



Microwave enhanced Fenton-like process for the treatment of high concentration pharmaceutical wastewater

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ABSTRACT

This paper explored a novel process for wastewater treatment, i.e. microwave enhanced Fenton-like process. This novel process was introduced to treat high concentration pharmaceutical wastewater with initial COD loading of 49,912.5 mg L⁻¹. Operating parameters were investigated and the optimal condition included as follows: microwave power was 300 W, radiation time was 6 min, initial pH was 4.42, H₂O₂ dosage was 1300 mg L⁻¹ and Fe₂(SO₄)₃ dosage was 4900 mg L⁻¹, respectively. Within the present experimental condition used, the COD removal and UV₂₅₄ removal reached to 57.53% and 55.06%, respectively, and BOD₅/COD was enhanced from 0.165 to 0.470. The variation of molecular weight distribution indicated that both macromolecular substances and micromolecular substances were eliminated quite well. The structure of flocs revealed that one ferric hydrated ion seemed to connect with another ferric hydrated ion and/or organic compound molecule to form large-scale particles by means of van der Waals force and/or hydrogen bond. Subsequently, these particles aggregated to form flocs and settled down. Comparing with traditional Fenton-like reaction and conventional heating assisted Fenton-like reaction, microwave enhanced Fenton-like process displayed superior treatment efficiency. Microwave was in favor of improving the degradation efficiency, the settling quality of sludge, as well as reducing the yield of sludge and enhancing the biodegradability of effluent. Microwave enhanced Fenton-like process is believed to be a promising treatment technology for high concentration and biorefractory wastewater.

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1. Introduction

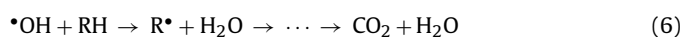
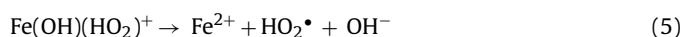
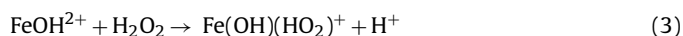
Recent studies indicated that antibiotics, which are specially designed to control bacteria in humans and animals, have been found in surface water [1,2] and sewage treatment plant effluents [3–5]. Treatment of pharmaceutical wastewater has always been troublesome to reach the desirable effluent standards due to the wide variety of the products produced in a drug manufacturing plant. The properties of pharmaceutical wastewater make it hard to be effectively eliminated by traditional biological treatment. Hence, biological wastewater treatment is insufficient for some recalcitrant pharmaceuticals. As a result, alternative treatment processes before and/or after biological treatment seem promising and even critical where pollution is present or anticipated.

Up until date, many researchers have been done a large number of investigations on advanced oxidation processes (AOPs) for the treatment of biorefractory wastewaters, including pharmaceutical wastewater [6–8]. Among these, Fenton's oxidation or Fenton-like reaction (FL) appeared to be the most promising one in terms of

cost-effectiveness and ease of operation. Recently, in a comprehensive review, Neyens and Baeyens [9] indicated that Fenton's oxidation was a very effective method in the removal of many hazardous organic pollutants in wastewaters. Fenton's oxidation could also be an effective pretreatment step by transforming constituents to by-products that were more readily to be biologically degraded and lower toxicity to microorganisms [10]. The suggested overall reaction for Fenton's oxidation is given as following [11]:



When the Fe²⁺ is substituted by Fe³⁺, the reaction of hydrogen peroxide with Fe³⁺ is referred as Fenton-like reaction. The mechanism of Fenton-like reaction accepted widely by most researchers is summarized as following [12,13]:



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Furthermore, the generated Fe^{2+} could react with hydrogen peroxide like reaction (1) to produce hydroxyl radicals. In addition, the Fenton-like reaction plays not only the role of oxidation but also coagulation by forming ferric–hydroxo complexes [14,15]. The ferric–hydroxo complexes would play the role like coagulants to remove some portions of organic contaminants. Less sludge would be produced in the Fenton-like reaction than that in traditional coagulation process [16].

Microwave (MW) have been widely used in organic synthesis [17] due to its special heating mechanism comparing with conventional heating. Conventional heating process relies on heat-transfer to supply energy into certain depth of a material. On the other hand, with respect to microwave process, the electric field exists in the body of the sample allows energy to be rapidly dissipated beyond the sample surface. Microwave heating does not therefore rely on heat-transfer, and consequently heating times can be up to three orders of magnitude lower than that of conventional heating [18]. A number of heating mechanisms exist depending on the material and microwave frequency, although the most common one is dipolar polarisation. In this case, a dipolar molecule such as water tries to align itself with the electric field component of the microwave. At the defined microwave frequencies of 300 MHz–3 GHz the electric field alternates, the polarised molecule attempts to rotate in phase with the alternating field. Frictional resistance to the molecular rotation gives rise to heating, and this mechanism is utilized in the domestic microwave oven where water acts as the microwave receptor. Other heating mechanisms are also proposed in the presence of ions (e.g. salt water) and free electrons (e.g. metal powders), which are also influenced by the alternating electric field [19]. In recent years, more and more reports have been appearing concerning the use of microwave to promote the oxidative degradation of biorefractory wastes [20–23] due to its advantages of swiftness, high-efficiency and no pollution to environment. These investigations suggested that MW was in favor of promoting the degradation efficiency of traditional treatment methods. Cravotto et al. [24] have been reported the combination of MW with Fenton-like for the treatment of POPs in soil. This paper displayed a better treatment efficiency of the combination processes than single Fenton-like reaction. The advantage of MW-enhanced degradation processes stimulates us to utilize MW-Fenton-like reaction for the treatment of pharmaceutical wastewater.

In the present work, the applicability of microwave enhanced Fenton-like reaction (MW-Fenton-like) for the treatment of pharmaceutical wastewater was tested under laboratory conditions. Operational parameters such as MW power, radiation time, initial pH, H_2O_2 dosage and $\text{Fe}_2(\text{SO}_4)_3$ dosage were optimized to obtain the maximum removal of organics. The structure of flocs was investigated in terms of transmission electron micrograph (TEM). Finally, the difference among the MW-Fenton-like, traditional Fenton-like reaction performed at ambient temperature and conventional heating assisted Fenton-like (CHFL) reaction performed at water bath was compared.

2. Experimental

2.1. Wastewater and reagents

Pharmaceutical wastewater was collected from Harbin pharmaceutical manufacturing group in China. The compositions of the solution were: ferment ramification, remnant penicillin and several of remnant menstrum, acetone, amyl butyric ester, formaldehyde etc. The characteristics of raw water are as following: COD (chemical oxygen demand) is $49,912.5 \text{ mg L}^{-1}$, TOC is $11,540 \text{ mg L}^{-1}$, pH is 4.42, UV_{254} is 1.491, Zeta potential is -30.1 and (biochemical oxygen demand) BOD_5/COD is 0.165, respectively. It should mention

that the UV_{254} was determined after the solution was diluted by 100 times. The COD is extremely high and biodegradability is very low, which indicates that this kind of wastewater belongs to high concentration and biorefractory wastewater.

Main reagents such as hydrogen peroxide (H_2O_2), ferric sulfate ($\text{Fe}_2(\text{SO}_4)_3$) were analytical grade and used as received without further purification. Solutions were prepared using deionized Milli-Q water. SANYO800 ordinary family microwave oven equipped with a condenser tube was used as experimental oven.

2.2. Analytical methods

Analyses of chemical oxygen demand and 5-day biochemical oxygen demand were carried out to investigate biodegradability of the pharmaceutical effluents after treatment. COD was measured by a titrimetric method using dichromate as the oxidant in acidic solution at 458 K for 2 h (Hachi). The BOD_5 of each sample was measured following Standard Methods [25]. The TOC of the system was analyzed using a TOC Analyzer (SHIMADZU TOC-VCPN). pH measurements were performed using a pH meter (pH-3C, Leici, Shanghai, China). UV_{254} was used as indicator of aromatic compounds and measured with a 752 UV-Vis Spectrophotometer analyzer (Shanghai, China) at wavelength of 254 nm. Zeta potential measurements were also performed in order to interpret the obtained results. The determinations of Zeta potential and conductivity were carried out using Zeta potential meter (Malvern, Zetasizer 2000, U.K.). Molecular weight distribution (MWD) was measured by the means of high-performance liquid chromatography (HPLC) equipped a UV-spectrophotometer (190–360 nm). The separation was performed using a Vp-ODS reversed phase column (mobile phase, pure water; flow rate, 0.4 mL min^{-1} ; injection, $100 \mu\text{L}$). UV wavelength was set to 210 nm. The morphology of the sediment sludge was observed with a H7500 transmission electron micrograph (TEM, Hitachi, Japan) with accelerated voltage of 80 kV. Liquid/solid ratio (L/S) was measured as the following steps: transported post-treatment effluent to a 50 mL measuring cylinder and stood for 1 h. Then, we measured the volumes of the supernatant and precipitated sludge. The ratio between the two values was denoted as L/S. Settlement rate (SR) was used as an indicator for the settling quality of sludge. This index was measured as follows: transported post-treatment effluent to a 50 mL measuring cylinder and determined the increasing volume of the supernatant in the first 10 min. The ratio of the increasing volume versus time was denoted as SR. The concentration of ferric ions was monitored by using ICP-OES (Optima 5300 DV, PerkinElmer).

In order to classify the aqueous species of Fe(III), a ferron-complexation timed spectrophotometric method was used on the basis of previous studies [26–28]. Three kinds of ferric species, which represented their different extent of hydrolysis and polymerization, was denoted as Fe(a), Fe(b) and Fe(c), respectively. Fe(a) included the simple monomeric and oligomeric species which reacted almost instantly with ferron. Fe(b) appeared to include the transitional low polymeric species which reacted with ferron gradually. Fe(c) consisted of more stable high polymeric species which did not react with ferron basically. The preparation of ferron reagent and standard ferric solution was followed the instruction of the literature [27].

2.3. Batch test

50.0 mL of sample was added into a beaker flask, and then mixed with some dosages of H_2O_2 and $\text{Fe}_2(\text{SO}_4)_3$ under atmospheric pressure. After being mixed well, the sample was put into MW oven and radiated with different power for some time. Then the L/S, SR, COD, TOC, BOD_5 , Zeta potential, MWD and pH of supernatant were determined after sedimentation. Traditional Fenton-like reaction

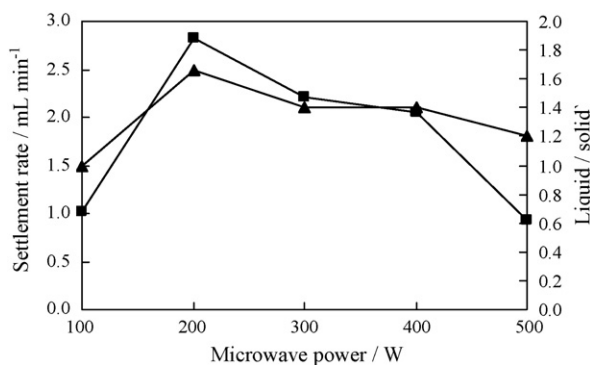


Fig. 1. Effect of microwave power on the variation of SR (▲) and L/S (■): pH 4.42; radiation time 6 min; $\text{H}_2\text{O}_2 = 1300 \text{ mg L}^{-1}$; $\text{Fe}_2(\text{SO}_4)_3 = 4900 \text{ mg L}^{-1}$.

was performed at ambient temperature with the same pH, H_2O_2 dosage and $\text{Fe}_2(\text{SO}_4)_3$ dosage as MW-Fenton-like reaction. Conventional heating assisted Fenton-like reaction experiment was carried out in water bath at the temperature identical to that of effluent of MW-Fenton-like, and the other parameters were same as the latter. All of experimental runs were performed in triplicate to diminish errors.

3. Results and discussion

3.1. Effect of MW power on removal efficiency

Fixing other parameters, MW power was adjusted from 100 W to 500 W to investigate its effect on degradation efficiency.

It can be seen in Fig. 1 that both liquid/solid ratio (L/S) and settlement rate increased firstly and then decreased as the increment of MW power. Excessive high or low power went against the sedimentation of flocs and resulted in the formation of massive sludge. As shown in Fig. 2, COD removal and BOD_5/COD (B/C) reached their maximum value when MW power was set at 300 W. Similarly, excessive high or low power was adverse to the removal of organic contaminants of wastewater.

Both oxidation and coagulation functions exist in the process of Fenton-like reaction. As the MW power increasing, the amount of solid which was produced by the means of coagulation decreased. In addition, in the range from 200 W to 400 W, the size of flocs with high SR was large, which indicated that appropriate MW power was in favor of the formation and sedimentation of coagulation flocs. To our knowledge, the main mechanism of coagulation of ferric salt contains charge neutralization and net rooling-sweeping action [29]. Differ from polyelectrolytes, the molecular weight multinuclear hydrolysates of ferric salt is not large enough, so that the

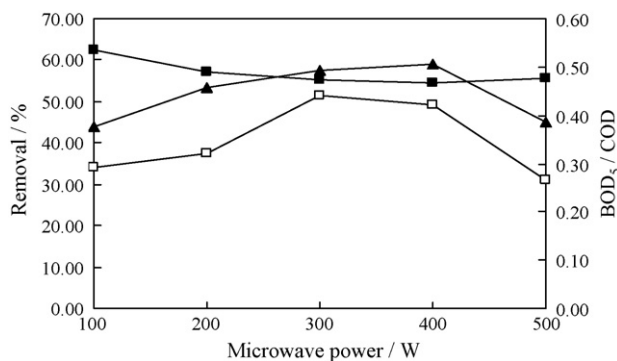


Fig. 2. Effect of microwave power on the evolution of COD and UV_{254} removal and B/C (▲, COD; ■, UV_{254} ; □, B/C): pH 4.42; radiation time 6 min; $\text{H}_2\text{O}_2 = 1300 \text{ mg L}^{-1}$; $\text{Fe}_2(\text{SO}_4)_3 = 4900 \text{ mg L}^{-1}$.

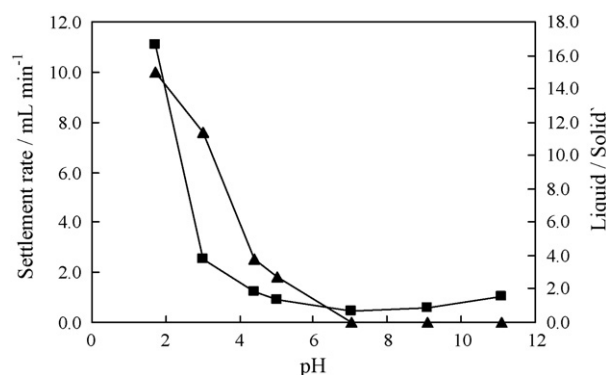


Fig. 3. Effect of initial pH on the variation of SR (▲) and L/S (■): microwave power 300 W; radiation time 6 min; $\text{H}_2\text{O}_2 = 1300 \text{ mg L}^{-1}$; $\text{Fe}_2(\text{SO}_4)_3 = 4900 \text{ mg L}^{-1}$.

mechanism of coagulation of ferric salt has nothing to do with adsorption bridging. The Zeta potentials of all effluents was about -30 which were identical to that of raw water, which indicated that Zeta potential was independent of the MW power. Therefore, it is suggested that the removal of colloidal substances was mainly attributed to net rooling-sweeping action in the present system.

The pH of raw water was 4.42 and then descended to 3.73 after being treated at 300 W. The variation of pH might reveal the formation of micromolecular organic acids due to the decomposition of macromolecular compounds. The B/C of wastewater ascended from 0.165 of raw water to 0.443 of effluent, suggesting that the effluent was suitable to successive biological treatment. In light of the evolution of UV_{254} , aromatic compounds were effectively eliminated as well in the present system. As a consequence, the MW power was selected 300 W in subsequent experiments.

3.2. Effect of initial pH on removal efficiency

As the increase of initial pH of solutions, L/S and SR descended gradually shown in Fig. 3. When initial pH of solutions was neutral or alkaline, the settlement of sludge was extremely bad and the formed flocs were small and loose, resulting in poor separation of liquid and solid. Fig. 4 shows that the removal of COD, aromatic compounds and B/C reached maximum in the range of pH from 4 to 5.

As displayed in Section 2.1, the colloidal particles in raw water were negatively charged and had thick diffusion layer. The repulsive force between these particles played dominant role so that these particles were in stable state. In order to neutralize the surface charges of colloidal particles for the purpose of destabilizing and settling, we should add some coagulants with positive charges.

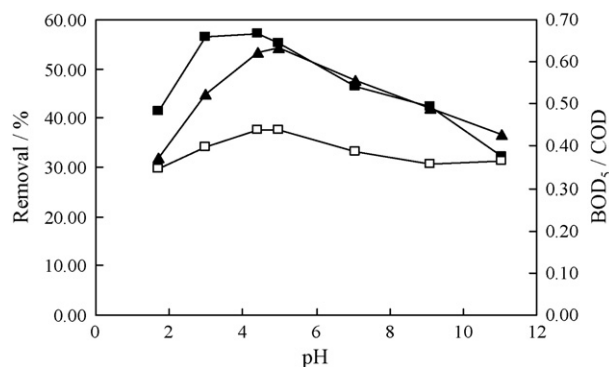


Fig. 4. Effect of initial pH on the evolution of COD and UV_{254} removal and B/C (▲, COD; ■, UV_{254} ; □, B/C): microwave power 300 W; radiation time 6 min; $\text{H}_2\text{O}_2 = 1300 \text{ mg L}^{-1}$; $\text{Fe}_2(\text{SO}_4)_3 = 4900 \text{ mg L}^{-1}$.

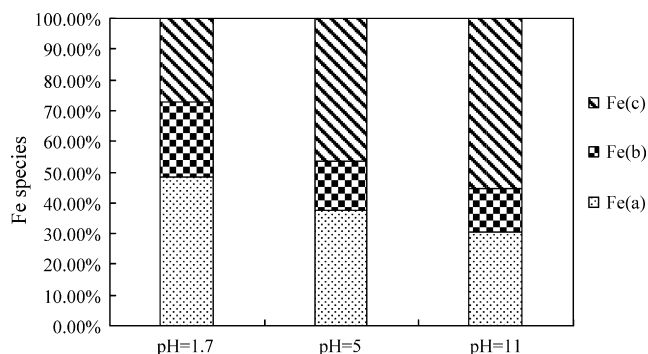


Fig. 5. Distribution of ferric species at different pH: microwave power 300 W; radiation time 6 min; $\text{H}_2\text{O}_2 = 1300 \text{ mg L}^{-1}$; $\text{Fe}_2(\text{SO}_4)_3 = 4900 \text{ mg L}^{-1}$.

From Fig. 5, it can be seen that the distribution of ferric species was of evident difference at different pH. In the strong acid (i.e. pH 1.7), Fe(a), both simple monomeric and oligomeric species, accounted for half of ferric species. According to previous study [30], ferric ion was speculated to be mainly in the form of Fe^{3+} , mononuclear $\text{Fe}(\text{OH})^{2+}$ and dimer $\text{Fe}_2(\text{OH})_2^{4+}$. These micromolecular formations had weak capacity of net rooling-sweeping action to colloidal substances so that reduced the efficiency of coagulation. Consequently, few organic compounds were removed via coagulation. Under this condition, degradation of organics was mainly ascribed to the oxidation of hydroxyl radicals generated by the catalytic oxidation of ferric ions to hydrogen peroxide. However, macromolecular compounds were hard to be oxidized, so the removal of COD was low and B/C elevated in a narrow range. In strong alkaline (pH 11), the amount of more stable high polymetric species, namely, Fe(c), exceeded 50%. In this condition, ferric ion was believed to be mainly in the form of $\text{Fe}(\text{OH})_3$ and $\text{Fe}(\text{OH})_4^-$ [30,31], so that the amount of positive charge decreased which led to reduce the charge neutralization to colloidal particles. The formation of large deals of flocs was dependent on net rooling-sweeping action due to the ferric hydroxide precipitation. Meanwhile, the hydrolyzation of ferric ions resulted in the formation of complex compounds between ferric and macromolecules, which reduced the catalytic activity of ferric ions and decreased the oxidation capacity of system, resulting in low removal [32]. In a mild medium (pH 5), the contents of Fe(a) and Fe(c) were near 40% and 50%, respectively. The main form of ferric was assumed to be $\text{Fe}_3(\text{OH})_4^{5+}$ [30], namely, both coagulation of hydroxyl-ferric and catalytic oxidation of ferric existed in such MW-Fenton-like system. Some portions of colloidal particles were removed in terms of coagulation of hydroxyl-ferric compounds, while other parts of organics were eliminated by means of the oxidation of hydroxyl radicals [33].

In addition, hydroxyl radicals produced via the catalytic oxidation of hydrogen peroxide by ferric could oxidize organic compounds in solution. Previous study [34] revealed that $\text{Fe}(\text{OH})^+$ was formed at pH in the range from 2 to 4. This species had high activity for catalytic decomposition of H_2O_2 to produce hydroxyl radicals. Buxton et al. [35] reported that at a pH around 2–3, the oxidation potential of hydroxyl radicals was 2.8 V, whereas, at a pH near 7, it was 1.9 V, decreasing the capacity of degradation of organic substances. On the other hand, the characteristic of some organic compounds in the wastewater would be changed at different pH conditions. Some organic compounds with special groups, such as $-\text{OH}$, $-\text{COOH}$, were deprotonated, resulting in higher negative charge at neutral or alkaline condition. Differently, these compounds had more neutral sites at acidic condition [32], which were easier to be removed by coagulation process. As a consequence, under this condition both the removal efficiency of pollutants and biodegradability of effluent were better and the

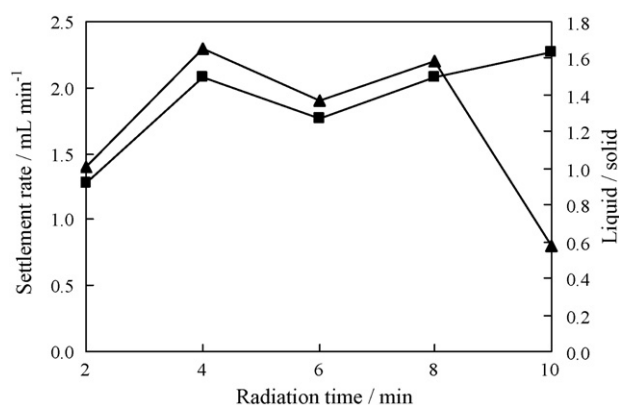


Fig. 6. Effect of radiation time on the variation of SR (▲) and L/S (■): microwave power 300 W; pH 4.42; $\text{H}_2\text{O}_2 = 1300 \text{ mg L}^{-1}$; $\text{Fe}_2(\text{SO}_4)_3 = 4900 \text{ mg L}^{-1}$.

amount of generated sludge was less. To some extent, both coagulation and oxidation could decrease the quantity of organics in solution and increase the biodegradability of effluent. Therefore, initial pH should meet the requirement of coagulation and oxidation at the same time to achieve high synthetic removal efficiency. The initial pH of raw water was 4.42 so that we needed not adjust it any more.

3.3. Effect of radiation time on removal efficiency

As depicted in Fig. 6, the yield of sludge was independent of the MW radiation time. However, the excessively long radiation time would result in a loose structure of flocs and make its settling quality bad, namely lower the SR. It can be seen in Fig. 7 that radiation time had no effect on removal of UV_{254} , but COD removal and B/C came to maximum at radiation time of 6 min. Therefore, the radiation time was chosen as 6 min in following experiments.

3.4. Effect of H_2O_2 dosage on removal efficiency

Fig. 8 shows that the removal of COD and TOC increased progressively when the H_2O_2 dosage increased to 3200 mg L^{-1} , and then the removal varied slightly from 3200 mg L^{-1} to $19,000 \text{ mg L}^{-1}$. At low H_2O_2 dosage, increasing the dosage of hydrogen peroxide would result in more production of hydroxyl radicals, which could enhance the oxidation capacity of the system, so that more organic compounds were eliminated. However, some of hydroxyl radicals would be scavenged by excess H_2O_2 through the following Eq. (7) [36,37]:

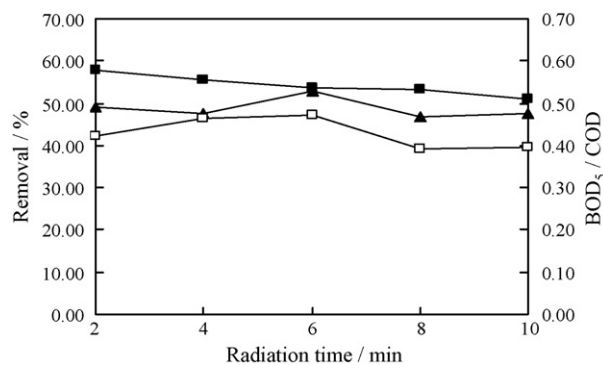


Fig. 7. Effect of radiation time on the evolution of COD and UV_{254} removal and B/C as a function of radiation time (▲, COD; ■, UV_{254} ; □, B/C): microwave power 300 W; pH 4.42; $\text{H}_2\text{O}_2 = 1300 \text{ mg L}^{-1}$; $\text{Fe}_2(\text{SO}_4)_3 = 4900 \text{ mg L}^{-1}$.

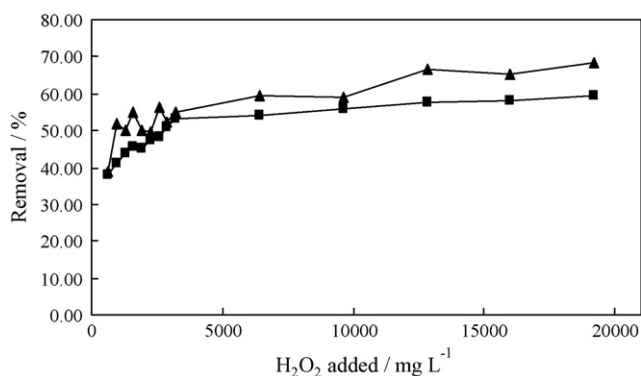


Fig. 8. Effect of H₂O₂ dosage on the evolution of COD and TOC removal (▲, COD; ■, TOC): microwave power 300 W; pH 4.42; radiation time 6 min; Fe₂(SO₄)₃ = 4900 mg L⁻¹.

In addition, Eq. (8) would become independent of hydrogen peroxide when excess H₂O₂ existed in the system [38]:



As a consequence, the variation of removal was slight when excess H₂O₂ was added into the system. Therefore, taking into account of cost and efficiency, 1300 mg L⁻¹ of H₂O₂ was chosen as the optimal dosage.

In the present system, the molar ratio of H₂O₂ to Fe³⁺ was 1.56:1, which was a low value for Fenton-like reaction comparing with other studies [39]. The theoretical mass ratio of removable COD to H₂O₂ is 470.6/1000. That is, 1000 mg L⁻¹ H₂O₂ theoretically removes 470.6 mg L⁻¹ COD by oxidation [37,40]. However, in our experiment, the mass ratio of removable COD to H₂O₂ was 61,021/1300, at H₂O₂ dosage of 1300 mg L⁻¹. It suggested that coagulation played a primary role in treatment of pharmaceutical wastewater, which was in agreement with other investigations [41,42].

3.5. Effect of Fe₂(SO₄)₃ dosage on removal efficiency

Fig. 9 shows that the yield of sludge increased as the increase of Fe₂(SO₄)₃ dosage, but the SR kept unchanging. Fig. 10 shows that the absolute value of Zeta potential decreased as the increase of Fe₂(SO₄)₃. It suggested that hydrolyzation products of ferric ions with positive charge weakened the repulsive force between colloidal particles owing to charge neutralization. Colloidal particles gathered together under the force of van der Waals force to form sludge. At the same time, as the increase of ferric dosage, a large number of mononuclear or multinuclear hydroxyl-complex ions and hydroxide precipitation formed. Colloidal particles were

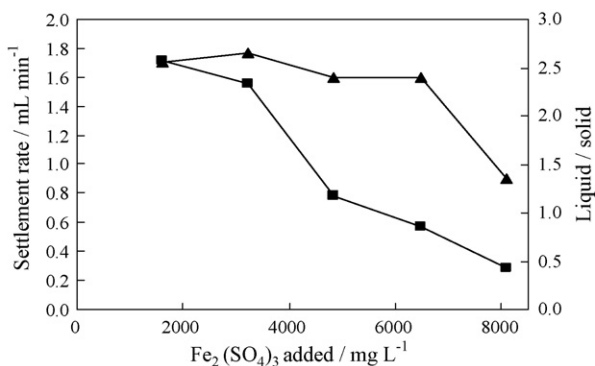


Fig. 9. Effect of Fe₂(SO₄)₃ dosage on the variation of SR (▲) and L/S (■): microwave power 300 W; pH 4.42; radiation time 6 min; H₂O₂ = 1300 mg L⁻¹.

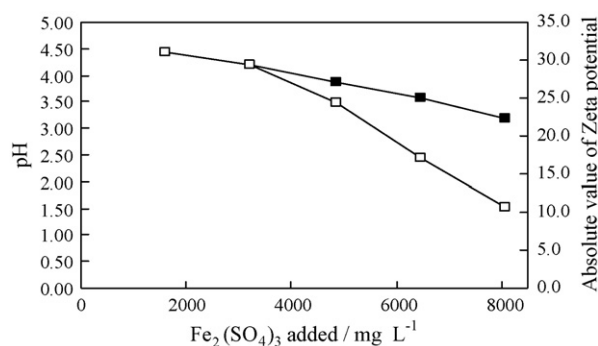


Fig. 10. Effect of Fe₂(SO₄)₃ dosage on the variation of pH and Zeta potential as a function of catalyst dosage (■, pH; □, Zeta potential): microwave power 300 W; pH 4.42; radiation time 6 min; H₂O₂ = 1300 mg L⁻¹.

trapped and tugged by these amorphous flocs and then were removed from solution. The combination of the two functions resulted in the yield of sludge increased as the increase of Fe₂(SO₄)₃. However, the variation of SR was slight, indicating that ferric dosage had no effect on the structure and morphology of flocs.

Fig. 11 shows the evolution of COD and UV₂₅₄ removal, demonstrating that the values of the two indicators increased as the increment of ferric dosage due to the improved coagulation of the system. While the B/C changed a little, it is inferred that the amount of H₂O₂ in the system was fixed so that the possible yield of hydroxyl radicals was limited and the organics which could be oxidized by hydroxyl radicals were finite as well. Therefore, the increase of ferric dosage would not lead to further elevation of B/C. Hence, the decrease of pH shown in Fig. 10 was mainly attributed to the hydrolyzation of ferric ions which increased the amount of H⁺. When the Fe₂(SO₄)₃ dosage was 4900 mg L⁻¹, the best removal efficiency was obtained. Therefore, in successive experimental runs, the Fe₂(SO₄)₃ dosage was selected as the above value.

According to the above mentioned experimental runs, the optimal operational condition of MW-Fenton-like system for the treatment of pharmaceutical wastewater was: MW power was 300 W, radiation time was 6 min, initial pH was 4.42, Fe₂(SO₄)₃ dosage was 4900 mg L⁻¹ and H₂O₂ dosage was 1300 mg L⁻¹, respectively. The COD removal, UV₂₅₄ removal were 57.53% and 55.06%, respectively, and BOD₅/COD was enhanced from 0.165 to 0.470 under this optimal condition.

3.6. Variation of MWD and structure of flocs

Fig. 12 shows the variation MWD before and after treatment under optimal operating condition of MW-Fenton-like reaction. One can see that both macromolecular substances (peaks at less

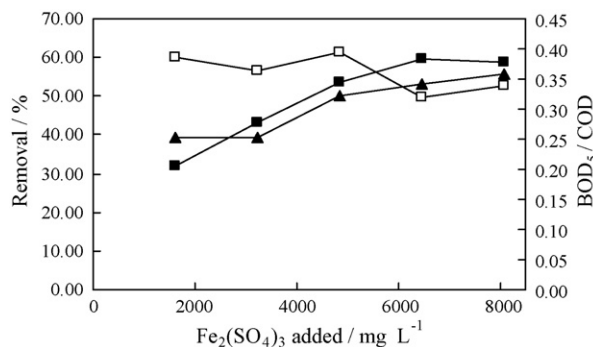


Fig. 11. Effect of Fe₂(SO₄)₃ dosage on the evolution of COD and UV₂₅₄ removal and B/C as a function of catalyst dosage (▲, COD; ■, UV₂₅₄; □, B/C): microwave power 300 W; pH 4.42; radiation time 6 min; H₂O₂ = 1300 mg L⁻¹.

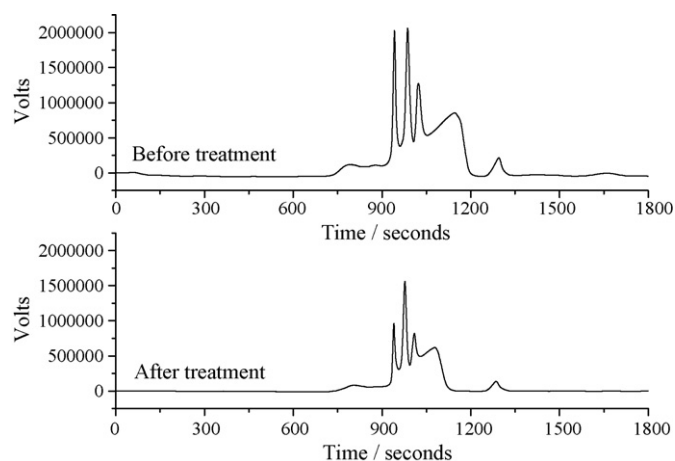


Fig. 12. Variation of MWD before and after treatment under optimal operating condition.

than 900 s) and micromolecular substances (peaks at more than 900 s) were eliminated quite well. To the best of our knowledge, in the course of Fenton-like reactions, generated hydroxyl radicals reacted with organic compounds and decomposed them into micromolecular substances, even organic acids [9,41,43,44]. As shown in this figure, almost all the macromolecular substances were degraded. It was speculated that these compounds were transformed into micromolecular substances, even organic acids, which enhanced the biodegradability of effluent. According to the removal of UV_{254} , more than half of aromatic compounds in wastewater were eliminated by means of oxidation and coagulation.

The structure of flocs was monitored by means of TEM, shown as in Fig. 13. It can be seen from this figure that all of particles linked with each other quite well. This would be attributed to the reason that one ferric hydrated ion seemed to connect with another ferric hydrated ion and/or one organic compound molecule to form large-scale particles by means of van der Waals force and/or hydrogen bond. Finally, these particles aggregated to form flocs and settled down.

3.7. Comparison with ambient temperature and conventional heating conditions

With the same reaction time, initial pH, H_2O_2 dosage and $Fe_2(SO_4)_3$ dosage, the result of MW-Fenton-like system was compared with those of traditional Fenton-like reaction and conventional heating assisted Fenton-like reaction experiments. As for the conventional heating experiment, its reaction temperature was identical to that of effluent of MW-Fenton-like system. The comparison was listed in Table 1.

According to the Zeta potential of effluents, one can see that the absolute values obtained in MW-Fenton-like system and CHFL condition were larger than that of ambient temperature condition. It elucidated that increment of temperature was adverse to the charge neutralization, which was ascribed to the reason that the hydrolyzation products of ferric ions were different at high temperature and room temperature. High temperature would lower the viscosity of water, which resulted in improving Brownian Motion. Kinetic energy increased with the increasing of temperature, as well as the collision between colloidal particles, which would enlarge the possibility for forming flocs. Taking into account of these reasons, net roiling-sweeping action played a dominant role at higher temperature in the course of coagulation.

Observed by naked eyes, the flocs formed in CHFL were larger than those in FL, but the flocs formed in the former condition were not uniform in size and looked like cotton, which resulted in poor settling quality as well. Regarding to the effluent of FL, the poor settling quality of sludge was dependent of the loose structure and extremely small size of flocs. However, the flocs formed in MW-Fenton-like system were uniform and compact, resulting in high settling quality. Therefore, the sludge in MW-Fenton-like system was prone to be separated compared with those formed in conventional heating and ambient temperature conditions. In these two heating systems, wastewater boiled in MW-Fenton-like system while the wastewater did not boil in CHFL system at the same effluent temperatures. This could be attributed to the distinctive heating mechanisms for these two heating methods. In MW heating progress, thermal cracking was produced by means of superheating, which would result in boil of wastewater [21]. At the status of boiling, the opportunity of collision between the hydrolyzation products of ferric ions was enlarged so that compact flocs were formed and the settling quality was improved. It can be speculated that during the course of coagulation of colloidal substances, microwave energy could promote the formation of ferric hydroxide and the hydrolyzation products of mononuclear or multinuclear of ferric. These complexes would react with colloidal particles by means of net roiling-sweeping action to form compact flocs which could settle promptly. Furthermore, MW energy could reduce the apparent volume of precipitates.

In previous study [45], membrane separation was introduced during the process of Fenton reaction due to the poor settling quality of sludge produced in Fenton process. In the present investigation, there is no need to use membrane separation because of the high settling quality of sludge produced in MW-Fenton-like system. The additional cost in MW-Fenton-like system was calculated in terms of the electric consumption per gram COD removal, i.e. $0.0209 \text{ kWh g COD}^{-1}$. This indicated that the additional electric consumption in MW-Fenton-like system was slight. On the other hand, the introduction of microwave could enhance the settling quality of sludge which was in favor of the separation between liq-

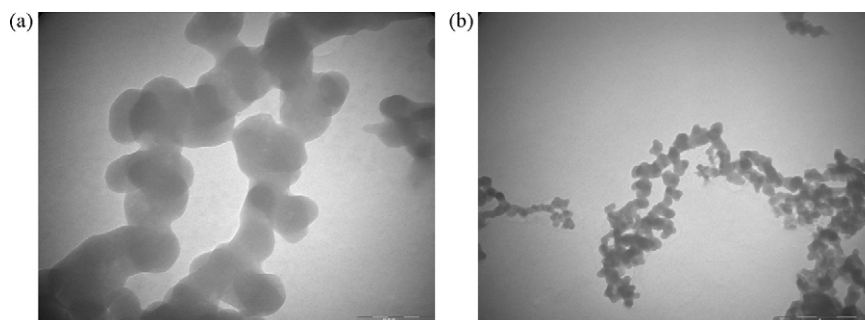


Fig. 13. TEM micrographs of flocs: (a) 200,000 \times and (b) 50,000 \times .

Table 1
Comparison of MW-Fenton-like system with ambient temperature and conventional heating.

Process	Settlement rate (mL.min ⁻¹)	Liquid/solid ratio	COD removal (%)	Zeta potential	B/C	Ferric residual (mg.L ⁻¹)
MW-Fenton-like	2.1	1.476	57.53	-32.0	0.470	154.300
CHFL	0	0.0196	52.05	-30.5	0.2933	179.700
FL	0	0	54.79	-22.0	0.3758	135.600

uid and solid phases. This advantage would result in diminishing the cost spent in successive separation and sludge treatment.

Moreover, the COD removal of MW-Fenton-like system was slightly higher than CHFL and FL, but B/C was enormously larger. The amounts of ferric residual of the three systems were almost equivalent (shown in Table 1). The molar ratio of H₂O₂ to Fe³⁺ of the three systems was in the range of 12:1 to 16:1, which was in agreement with those reported in the literatures with respect to Fenton or Fenton-like systems [37,39]. This indicated that at the same molar ratio of H₂O₂ to Fe³⁺, the high biodegradability of MW-Fenton-like system would be ascribed to the reason that microwave enhanced the oxidation capacity of the system. In addition, superior coagulation capacity of MW-Fenton-like system would also enhance the biodegradability of effluent by eliminating biorefractory macromolecular compounds [46,47]. COD removal and B/C in CHFL were inferior to those in FL, which might be attributed to the fact as follows. The flocs with larger size formed in CHFL had smaller specific surface area at this temperature, resulting in worse adsorption of organic compounds. Consequently, the degradation efficiency of wastewater was slightly worse in CHFL.

With regard to the above mentioned results, it could proclaim that MW was in favor of improving degradation efficiency of Fenton-like reaction comparing with Fenton-like reaction performed at ambient temperature and conventional heating. MW-Fenton-like reaction was beneficial to enhance the settling quality of sludge, reduce the production of sludge and improve the biodegradability of effluent.

4. Conclusions

In this work, microwave enhanced Fenton-like reactions for the treatment of pharmaceutical wastewater with high COD loading and poor biodegradability were studied systematically. Operational parameters such as microwave power, radiation time, initial pH, H₂O₂ dosage and Fe₂(SO₄)₃ dosage were optimized to obtain the maximum removal of organics. The optimal operational condition of microwave-Fenton-like system included microwave power 300 W, radiation time 6 min, pH 4.42, H₂O₂ 1300 mg.L⁻¹ and Fe₂(SO₄)₃ 4900 mg.L⁻¹, respectively. The COD removal, UV₂₅₄ removal were 57.53% and 55.06%, respectively, and BOD₅/COD was enhanced from 0.165 to 0.470 under this optimal condition. In addition, we investigated the variation of molecular weight distribution and the structure of flocs as well. The result of variation of molecular weight distribution indicated that both macromolecular and micromolecular substances were eliminated quite well. The structure of flocs revealed that one ferric hydrated ion seemed to connect with another ferric hydrated ion and/or one organic compound molecule to form large-scale particles by means of van der Waals force and/or hydrogen bond. Subsequently, these particles aggregated to form flocs and settled down. Eventually, traditional Fenton-like reaction and conventional heating assisted Fenton-like reaction were performed at the same reaction time, H₂O₂ dosage and Fe₂(SO₄)₃ dosage as microwave-Fenton-like reaction. The results indicated that microwave was in favor of improving degradation efficiency, the settling quality of sludge as well as reducing the yield of sludge and enhancing the biodegradability of effluent. Microwave enhanced Fenton-like process is believed to be a promising pretreatment technology for high concentration biore-

fractory wastewater and enables the effluent suitable for successive bio-treatment processes.

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