentration of the OPD solution was 0.04 mol L⁻¹ and the volume was 200 mL. The pH was adjusted to 7.8 and the initial reaction temperature was 30°C. The concentration of Fe²⁺ was 10 mmol L⁻¹ and the reaction time was 100 min. The experimental results are shown in Figs. 4 and 5. Fig. 2 shows that ΔT increases with [H₂O₂] during the degradation of OPD by a homogeneous Fe²⁺/H₂O₂ Fenton system. The ΔT was 3.2°C when the [H₂O₂] = 0.05 mol L⁻¹, and ΔT was 19.6°C when the [H₂O₂] = 0.4 mol L⁻¹. Furthermore, η initially increased and then decreased with increasing [H₂O₂] [7,21]. Moreover, it was observed that η was 53.24%, 94.19%, and 84.63% when the [H₂O₂] was 0.05, 0.15, and 0.4 mol L⁻¹, respectively. Fig. 5, shows that T increased from 4.0 to 39.3 min when the [H₂O₂] increased from 0.05 to 0.4 mol L⁻¹, which indicates that T increases with increasing [H₂O₂]. Therefore, the degradation of OPD by the Fe²⁺/H₂O₂ system is an exothermic reaction, and both the amount of heat released and the duration of heat release increase with increasing [H₂O₂].

Based on the mechanisms of the Fenton reaction [21], Eqs. (4)–(8) will be relatively weak if the [H₂O₂] is low. Therefore, only a small number of •OH and HO₂• radicals will be present in the solution. Therefore, they are only able to partially degrade the OPD molecules. Under these conditions, ΔT , η , and T will be low. As the [H₂O₂] increases, the number of •OH and HO₂• radicals generated by the Fenton system will increase, thus increasing the number of OPD molecules that are degraded by the system. Under these conditions, ΔT , η , and T will increase with increasing [H₂O₂] [22]. When the concentration of H₂O₂ is increased to a certain value, the amount of self-consumption due to reactions (7)–(9) increases, and the decomposition of hydrogen peroxide occurs [13,23]. Consequently, the number of

$\cdot\text{OH}$ and $\text{HO}_2\cdot$ radicals that are available to react with OPD will decrease, and η will decrease with increasing $[\text{H}_2\text{O}_2]$.

However, Fig. 4 shows that the ΔT plot continues to rise even after the η plot declines. This indicates that the rise in solution temperature is not significantly affected by the decrease in OPD molecules participating in reaction (6) and the increase in radical termination reactions. Therefore, it may be deduced that the heat produced by the reaction of free radicals (like $\cdot\text{OH}$ and $\text{HO}_2\cdot$) with OPD is similar to the heat produced by the radical termination reactions. In Fig. 4, it can be seen that ΔT is approximately directly proportional to the $[\text{H}_2\text{O}_2]$, as the ΔT that corresponds to the $[\text{H}_2\text{O}_2] = 0.4 \text{ mol L}^{-1}$ is 6.125 times greater than the ΔT corresponding to the $[\text{H}_2\text{O}_2] = 0.05 \text{ mol L}^{-1}$. Hence, the $[\text{H}_2\text{O}_2]$ is an important factor controlling the rise in solution temperature.

3.3. Effects of the concentration of Fe^{2+}

To study the effect of Fe^{2+} concentration on ΔT , η , and t , the reaction conditions were as follows: the concentration of the OPD solution was 0.04 mol L^{-1} and the volume was 200 mL. The pH was 7.8, and the initial reaction temperature was 30°C . The concentration of H_2O_2 was 0.2 mol L^{-1} and the reaction time was 30 min. The experimental results are shown in Figs. 6 and 7. Fig. 6, shows that an increase in the $[\text{Fe}^{2+}]$ from 5 to 10 mmol L^{-1} resulted in a rapid increase in ΔT , from 6.5°C to 11.3°C . Further increases in the $[\text{Fe}^{2+}]$ only led to a small increase in ΔT . The values of η were 91.96%, 93.75%, and 89.71% when the $[\text{Fe}^{2+}]$ was 5, 10, and 30 mmol L^{-1} , respectively. Therefore, η initially increased and then decreased with increasing $[\text{Fe}^{2+}]$ [24]. As seen in Fig. 7, T decreased from 83.5 min to 1.3 min when the $[\text{Fe}^{2+}]$ increased from 5 to 30 mmol L^{-1} , which shows that T decreases rapidly with increases in the $[\text{Fe}^{2+}]$. This indicates that the $[\text{Fe}^{2+}]$ is an extremely significant factor for controlling the rate of heat release from the reaction. The greater the concentration of Fe^{2+} , the faster the rate of heat release from the reaction, and the shorter the temperature rise time, T .

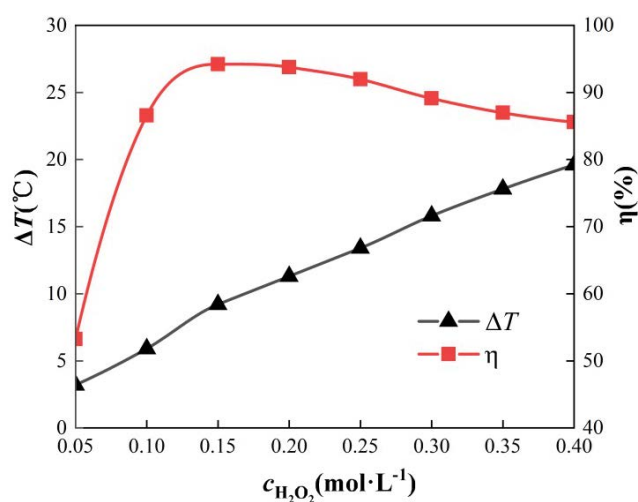


Fig. 4. Effect of dosing concentration of hydrogen peroxide on ΔT and η .

If the $[\text{Fe}^{2+}]$ is very low, the cyclic reactions between H_2O_2 , Fe^{2+} , and Fe^{3+} will be slow, which inhibits the rate of free radical ($\cdot\text{OH}$ and $\text{HO}_2\cdot$) generating reactions, OPD-free radical reactions, and reactions (7)–(8) (the radical consuming reactions) [25,26]. This effectively increases t . The cyclic reactions between H_2O_2 , Fe^{2+} , and Fe^{3+} are accelerated by an increase in the $[\text{Fe}^{2+}]$, which increases the number of free radicals in the solution, thus increasing the number of OPD molecules that are degraded by free radicals. This increases ΔT and η . When the $[\text{Fe}^{2+}]$ increases beyond a certain threshold, the cyclic reactions between H_2O_2 , Fe^{2+} , and Fe^{3+} are further accelerated, which leads to the production of large amounts of $\cdot\text{OH}$ and $\text{HO}_2\cdot$ radicals that react with OPD. However, the rate of radical termination reactions is also accelerated, which reduces the number of $\cdot\text{OH}$ and $\text{HO}_2\cdot$ radicals that are available to react with OPD and increases the number of radicals lost to radical termination reactions, thus decreasing η . Further

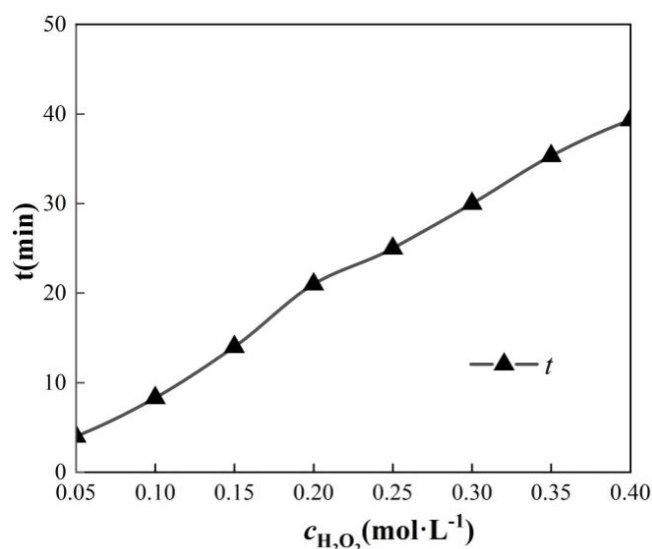


Fig. 5. Effect of dosing concentration of hydrogen peroxide on t .

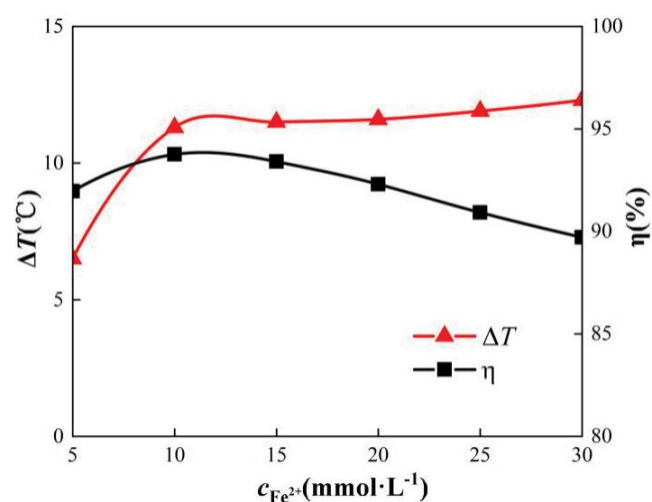


Fig. 6. Effect of dosing concentration of Fe^{3+} on ΔT and η .

increases in the $[\text{Fe}^{2+}]$ will accelerate the reactions of the system; however, η will continue to decrease. Fig. 6 shows that ΔT still rises slightly even when the η plot begins to decline. Therefore, it may be deduced that the exothermicity of the OPD and free radical ($\cdot\text{OH}$ and $\text{HO}_2\cdot$) reactions is slightly less than that of the radical termination reactions.

3.4. Effects of initial reaction temperature

In order to study the effect of initial reaction temperature on ΔT , η , and t , the reaction conditions were as follows: the concentration of OPD solution was 0.04 mol L^{-1} and the volume was 200 mL. The pH was 7.8, the concentration of H_2O_2 was 0.2 mol L^{-1} , the concentration of Fe^{2+} was 10 mmol L^{-1} , and the reaction time was 70 min. The experimental results are shown in Figs. 8 and 9. Fig. 8 shows that η was 94.85% and ΔT was 6.2°C when the initial reaction temperature was 10°C . When the initial reaction temperature was increased to 60°C the ΔT was 12.2°C and η was 88.79%. Therefore,

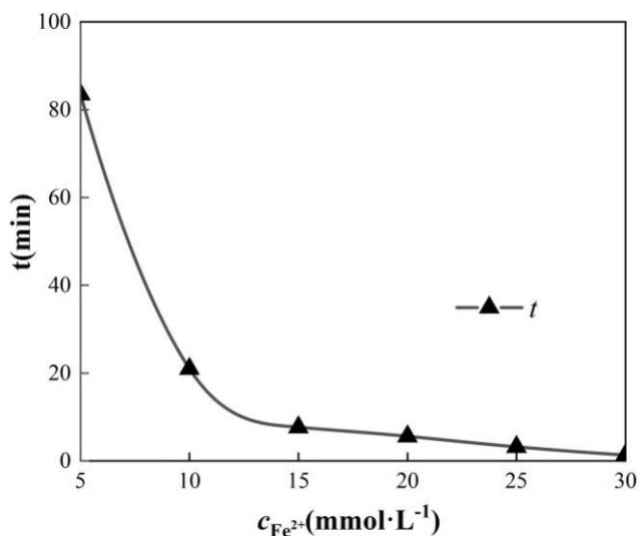


Fig. 7. Effect of dosing concentration of Fe^{3+} on t .

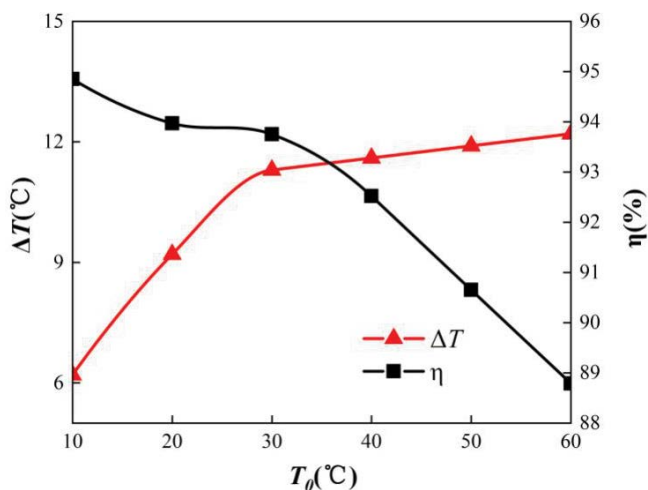


Fig. 8. Effects of initial reaction temperature on ΔT and η .

an increase in initial reaction temperature increased ΔT but decreased η [27]. This is mainly because increases in temperature simultaneously accelerate the oxidation of OPD by $\cdot\text{OH}$ and $\text{HO}_2\cdot$, the radical termination reactions, and the thermal decomposition of H_2O_2 into O_2 and H_2O . This acts to decrease the number of $\cdot\text{OH}$ and $\text{HO}_2\cdot$ radicals available to react with OPD as well as the number free radicals lost to radical termination reactions. This has the effect of increasing ΔT and decreasing η . Fig. 9 shows that T decreases from 67.5 to 1.67 min when the initial reaction temperature is increased from 10°C to 60°C . This is because an increase in initial reaction temperature increases the number of active molecules in the solution, which increases reaction rates, thus decreasing reaction time.

3.5. Effect of solution pH

In order to study the effect of pH on ΔT , η , and t , the reaction conditions were as follows: the concentration of the OPD solution was 0.04 mol L^{-1} and the volume was 200 mL. The initial reaction temperature was 30°C , the concentration of H_2O_2 was 0.2 mol L^{-1} , the concentration of Fe^{2+} was 10 mmol L^{-1} , and the reaction time was 30 min. The experimental results are shown in Figs. 10 and 11. Fig. 10 shows that the temperature of the solution increased at all pH values. The ΔT decreased with increasing pH, whereas η initially increased and then decreased with increasing pH [19]. The degradation of OPD increased from 85.90% to 94.32% when pH increased from 1.0 to 5.0, but decreased with further increases in pH. The OPD degradation rate decreased to 61.28% when the pH was 11.0. These observations may be explained as follows: at excessively low pH levels, Fe^{3+} cannot be reduced to Fe^{2+} due to the excessive concentration of H^+ in the solution. This hinders the catalytic reaction and thus decreases the percentage of OPD degradation. An increase in pH effectively decreases H^+ concentration to a more suitable level, which accelerates the reactions between Fe^{2+} , Fe^{3+} and H_2O_2 , thus increasing the generation of reactive species like

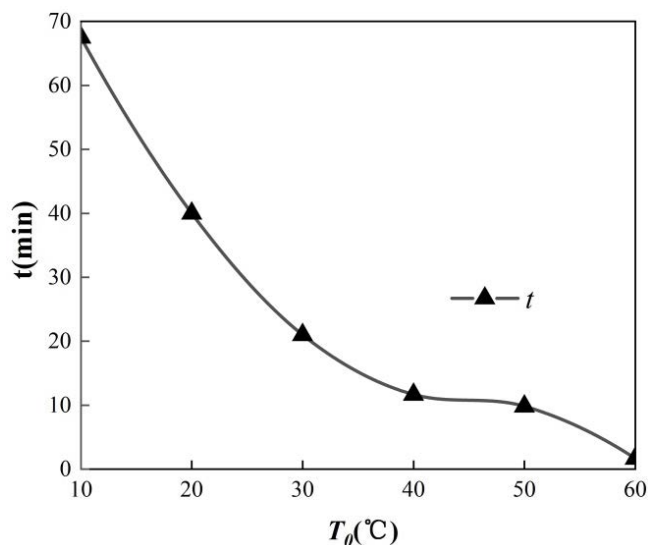


Fig. 9. Effects of initial reaction temperature on t .

$\cdot\text{OH}$. This increases the percentage of OPD degradation. However, at excessively high pH values, the Fe^{2+} ions in the solution will precipitate as oxides and lose their catalytic ability, thus resulting in dramatic decreases in the percentage of OPD degradation [7,28]. Fig. 11 shows that T increases with pH, which indicates that the rate of heat release by the degradation of OPD by the $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ system decreases with increases in pH. This is because the Fe^{2+} ions in the solution undergo a change in state when pH increases, which directly slows the rate of the Fenton reaction. At low pH values, Fe(II) generally exists as Fe^{2+} ions in solution. The higher the concentration of Fe^{2+} , the faster the reactions of the Fenton system and the shorter the solution-temperature rise time, T . However, Fe(II) mainly exists as $\text{Fe}(\text{OH})$ and $\text{Fe}(\text{OH})_2$ at higher pH values. Therefore, an increase in pH decreases the concentration of Fe^{2+} in the solution, which reduces the generation of $\cdot\text{OH}$ and slows the reactions of the Fenton system [6,29].

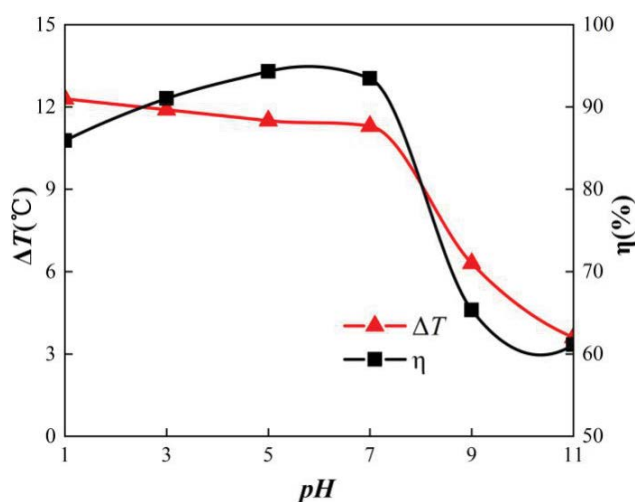


Fig. 10. Effects of pH on ΔT and η .

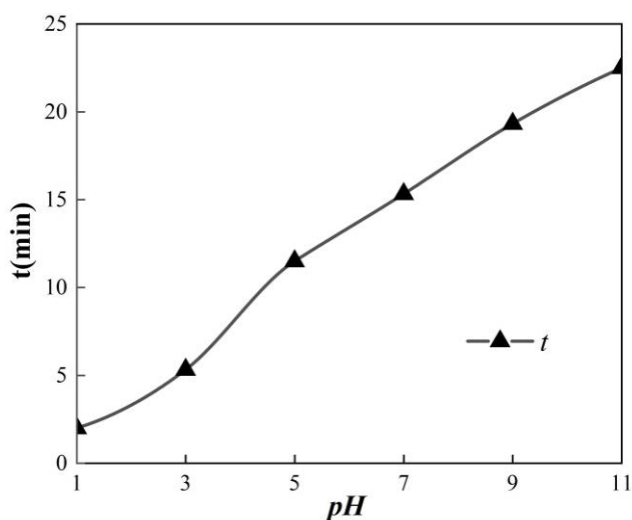


Fig. 11. Effects of pH on t .

Fig. 11 shows that in the pH range of 1.0 to 11.0, the exothermic time of the reaction increases with the increase of pH, this is because the reaction rate is affected by pH, the higher the pH, the slower the exothermic reaction rate.

3.6. Analysis of reaction synchronicity

An experiment was performed to examine the synchronicity of the exothermic reactions and the degradation reactions during the degradation of OPD by the $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ Fenton system. The conditions of this experiment were as follows: $[\text{OPD}] = 0.04 \text{ mol L}^{-1}$, $\text{pH} = 7.8$, initial reaction temperature = 30°C , $[\text{H}_2\text{O}_2] = 0.2 \text{ mol L}^{-1}$, $[\text{Fe}^{2+}] = 10 \text{ mmol L}^{-1}$, and the reaction time was 60 min. The results of this experiment are illustrated in Fig. 12. Here, it is shown that the ΔT and η plots can be divided into a rapidly rising stage, a gradually rising stage, and a plateau stage. During the initial stages of the reaction, the solution has high concentrations of OPD, H_2O_2 , and Fe^{2+} . Therefore, the cyclic reactions between Fe^{2+} , Fe^{3+} , and H_2O_2 will proceed rapidly during this stage, thus generating large amounts of SOH and $\text{HO}_2\cdot$. The radicals $\cdot\text{OH}$, $\text{HO}_2\cdot$, and the OPD will then react rapidly with each other, which results in the degradation of the OPD, and in large amounts of heat being released. This will cause ΔT and η to rise rapidly. Under the conditions of this experiment, the period where ΔT and η rose rapidly is almost 20 min long. As the reaction continued to progress, the H_2O_2 and OPD concentrations in the solution rapidly decreased, thus slowing the reaction. This caused ΔT and η to increase more slowly, and ΔT and η both approached their maximum values when the reaction reached 30-min. After 30 min of reaction time, the concentration of OPD and H_2O_2 in the solution approached depletion, which caused the reaction to become very slow. Consequently, ΔT and η remained almost unchanged even as reaction time continues to increase. Based on the analysis above, the trends of the ΔT and η plots were nearly identical. Therefore, the degradation reactions and exothermic reactions that occur during the degradation of OPD by the $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ Fenton system are practically synchronous.

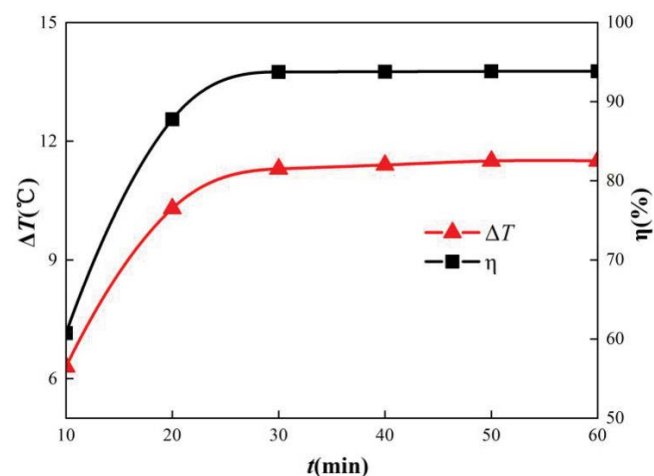


Fig. 12. Effects of reaction time on ΔT and η .

4. Conclusions and outlook

The following conclusions were obtained from our study of the heat-releasing behaviors of the homogeneous $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ Fenton system during the degradation of OPD solutions: (1) When the concentration of OPD wastewater increases from 0.01 to 0.04 mol L^{-1} , the ΔT after O_3 degradation of OPD wastewater increases from 2.5°C to 9.5°C, and ΔC increases from 1,497.9 to 5,187.3 mg L^{-1} ; The ΔT of the homogeneous $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ Fenton reagent degraded OPD wastewater increased from 9.1°C to 11.3°C, and the ΔC increased from 1,795.7 to 7,541.8 mg L^{-1} . Compared with O_3 , homogeneous $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ Fenton reagent exhibits better degradation and exothermic performance. (2) The process of O_3 degradation of OPD wastewater is a single oxidation exothermic process. In the process of $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ homogeneous Fenton degradation of OPD wastewater, Fe^{2+} , Fe^{3+} catalyze the cyclic reaction of H_2O_2 to produce $\cdot\text{OH}$ radicals, the oxidation reaction of OPD oxidation by $\cdot\text{OH}$ radicals and the quenching reaction of H_2O_2 , the consumption of $\cdot\text{OH}$ and $\text{HO}_2\cdot$ radicals themselves, there are three reaction processes in the quenching reaction, the superposition of multiple reaction heats is the main reason for the effective increase of sewage temperature in the degradation process of homogeneous $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ Fenton system. (3) The homogeneous $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ Fenton system exhibits excellent degradation and exothermic characteristics during the degradation of OPD wastewater. Under the condition that $[\text{H}_2\text{O}_2]$ is 0.2 mol L^{-1} , $[\text{Fe}^{2+}]$ is 10 mmol L^{-1} , and $T_0 = 30^\circ\text{C}$, the ΔT of 200 mL OPD sewage with a concentration of 0.04 mol L^{-1} is 11.3°C, and η is 93.75%, T is 21 min.

This paper summarizes the heat release law of the process of homogeneous $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ Fenton degradation of OPD wastewater, which is of positive significance for the energy utilization of wastewater treatment.

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