



## Efficiency optimization of a microwave-assisted Fenton-like process for the pretreatment of chemical synthetic pharmaceutical wastewater

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### ABSTRACT

Chemical synthetic pharmaceutical wastewater was treated using a microwave-assisted Fenton-like (MW-Fenton-like) process with satisfactory efficiency. Firstly, based on the MW power chosen, three factors, namely ferric sulfate dose, hydrogen peroxide dose, and total organic carbon (TOC) concentration were used to investigate the improvement in the efficiency of the MW-Fenton-like process for pharmaceutical wastewater pretreatment. Ferric sulfate and hydrogen peroxide doses (ferric sulfate 1.5 mg/L and hydrogen peroxide 10 mL/L) were low, after mixing well, oxidation decomposition was explored without acidification, this time was short (6 min). Under optimal conditions, the removal rate of TOC was with satisfactory effects (57.5%). Furthermore, the initial pH value was selected without adjustment when the MW radiation started. It was unnecessary to extend the radiation time because no hydrogen peroxide existed in system with the radiation time of 8 min. The influent was unnecessary to be diluted. Biodegradation of the wastewater could be elevated well (BOD<sub>5</sub>/COD arose from 0.23 to 0.40). Moreover, all of coloration from Riboflavin sodium phosphate dissolved (<15 mg/1 L wastewater) was completely removed in the sample. Finally, according to the TOC removal, the second step (flocculation precipitation) was as equally important as the first step (oxidation decomposition), though ferric sulfate dose was low. The effect of biological treatment was unsatisfactory compared with MW-Fenton-like process.

*Keywords:* Fenton-like; Microwave; Pharmaceutical; Wastewater

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### 1. Introduction

Chemical synthetic pharmaceutical wastewater is a common industrial form of wastewater. It is characterized by its biorefractory nature, and a relatively high degree of coloration [1,2]. Such industrial waste is hazardous if not properly treated and disposed of.

Recently, the effective treatment of pharmaceutical wastewater has become a challenging task for environmental safety. With regard to pharmaceutical wastewater of good biodegradability, anaerobic/aerobic biological process was explored. Otherwise, physical method, chemical method, physical-chemical method was explored as pretreatment to elevate biodegradability of the wastewater. When the effluent

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from biological process did not reach specified standard, post-processing was required to reach the object [3–8].

Advanced oxidation processes are effective in treating pharmaceutical wastewater [9,10], among which the Fenton method is one of the most popular. The mechanism of the classic Fenton method has been widely discussed in the literature [11]. This method uses ferrous ions ( $\text{Fe}^{2+}$ ) and hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) under acidic pH conditions (2–5) to yield hydroxyl radical ( $\cdot\text{OH}$ ) and considers the potential flocculation capability of Fenton's reagent by hydroxyl–ferric complexes [12]. The standard electric potential of  $\cdot\text{OH}$  is 2.80 V, which falls between the electric potentials of fluorine gas ( $\text{F}_2$ ) and ozone gas ( $\text{O}_3$ ). The oxidizability of  $\cdot\text{OH}$  is notably much more powerful than that of  $\text{H}_2\text{O}_2$ , whose standard electric potential is 1.77 V only [13,14].

However, industrial wastewater contains various inorganic or organic interferents that can retard the catalytic reactions in the classic Fenton process by reacting with  $\text{Fe}^{2+}$  or  $\text{H}_2\text{O}_2$  [15–18]. The complicated compositions of wastewater result in the loss of radicals,  $\text{H}_2\text{O}_2$ , or the activity of a homogenous catalyst (e.g.  $\text{Fe}^{2+}$ ). Therefore, Fenton-like processes, which use catalysts other than  $\text{Fe}^{2+}$  have been widely studied and used in industrial wastewater treatment. Fenton-like reactions are complex and capable of generating both  $\cdot\text{OH}$  and higher oxidation states of iron [19]. During the whole course of the reaction, newly generated ferrous ions exist more stably in the wastewater system; in addition, ferric hydrolysis or complexes generated by the combination of  $\text{Fe}^{3+}$  with some pollutants or intermediates also serve as catalysts for Fenton-like reactions [20,21]. Therefore, the efficiency of radical chains in a Fenton-like method is much higher than that in the classic Fenton process. In a Fenton-like method used for industrial wastewater treatment, the initial oxidant (i.e.  $\text{H}_2\text{O}_2$ ) can be more efficiently transferred into  $\cdot\text{OH}$  and higher oxidation states of the iron, with the process being more stable compared with the classic Fenton method.

The common reaction time for a single Fenton-like process lasts more than 20 min, which is still a long time in modern industry. Microwave-assisted Fenton-like (MW-Fenton-like) processes not only can achieve treatment efficiency similar to that of stand-alone Fenton-like processes, but also may reduce reagent dosage and shorten the reaction time. As known, MW frequency was between 300 and 300,000 MHz, and the most common frequency was 2,450 MHz, MW could alter ion migration and the rotation of dipoles of ions but not change molecule structure [22]. Thus, through improvement of ferric ion or hydrogen peroxide

vibration with the help of MW, the efficiency of Fenton-like process could be enhanced much more.

Environmental reactions are widely known to be more complex and confusing than ordinary chemical reactions. This study explored the key characteristics of MW-Fenton-like process and then optimized the efficiency of the process. Total organic carbon (TOC) is used to quantitatively evaluate the extent of final degradation (mineralization) in reactions [23,24]. In this study, we used ferric sulfate [ $\text{Fe}_2(\text{SO}_4)_3$ ] instead of ferrous sulfate [ $\text{FeSO}_4$ ] as the catalyst in the MW-Fenton-like reaction, because the former compound has a much lower hydrolysis pH level than the latter under MW radiation.

Chemical synthetic pharmaceutical wastewater with special characteristics was introduced as above and MW-assisted Fenton-like process was explored with distinctive advantages. Key characteristics about such advantages were depicted as below: low amount of  $\text{Fe}_2(\text{SO}_4)_3$  and  $\text{H}_2\text{O}_2$ , unwanted acidification of the initial reaction system (i.e. wastewater mixed with  $\text{Fe}_2(\text{SO}_4)_3$  and  $\text{H}_2\text{O}_2$ ), short reaction time (i.e. MW radiation time), well decomposition of organic pollutants, favorable improvement of biodegradation, satisfactory coloration removal, moreover, at the end of oxidation decomposition, flocculation precipitation was conducted to remove the organic pollutants in coordination with oxidation decomposition, the former was as equally important as the latter, though ferric sulfate dose was low. The study was conducted in Tianjin of China in the year of 2013.

## 2. Materials and methods

### 2.1. Wastewater and materials

Chemical synthetic pharmaceutical wastewater was collected from a pharmaceutical factory in Tianjin, China. The main products of the factory were cephalosporin and preparations thereof, cephalosporin intermediate, and several chemical raw materials, such as GCLE (7-Phenglacetamido-3-chloromethyl-3-cephem-4-carboxylic acid p-methoxybenzyl ester, Cephalosporin intermediate) and Riboflavin sodium phosphate, for curing special diseases. The wastewater was filtered using quantitative filter paper to remove the suspended solids and stored at 4°C with homogeneous properties. Its properties are listed in detail in Table 1.

All other chemicals used in this study were of analytical grade and used without further purification. The effects of  $\text{Fe}_2(\text{SO}_4)_3$  and  $\text{H}_2\text{O}_2$  (30%, w/w) were analyzed. An ordinary Midea MW oven was used as an MW emitter.

Table 1  
Properties of the filtered pharmaceutical wastewater

Item	COD (mg/L)	BOD <sub>5</sub> /COD	TOC (mg/L)	SS (mg/L)	pH	NH <sub>4</sub> <sup>+</sup> -N (mg/L)	Coloration
Value	2,169	0.23	209.3	258	7.12	75	50

## 2.2. Experimental setup and methods

Batch experiments were carried out in series using 1-L beakers. One liter of wastewater was introduced into the reactor. Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> was then added to the wastewater to reach the desired Fe<sup>3+</sup> concentration. After Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> had dissolved, the appropriate H<sub>2</sub>O<sub>2</sub> was added to the wastewater to start the Fenton-like reaction. After being mixed well, the reactor was placed in the MW oven and irradiated at the appropriate power level (119, 281, 385, 539, or 700 W) for different times (2, 4, 6, and 8 min). The water system started boiling in 8 min under medium high level of MW radiation. Furthermore, flocculation was carried out during the radiation process and enhanced by adjusting the pH level to 10 at the end of the reaction to enable larger flocs for removing pollutants from the wastewater to form. The flocs were allowed to settle for 10 min to produce a clear supernatant. The supernatant was subsequently decanted and filtered using a quantitative filter paper to determine the concentrations of TOC and other items.

A total of 6.38 mL of H<sub>2</sub>O<sub>2</sub> as the theoretical stoichiometric amount to 2,169 mg/L COD is required for 1 L of wastewater [25]. In this study, we used 10 mL of H<sub>2</sub>O<sub>2</sub> as the reference amount (Table 2).

## 2.3. Analytical methods

Milli-Q water (Milli-Q Academic equipment with influent of nano-filtrated purified water) was used to dilute water samples when necessary. COD was measured using a COD rapid testing instrument with reagents named D and Eg (LianHua Technology

Company, Lanzhou, China), BOD<sub>5</sub> was determined using an IS6 BOD system (WTW Corporation), and TOC was analyzed using a TOC analyzer (SHIMADZU). Suspended solids, NH<sub>4</sub><sup>+</sup>-N, and coloration were determined according to standard methods [26]. pH measurements were performed using a pH meter (pH-3C; LeiCi, Shanghai, China).

## 3. Results and discussion

### 3.1. Efficiency optimization of the MW-Fenton-like process

#### 3.1.1. Choice of MW power for the MW-Fenton-like process

MW power levels varied as high (700 W), medium high (539 W), medium (385 W), medium low (281 W), and low (119 W). Oxidation decomposition and flocculation precipitation both occurred in the Fenton-like process. MW could alter ion migration and the rotation of dipoles of ions in water, but it had no effect on the molecular structure [22]. The different MW power levels affected the generation of hydroxyl radicals (-OH), the high-valence iron complex, and the efficiency of flocculation. The water samples containing 10 mL of H<sub>2</sub>O<sub>2</sub> (somewhat high level) and 2.0 g of Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> (somewhat high level) were irradiated at five MW power levels for 8 min to optimize the MW-Fenton-like process.

As shown in Fig. 1, the removal rate of TOC significantly increased from 34.2 to 57.7% as the MW power increased from low to medium high. However, a further increase in MW power from medium high to high reduced the removal rate of TOC to a limited

Table 2  
Experimental design for optimizing key factors of MW-Fenton-like process

Key factors	Intensity of each key factors					
	MW (W)	mFe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> (mg)	H <sub>2</sub> O <sub>2</sub> (mL)	TOC (mg/L)	T (min)	pH <sub>Flocculation precipitation</sub>
MW power	119–700	2.0	10	209.3	8	10
Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> dose	539	0.5–2.0	10	209.3	2–8	10
H <sub>2</sub> O <sub>2</sub> dose	539	1.5	2.5–15	209.3	2–8	10
TOC concentration	539	1.5	10	26.2–209.3	2–8	10
Flocculation pH	539	1.5	10	209.3	8	7–13

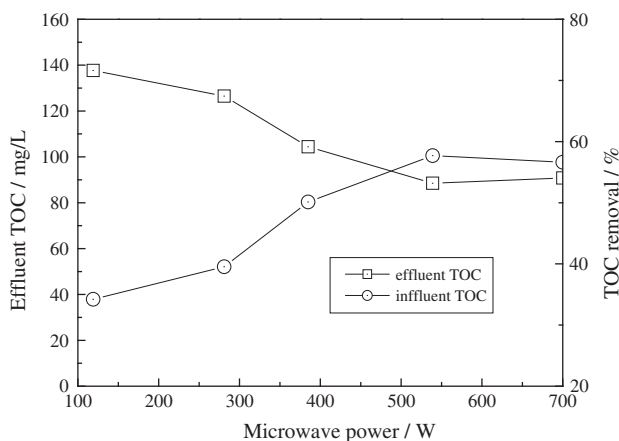


Fig. 1. Effect of MW power on TOC removal ( $\text{TOC}_0 = 209.3$  mg/L).

extent. This phenomenon was attributed to the fact that  $\text{H}_2\text{O}_2$  retained the properties of polar substances, allowing high MW power to excessively enhance the decomposition of  $\text{H}_2\text{O}_2$ . This was higher than 162 W as reported from literature, because actual wastewater has characteristic of many components and refractory pollutants [27]. Therefore, we chose medium high power (539 W) for optimal MW intensity. Hydrogen peroxide absorbed too much radiation energy under high level MW power which caused invalid decomposition of itself [28].

### 3.1.2. Effect of $\text{Fe}_2(\text{SO}_4)_3$ dose on the efficiency of the MW-Fenton-like process

Four 1-L samples with original concentrations were prepared to investigate the effect of  $\text{Fe}_2(\text{SO}_4)_3$  as a catalyst on the efficiency of the MW-Fenton-like process, which means the change in the TOC removal rate with reaction time under each  $\text{Fe}_2(\text{SO}_4)_3$  dose. Ten milliliters of  $\text{H}_2\text{O}_2$  were added to these samples, and  $\text{Fe}_2(\text{SO}_4)_3$  was introduced at the doses of 0.5, 1.0, 1.5, and 2.0 g, respectively. The MW power was set at medium high (539 W), and the reaction time was 8 min. Sampling was performed as described in the section of Experimental setup and methods.

At the  $\text{Fe}_2(\text{SO}_4)_3$  doses of 0.5, 1.0, 1.5, and 2.0 g/1 L wastewater, the removal rate of TOC peaked at 39.0% at 8 min, 49.7% at 8 min, 56.3% at 6 min, and 58.0% at 8 min, respectively. The data in Fig. 2 indicate that the efficiency of the MW-Fenton-like process was low when the  $\text{Fe}_2(\text{SO}_4)_3$  dose was insufficient (0.5 g). As the  $\text{Fe}_2(\text{SO}_4)_3$  dose increased, the efficiency of the process increased significantly. At higher doses (1.0 g), the efficiency of the process was maintained at

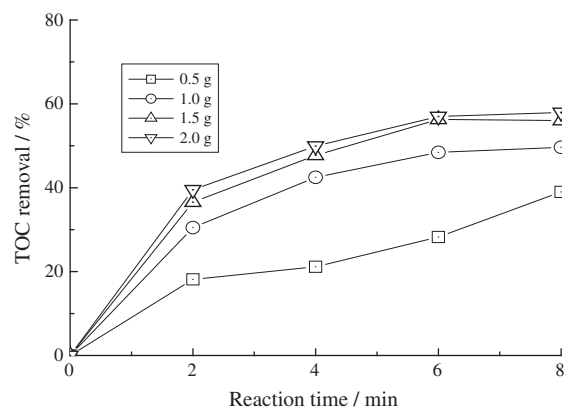


Fig. 2. Effect of  $\text{Fe}_2(\text{SO}_4)_3$  dose on TOC removal ( $\text{TOC}_0 = 209.3$  mg/L).

higher levels as well. When it was 1.5 g/1 L wastewater, the efficiency of the process approached the best states. Excessive  $\text{Fe}_2(\text{SO}_4)_3$  (2.0 g) did not alter the efficiency of the MW-Fenton-like process; however, the waste from reagents and the production of ferric sludge were severe. These indicate that the efficiency of the MW-Fenton-like process reached the ideal state at the  $\text{Fe}_2(\text{SO}_4)_3$  dose of 1.5 g/1 L wastewater. This regularity was similar to the data by other experiment on water distribution of single component or common wastewater [27].

### 3.1.3. Effect of $\text{H}_2\text{O}_2$ dose on the efficiency of the MW-Fenton-like process

To investigate the effect of  $\text{H}_2\text{O}_2$  as an oxidant on the efficiency of the MW-Fenton-like process, four 1-L samples with original concentrations were prepared. In total, 1.5 g of  $\text{Fe}_2(\text{SO}_4)_3$  was added to these samples, and  $\text{H}_2\text{O}_2$  was introduced at the corresponding doses of 2.5, 5, 10, and 15 mL. The MW power was set at medium high (539 W), and the reaction time was 8 min. Sampling was performed as described in the section of Experimental setup and methods.

At the  $\text{H}_2\text{O}_2$  doses of 2.5, 5, 10, and 15 mL/1 L wastewater, the removal rate of TOC peaked at 32.6% at 4 min, 50.1% at 8 min, 57.5% at 8 min, and 63.0% at 6 min, respectively. The efficiency of the MW-Fenton-like process was clearly unsatisfactory when the  $\text{H}_2\text{O}_2$  dose was insufficient (2.5 mL) compared with the theoretical dose (6.38 mL); Furthermore, the efficiency of the MW-Fenton-like process was satisfactory when the  $\text{H}_2\text{O}_2$  dose (10 mL) was somewhat greater than the theoretical stoichiometric amount of  $\text{H}_2\text{O}_2$ , thus, considering the cost of reagents, such  $\text{H}_2\text{O}_2$  doses could

be used for wastewater pre-treatment. In summary, as the  $\text{H}_2\text{O}_2$  dose (not involving excessive overdose) increased, the efficiency of the MW-Fenton-like process was improved obviously; moreover, the efficiency of the MW-Fenton-like process approached the ideal state at the  $\text{H}_2\text{O}_2$  dose of 10 mL/L wastewater. As many literatures reported, MW-Fenton or MW-Fenton-like process and traditional Fenton or Fenton-like process all required optimal hydrogen peroxide amounts [29–33] (Fig. 3).

### 3.1.4. Effect of TOC concentration on the efficiency of the MW-Fenton-like process

The four 1-L samples were yielded by diluting the whole original concentration as well as 1/2, 1/4, and 1/8 thereof with distilled water, with the corresponding TOC concentrations being 209.3, 104.7, 52.3, and 26.2 mg/L. They were treated using the MW-Fenton-like process as follows: 1.5 g of  $\text{Fe}_2(\text{SO}_4)_3$  was added to each sample, the  $\text{H}_2\text{O}_2$  dose was set at 10 mL, a medium high level (539 W) of MW power was selected, and the reaction time was fixed at 8 min. Sampling was performed as described in the section of Experimental setup and methods.

As shown in Fig. 4, when the sample was of 1, 1/2, 1/4, and 1/8 of the original concentration (209.3 mg/L), the removal rate of TOC peaked at 56.5% at 6 min, 58.9% at 6 min, 68.4% at 6 min, and 68.1% at 6 min, respectively. In the Fenton-like process, it is no help to increase the TOC removal of wastewater by diluting influent, therefore, it is unnecessary to dilute the influent by MW-Fenton-like process.

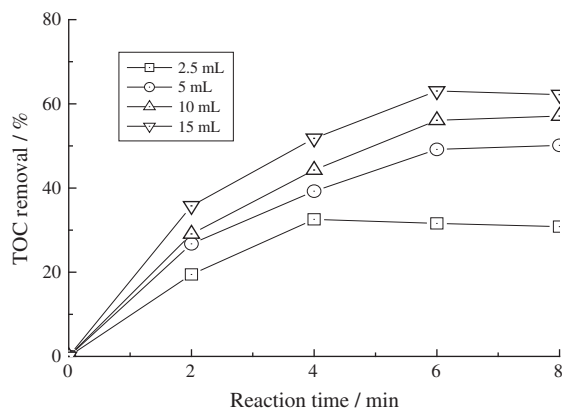


Fig. 3. Effect of  $\text{H}_2\text{O}_2$  dose on TOC removal ( $\text{TOC}_0 = 209.3$  mg/L).

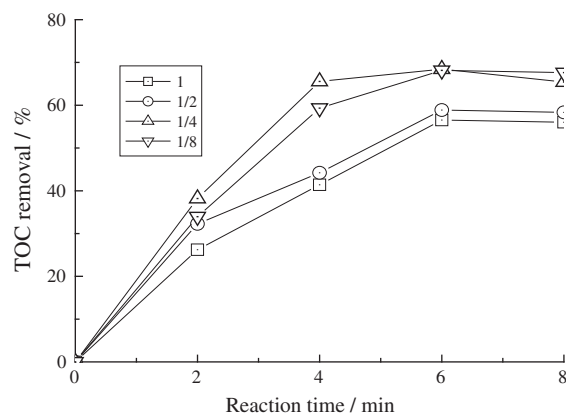


Fig. 4. Effect of TOC concentration on TOC removal ( $\text{TOC}_0 = 209.3$  mg/L).

### 3.1.5. Effect of initial pH value

The initial pH value of the wastewater was 7.12, 1.5 g/L ferric sulfate was added to the sample, the initial pH value was changed to 1.8, this was the pH value under normal condition. In order to investigate the effect of initial pH value on TOC removal of the wastewater by MW-Fenton-like process, the pH value of the system was adjusted to 2, 2.5, 3, 3.5, 4, and 4.5 by sodium hydroxide solution (5 mol/L) after ferric sulfate was added. Other conditions were depicted as below: 1.5 g of  $\text{Fe}_2(\text{SO}_4)_3$  was added to each sample, the  $\text{H}_2\text{O}_2$  dose was set at 10 mL, a medium high level (539 W) of MW power was selected, and the reaction time was fixed at 8 min. Sampling was performed as described in Section 3.2.

As shown in Fig. 5, the removal rate of TOC was 57.4, 56.2, 57.3, 52.2, 49.7, and 44.4%, respectively. The

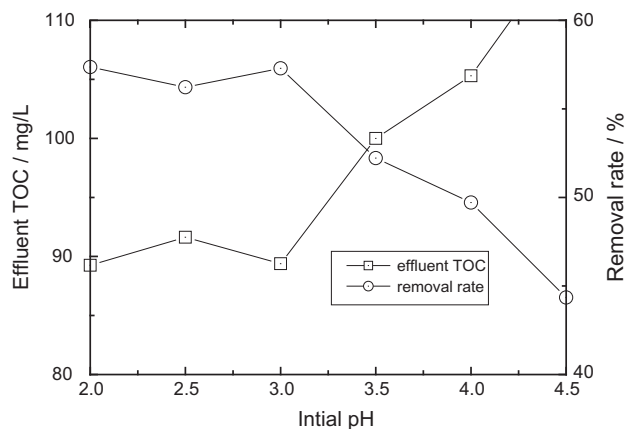


Fig. 5. Effect of initial pH on TOC removal ( $\text{TOC}_0 = 209.3$  mg/L).



removal rate of TOC was 57.5% corresponding to the pH value under normal condition. Therefore, at the beginning of the MW radiation, the initial pH value was selected after ferric sulfate was added with no adjustment.

### 3.1.6. Effect of the value of pH for flocculation precipitation on the efficiency of the MW-Fenton-like process

Five 1-L samples with original concentrations were prepared to investigate effect of the value of pH for flocculation precipitation on the efficiency of the MW-Fenton-like process. 1.5 g of  $\text{Fe}_2(\text{SO}_4)_3$  was added to each sample, the  $\text{H}_2\text{O}_2$  dose was set at 10 mL, a medium high level (539 W) of MW power was selected, and the reaction time was fixed at 8 min. Sampling was performed as described in Experimental methods.

As shown in Fig. 6, when the value of pH for flocculation precipitation was 10, 11, and 12, the removal rate of TOC was high (about 57.8%), in order to reduce the amount of NaOH solution (40 g/L), the value of pH was fixed at 10 as the optimal condition.

### 3.1.7. Effects of extending the radiation time after boiling

1.5 g of  $\text{Fe}_2(\text{SO}_4)_3$  was added to each sample, the  $\text{H}_2\text{O}_2$  dose was set at 10 mL, a medium high level (539 W) of MW power was selected, and the reaction time was fixed at 8 min, the system started to boiling. After boiling, radiation was explored continuously with the radiation time of 2, 4, 6, 8, and 10 min. The TOC concentration of the influent (i.e. original sample)

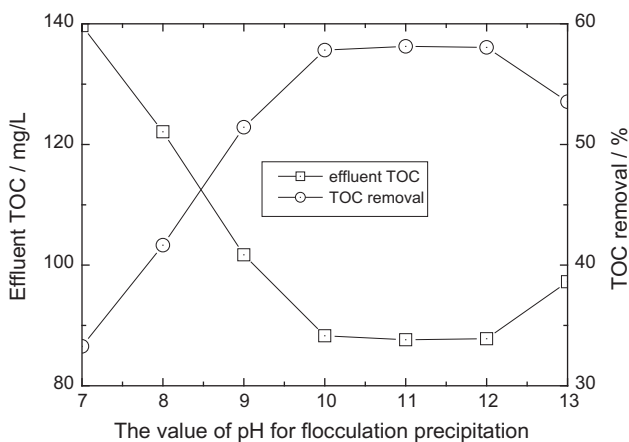


Fig. 6. Effect of the value of pH for flocculation precipitation on the efficiency of the MW-Fenton-like process ( $\text{TOC}_0 = 209.3 \text{ mg/L}$ ).

was 209.3 mg/L, the removal rate of TOC was 57.4, 57.4, 57.1, 54.1, 54.0, and 54.0%, respectively. The  $\text{BOD}_5/\text{COD}$  was all elevated from 0.23 to 0.4. Therefore, the consumption of hydrogen peroxide was accelerated by MW radiation, and no hydrogen peroxide existed in system with the radiation time of 8 min, meanwhile, the temperature was elevated from 19 min to boiling point (about  $94^\circ\text{C}$ ).

### 3.2. Change in $\text{BOD}_5/\text{COD}$ under optimal conditions

Four 1-L samples with original concentrations were prepared to investigate the change in  $\text{BOD}_5/\text{COD}$  under optimal conditions. 1.5 g of  $\text{Fe}_2(\text{SO}_4)_3$  was added to each sample, the  $\text{H}_2\text{O}_2$  dose was set at 10 mL, a medium high level (539 W) of MW power was selected, and the reaction time was fixed at 8 min. Sampling was performed as described in Experimental methods.

As shown in Fig. 7, The  $\text{BOD}_5/\text{COD}$  value of the former wastewater was 0.23, and effluent  $\text{BOD}_5/\text{COD}$  could peak at 0.40 at 6 min. Therefore, biodegradation of the wastewater could be improved obviously by the MW-Fenton-like process. According to pharmaceutical wastewater, the value of  $\text{BOD}_5/\text{COD}$  reached 0.40, and the biodegradability was satisfactory.

### 3.3. Degradation of the pollutant with high coloration in pharmaceutical wastewater treated using the MW-Fenton-like process under optimal conditions

The coloration of the wastewater was generated by Riboflavin sodium phosphate. Riboflavin sodium phosphate was added to the five 1-L samples at 0, 5, 10, 15, and 20 mg, respectively. After being completely dissolved, the wastewater was prepared for treatment by the MW-Fenton-like process. In total, 1.5 g of  $\text{Fe}_2(\text{SO}_4)_3$  and 10 mL of  $\text{H}_2\text{O}_2$  were added to the wastewater, which was then treated using the MW-Fenton-like process under medium high radiation (539 W) for 8 min. Supernatant was collected for TOC determination. It should be noted that Riboflavin sodium phosphate belonged to high color material and adding amount was low. Therefore, Figs. 7 and 8 illustrate that TOC of the influent was only slightly modified and the removal rate of TOC slightly changed in the five samples, while coloration changed with the addition of Riboflavin sodium phosphate.

This method of adding a standard material (i.e. target pollutant) can maintain the removal rate of TOC and help investigate the degradation of the pollutant with high coloration by the MW-Fenton-like process under optimal conditions. As shown in Fig. 9(a), the

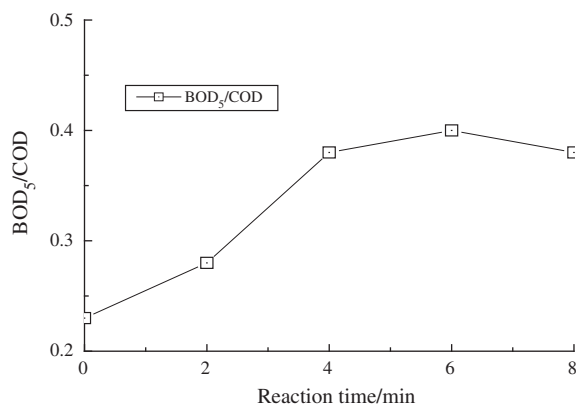


Fig. 7. Change in BOD<sub>5</sub>/COD under optimal conditions (MW power 539 W, ferric sulfate 1.5 mg/L and hydrogen peroxide 10 mL/L).

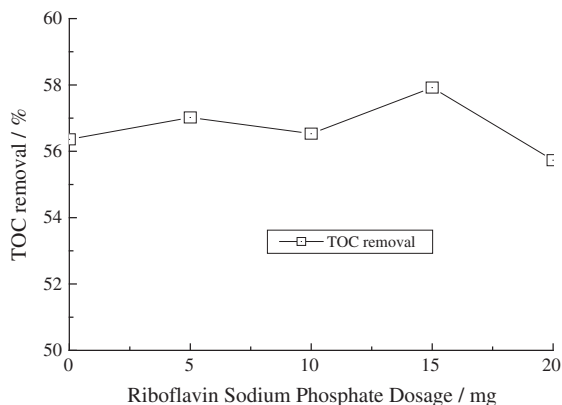


Fig. 8. TOC removal in the five samples treated using the MW-Fenton-like process under the same conditions (MW power 539 W, ferric sulfate 1.5 mg/L and hydrogen peroxide 10 mL/L).

five samples were scanned using an ultraviolet–visible spectrophotometer, with the characteristic peaks at approximately 266 and 350 nm in the ultraviolet band. Another peak at 444 nm was observed in the visible region. The five samples were treated using the MW-Fenton-like process under the same conditions. After the reaction, through visual colorimetry, the coloration of the effluent about the four samples at 0, 5, 10, 15 mg/L was completely removed (reach 0), while the coloration of the sample at 20 mg/L was 20. Furthermore, the effluent of the five samples was scanned using the ultraviolet–visible spectrophotometer. According to Fig. 9(b), indeed, adding a standard material under optimal conditions helped in the analysis of the degradation of the specified pollutant with high coloration, the results showed all of coloration from Riboflavin sodium phosphate dissolved

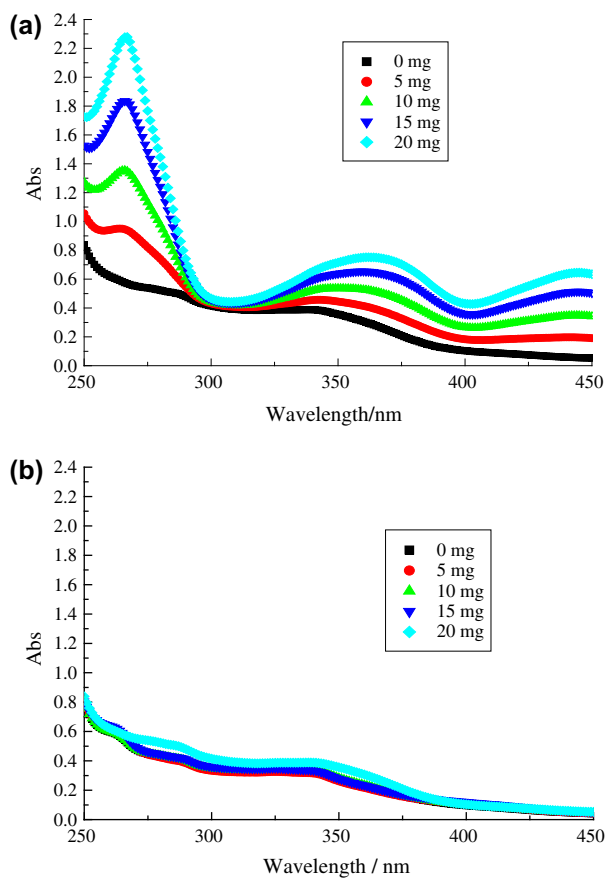


Fig. 9. UV scanning spectrum of the influent (a) and effluent (b) of the five samples treated using the MW-Fenton-like process (MW power 539 W, ferric sulfate 1.5 mg/L and hydrogen peroxide 10 mL/L).

(<15 mg/1 L wastewater) was completely removed in the experiment.

### 3.4. Comparison between oxidation decomposition and flocculation precipitation

The reaction of the MW-Fenton-like process included oxidation decomposition and flocculation precipitation. To compare these two effects, the wastewater was treated using single  $\text{Fe}_2(\text{SO}_4)_3$  flocculation precipitation; the MW power was set at medium high (539 W); and added  $\text{Fe}_2(\text{SO}_4)_3$  to the four samples at the doses of 0.5, 1.0, 1.5, and 2.0 g, respectively. The radiation time was 8 min, and the influent TOC was 209.3 mg/L. The corresponding effluent TOC concentrations were determined to be 155.4, 141.9, 140.9, and 140.2 mg/L. TOC removal is depicted in Fig. 10.

The removal rate of TOC increased from 25.7 to 33.0% as the dose of  $\text{Fe}_2(\text{SO}_4)_3$  increased from 0.5 to

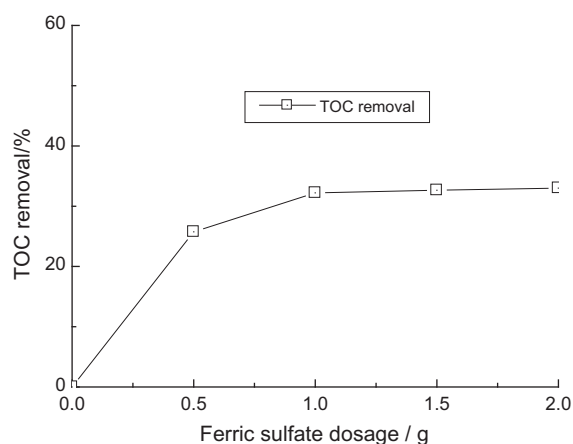


Fig. 10. Effect of  $\text{Fe}_2(\text{SO}_4)_3$  dose in single  $\text{Fe}_2(\text{SO}_4)_3$  flocculation precipitation ( $\text{TOC}_0 = 209.3 \text{ mg/L}$ ).

2.0 g/1 L wastewater. However, in the MW-Fenton-like process, the removal rate of TOC rose from 39.0 to 58.0%. Therefore, in MW-Fenton-like process, except oxidation decomposition, flocculation precipitation plays an important role in TOC removal of the wastewater, thus, it is important to explore flocculation precipitation by elevating the value of pH.

### 3.5. The comparison of biological treatment and MW-Fenton-like process for pretreatment

Sequence batch reactor was a typical bioreactor, which was chosen to treat the pharmaceutical wastewater. The sludge was taken from secondary sedimentation tank of one domestic wastewater plant in Tianjin. After proper settlement, concentrated liquid was gained, the MLSS was 6.5 g/L, MLVSS was 2.8 g/L. Two liter concentrated liquid (excessive dose) was introduced to three reactors having 5 L volume each, the biological treatment was explored for pretreatment respectively.

The influent was pharmaceutical wastewater, 1,000 mL wastewater was added to three reactors, full reaction time was 24 h, sampling was performed as described in Section 3.2. The treatment effect was unsatisfactory which was depicted as below:

The TOC concentration of effluent was 150.4, 154.2, and 148.5 mg/L, respectively. The removal rate of TOC was 28.2, 26.3, and 29.1%. The value of  $\text{BOD}_5/\text{COD}$  was all elevated from 0.23 to 0.30.

## 4. Conclusions

The MW-Fenton-like process used in this study is superior to that of classic Fenton process, as evidenced

by unnecessary dilution and acidification on influent, low chemical agent amount (ferric sulfate 1.5 mg/L and hydrogen peroxide 10 mL/L), short reaction time (6 min), improvement in reaction efficiency (the removal rate of TOC 57.5%). Moreover, no hydrogen peroxide existed in system with the radiation time of 8 min, it was unnecessary to extend the radiation time after boiling.

The  $\text{BOD}_5/\text{COD}$  value of the former wastewater was 0.23, and effluent  $\text{BOD}_5/\text{COD}$  could be elevated to 0.40 by the MW-Fenton-like process under optimal conditions.

Adding a standard material under optimal conditions helped in the analysis of the degradation of the specified pollutant with high coloration. The results showed all of coloration from Riboflavin sodium phosphate dissolved (<15 mg/1L wastewater) was completely removed in the experiment.

Moreover, comparative analysis of oxidation decomposition and flocculation precipitation revealed that not only oxidation decomposition but also flocculation precipitation played an important role in the MW-Fenton-like process.

Comparative analysis of biological treatment and MW-Fenton-like process for pretreatment showed that the effect of biological treatment was unsatisfactory which was depicted as below: The removal rate of TOC was 28.2, 26.3, and 29.1%. The value of  $\text{BOD}_5/\text{COD}$  was elevated from 0.23 to 0.30.

Water quality of the effluent was qualified to the demand of pharmaceutical wastewater pretreatment with some distinctive advantages as above.

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