



Species distribution of ferric hydrolysates in microwave enhanced Fenton-like process and possible mechanism

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ABSTRACT

In the present work, the investigations were firstly focused on the effect of microwave on the species distribution of ferric hydrolysates, as well as the effect of hydrolysates speciation on the treatment efficiency of organic compounds in the process of coagulation. A ferron-complexation timed spectrophotometric method was used to classify the Fe(III) speciation under different reaction conditions. Effects of microwave power, initial pH and reaction temperature on species distribution were intensively investigated. When microwave power and initial pH were 300 W and 5, respectively, the amount of high polymeric ferric species, so-called Fe(c), reached its maximum. The increment of reaction temperature resulted in an increasing formation of Fe(c), and microwave was able to generate more Fe(c) than that of thermostatic method at the same temperature. Comparing with the treatment of pharmaceutical wastewater, the results indicated that Fe(c) facilitated the net rolling-sweep action for organic molecules in coagulation process, which enhanced the removal efficiency of entire reaction system.

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1. Introduction

Fenton or Fenton-like reactions have been widely investigated and developed for wastewater treatment for many years [1–5]. As we know, in the Fenton process, ferrous or ferric ions and hydrogen peroxide are employed under acidic pH conditions to produce strong oxidative hydroxyl radicals [6,7], as well as hydroxyl-ferric complexes which accounted for the coagulation capability of Fenton reagents [8–11]. In our previous work [12], we explored a novel process for the treatment of high concentration pharmaceutical wastewater, i.e. microwave enhanced Fenton-like process. This process was successfully used to treat high concentration pharmaceutical wastewater with initial COD of 49912.5 mg L⁻¹ under optimal operating parameters. In that work, we got a primary conclusion that 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. In order to figure out the mechanism, it should carry out tests to examine the procedures of ferric hydrolysis.

With regard to the investigation of ferric hydrolysis, it has been carried out since 1930s [13]. Under strong acidic condition, there is no simple Fe³⁺ but Fe(H₂O)₆³⁺, which contains six coordinated H₂O molecules [14,15]. Besides hydrolysis, polymerization of Fe(III) also takes place, as shown in elsewhere [14].

In view of the investigation of Fe(III) hydrolysis, Hedstrom confirmed the existence of FeOH²⁺, Fe(OH)₂⁺ and Fe₂(OH)₂⁴⁺ [16]. Biedermann and Schindler [17] also detected the existence of trimer Fe₃(OH)₄⁵⁺ in the course of Fe(III) hydrolysis. Generally, monomers of ferric hydrolysates had strong tendency to form polymers, of which the simplest one was dimmer Fe₂(OH)₂⁴⁺. This species possessed remarkable stability and played important role in the process of coagulation due to its special stereoscopic structure [18,19].

As for the determination of ferric hydrolysates, ferron-complexation timed spectrophotometric method has been widely studied and applied [20,21]. 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) was consisted of more stable high polymeric species which did not react with ferron. Therefore, on the basis of the variation of absorbance with time, three kinds of ferric species could be determined quantitatively.

However, to the best of our knowledge, there has not yet been any work focused on the investigation of the effect of microwave on ferric hydrolysis. And there is few researches reported the role of species of ferric hydrolysates played in the course of coagulation. Therefore, in the present work, we aimed to study the effect of microwave on species distribution of ferric hydrolysate, as well as the effect of the hydrolysis speciation on the treatment

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efficiency of high concentration pharmaceutical wastewater in a microwave enhanced Fenton-like reaction (FL-M) system. A ferron-complexation timed spectrophotometric method was used to classify the Fe(III) speciation under different reaction conditions. Effects of microwave power, initial pH and reaction temperature on species distribution were intensively investigated.

2. Experimental

Pharmaceutical wastewater was collected from Harbin pharmaceutical manufacturing group in China. The compositions of the solution included ferment ramification, remnant penicillin and several of remnant menstruum, acetone, amyl butyric ester, formaldehyde, etc. The characteristics of raw water were as following: COD was 49912.5 mg L⁻¹, UV₂₅₄ was 1.491, pH was 4.42, zeta potential was -30.1 and BOD₅/COD was 0.165, respectively.

Main reagents such as hydrogen peroxide, ferric sulfate and ferron agent 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.

The methods of determination of COD, BOD₅, Zeta potential, UV₂₅₄ could be seen in our previous work [12]. As for the ferron-complexation timed spectrophotometric method, the specific procedures are as follows: the preparation of solutions and standard curve could be seen in elsewhere [20,22,23]. Sample was taken from reactor and diluted by 10 times. Then 1 mL of the diluted solution was drawn out and transferred into a 50 mL colorimetric tube, followed by 0.5 mL of hydrochloric acid (1:1), 4 mL of 20% NaAC and 5 mL of 0.2% Ferron agent. Afterward, this mixture was diluted to 50 mL. Mixing of the solution was achieved by manual shaking. Solution without ferric ion was used as the blank. Timed spectrophotometric tests were conducted at 600 nm at a certain interval.

50 mL of distilled water and/or wastewater was added into a breaker flask, and then mixed with 1.5 mL of 0.8 mol L⁻¹ Fe₂(SO₄)₃ and 0.2 mL of 30% H₂O₂. pH was adjusted by 0.5 mol L⁻¹ H₂SO₄ and 0.5 mol L⁻¹ NaOH. After being mixed well, the sample was put into microwave oven and radiated with different power for some time. After cooling down, samples were drawn out for determination. As for the investigation of reaction temperature, experiments were conducted by means of thermostatic heating. All of experimental runs were performed in triplicate to diminish errors.

3. Results and discussion

3.1. Effect of microwave power on species distribution

The effect of microwave power on species distribution, as well as coagulation efficiency, was studied. The profile of the variation of absorbance of Ferron-Fe as a function of microwave power (data not shown) reveals that the complex reaction of ferric hydrolysate was characterized by typical dynamic profiles. Absorbance increased sharply in initial time and then became slow gradually. After 1 or 2 h, the absorbance kept constant. It is also clearly shown in this figure that microwave mainly influenced the amount of Fe(a) and Fe(c). The amount of Fe(b) was extremely small and almost constant in any condition. The function of non-linear curve fitting analysis of Origin 7.5 was used to fit the kinetic curves of Ferron-Fe obtained from different microwave power. The results suggested that all the reactions could be described by pseudo-first-order reaction equation:

$$A = A_0 + A_1(1 - e^{-(t/t_1)}) + A_2(1 - e^{-(t/t_2)}) \quad (1)$$

Table 1
Effect of microwave power on proportion of ferric species.

Microwave power (W)	Fe(a) proportion (%)	Fe(b) proportion (%)	Fe(c) proportion (%)
100	56.30	0.27	43.42
200	32.08	0.22	67.70
300	26.74	0.65	72.61
400	29.39	0.61	70.01
500	38.95	0.00	61.05

where A is absorbance, A_0 is the absorbance of Fe(a), A_1 is the absorbance of Fe(b)₁, A_2 is the absorbance of Fe(b)₂, t is reaction time (s), t_1 is the reaction time spent by Fe(b)₁ and Ferron, t_2 is the reaction time spent by Fe(b)₂ and Ferron. It should note that both Fe(b)₁ and Fe(b)₂ belong to Fe(b). The former contains hydroxyl-bridging low oligomers, which are of high activity. The latter includes high polymers, which are of low activity. Based on the equation, these parameters were calculated.

Substituting these fitted parameters into Eq. (1), the kinetic formulae of Ferron-Fe reaction at different microwave power would be obtained. According to these formulae, the amount of Fe(a) could be obtained by calculating the absorbance within 1 min. Meanwhile, the proportion of various ferric species in Fe_T (total ferric) was able to calculated on the basis of the following equations:

$$\text{Fe}_T = \text{Fe(a)} + \text{Fe(b)} + \text{Fe(c)}; \quad \text{Fe(a)\%} = \frac{\text{Fe(a)}}{\text{Fe}_T} \quad (2)$$

$$\text{Fe(b)} = (\text{Fe(a)} + \text{Fe(b)}) - \text{Fe(a)}; \quad \text{Fe(b)\%} = \frac{\text{Fe(b)}}{\text{Fe}_T} \quad (3)$$

$$\text{Fe(c)} = \text{Fe}_T - (\text{Fe(a)} + \text{Fe(b)}); \quad \text{Fe(c)\%} = \frac{\text{Fe(c)}}{\text{Fe}_T} \quad (4)$$

Table 1 shows the proportion of different ferric species at different microwave power. It can be seen from this figure that the amount of Fe(a) decreased and then increased as the increase of microwave power. Contrarily, the variation of the amount of Fe(c) displayed an opposite trend comparing with that of Fe(a). The amount of Fe(b) almost kept constant. When the microwave power was set at 300 W, Fe(c) reached its maximum, which indicated that proper microwave power favored the formation of high polymeric ferric in the present reaction system.

When microwave power was 100 or 500 W, the amount of Fe(a) was somewhat high, suggesting that the amount of ionic oligomeric ferric was large. However, at 100 W, the amount of mononuclear and primary polymeric ferric with positive charge was larger. Under this condition, the removal of organic compounds was mainly ascribed to the oxidation of hydroxyl radicals generated by means of ferric catalytic oxidation of hydrogen peroxide. Nevertheless, due to the weak net rolling-sweeping ability, coagulation did not play an important role at this condition. On the other hand, the amount of mononuclear and primary polymeric ferric with negative charge was larger at 500 W. Under this condition, because of the weak function of catalytic oxidation, the elimination of organic compounds was mainly attributed to the net rolling-sweeping action. Hence, neither of the conditions was able to achieve high removal efficiency.

Comparing with the treatment efficiency of pharmaceutical wastewater (as shown in Fig. 1 [12]), it could be found that COD removal achieved its summit, i.e. 58%, when microwave power was set at 300 or 400 W. Under the same microwave power, the proportion of Fe(c) also reached its maximum, as high as 72%, as shown in Table 1. This result indicated that at this range of microwave power, the amount of high polymeric ferric hydrolysates increased. These macromolecular compounds had three-dimensional stereoscopic structure, which was suitable to capture colloidal particles. As the volume of high polymeric ferric hydrolysates shrank, these

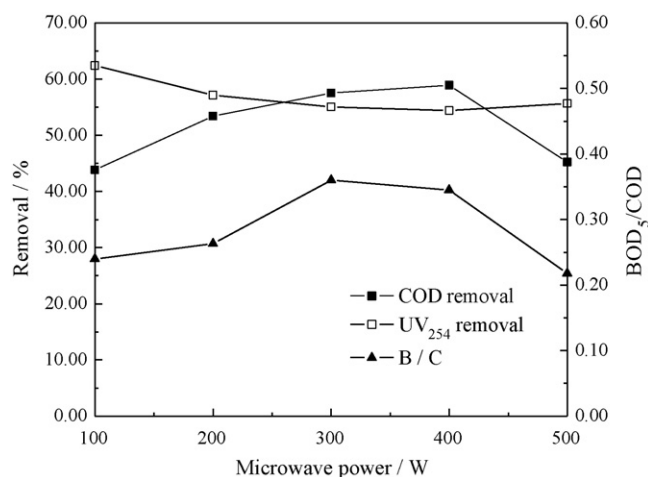


Fig. 1. Effect of microwave power on COD, UV₂₅₄ removal and B/C.

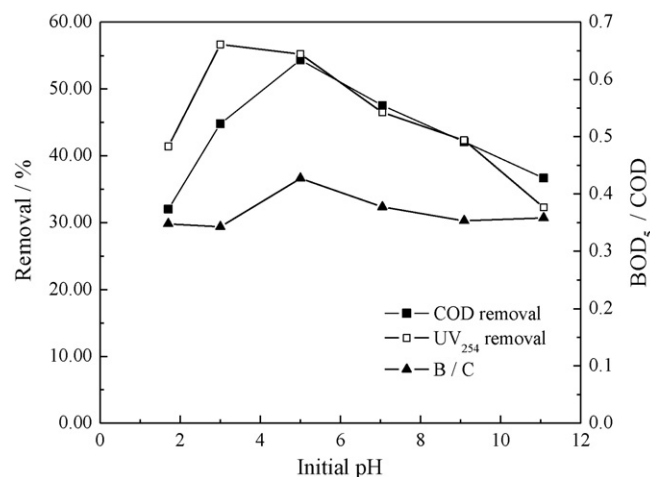


Fig. 2. Effect of initial pH on COD, UV₂₅₄ removal and B/C.

hydrolysates, including precipitates and suspended matters, like porous nets, could sweep down the colloidal and suspended particles to form flocule. This function favored to enhance the coagulation efficiency of reaction system, so that removed organic compounds in solution. At the same time, due to the polymerization of high polymeric ferric, the size of flocs also enlarged, which were prone to subside and accelerate the settlement rate. Consequently, it could be inferred that the increase of the amount of Fe(c) facilitate the net rolling-sweeping action, which enhanced the removal efficiency of macromolecular organics in coagulation system.

3.2. Effect of initial pH on species distribution

As we know, both oxidation and coagulation exist in Fenton system [10,11,24]. Therefore, the influence of initial pH was investigated. It can be seen from the figure depicted the effect of initial pH on species distribution (data not shown) that in strong acid, the variation of ferric species was of evident difference. When pH was higher than 5, the species distribution was almost the same. Based on Eq. (1), parameters were calculated. Subsequently, the proportion of various ferric species calculated on the basis of Eqs. (2)–(4) and listed in Table 2. One can see from this table that most of ferric hydrolysates were consisted of Fe(a) while only small portion of Fe(c) in strong acid condition. With the increase of pH, the amount of Fe(c) began to ascend while Fe(a) descended step by step. When pH exceeded 5, the variation of Fe(c) was slight. In order to compare the effect of ferric hydrolysates on removal efficiency of organic compounds, Fig. 2 shows the effect of initial pH on removal efficiencies during treatment of pharmaceutical wastewater [12].

Comparing Table 2 and Fig. 2, one can find the dependence of COD removal on ferric species. At extremely low pH (pH < 2), the COD removal efficiency was only 32%, the lowest of all. Within this condition, it was believed that Fe³⁺ was hard to react with hydrogen peroxide [25]. Therefore, the removal of organic compounds was mainly dependent on charge neutralization of ferric

hydrolysates with positive charge, other than the oxidative capacity of system. When pH was a little higher (pH 3.05), the COD removal was also somewhat higher (ca. 44%) than that of former condition. Due to the weak capacity of net rolling-sweeping action to colloidal substances of ferric hydrolysates in such pH condition [26], small portion of organic compounds were removed by means of coagulation and the amount of sludge was accordingly small. According to previous studies [27], the optimal pH value for Fenton or Fenton-like reaction was in the range of 3–5. Hence, it could be concluded that degradation of organics was mainly ascribed to the oxidation of hydroxyl radicals generated by the catalytic oxidation of ferric ions to hydrogen peroxide. In basic solution (pH > 7), as shown in Table 3, large amount of high polymeric species generated by means of ferric hydrolysis. In this condition, the formation of large deals of flocs was dependent on net rolling-sweeping action due to the ferric hydroxide precipitation [26,28]. With regard to oxidative aspect, according to the result of Deng and Englehardt [25], due to the lack of H⁺, the decomposition of H₂O₂ to generate hydroxyl radicals was suppressed. Meanwhile, the oxidative capacity of hydroxyl radicals was dependant on the pH of solution. When pH was zero, the redox potential of hydroxyl radicals was 2.8 V. While at pH 14, redox the potential declined to 1.95 V. Therefore, the oxidative capacity of hydroxyl radicals descended as the increase of pH [25]. Summarily, when pH was more than 7, the oxidation capacity of system was weakened and the elimination of organics was mainly dependent on net rolling-sweeping action of ferric hydrolysates, resulting in low removal efficiency, only 25–30%.

In the mild condition (pH = ca. 5), the amount of Fe(c) reached its summit. Therefore, organic pollutants were eliminated by means of coagulation, as well as oxidation. As mentioned before [27], researchers pointed out that in the range of pH 3–5, the oxidation capacity of Fenton system varied a little, indicating that the catalytic activity of ferric ions was unchanged in that range. Hence, some portions of colloidal particles were removed in terms of coagulation of hydroxyl-ferric compounds, while other parts of organics

Table 2
Effect of initial pH on proportion of ferric species.

Initial pH	Fe(a) proportion (%)	Fe(b) proportion (%)	Fe(c) proportion (%)
1.71	62.67	0.19	37.135
3.05	40.39	1.63	57.981
5.17	36.05	0.15	63.802
7.08	36.68	0.19	63.125
9	35.83	0.91	63.261
11	36.71	0.44	62.855

Table 3
Effect of reaction temperature on proportion of ferric species.

Reaction temperature (°C)	Fe(a) proportion (%)	Fe(b) proportion (%)	Fe(c) proportion (%)
20	75.29	0.93	23.77
40	74.10	1.41	24.50
60	80.72	0.86	18.43
70	66.01	0.39	33.60
80	58.67	1.23	40.10
90	51.92	0.18	47.90

Table 4
Comparison of FL-M system with FL-T.

Process	COD removal (%)	Zeta potential	B/C
FL-T ^a	52.05	−30.5	0.2933
FL-M ^b	57.53	−32.0	0.470

^a FL-T is short for Fenton-like thermostatic.

^b FL-M is short for microwave enhanced Fenton-like process.

were eliminated by means of the oxidation of hydroxyl radicals [29]. Consequently, the optimal COD removal efficiency achieved in this condition, which was 54%.

3.3. Effect of reaction temperature on species distribution

The effect of reaction temperature on species distribution was obtained (data not shown). Based on Eq. (1), parameters were calculated. Subsequently, the proportion of various ferric species in Fe_T was calculated on the basis of Eqs. (2)–(4) and listed in Table 3.

It can be seen from this table that as the increase of reaction temperature, the proportion of Fe(c) increased and that of Fe(a) decreased gradually. The result elucidated that the increase of reaction temperature facilitated the formation of high polymeric ferric species.

3.4. Possible mechanism of microwave on ferric hydrolysis

As shown in Table 3, the amount of Fe(a), Fe(b) and Fe(c) under different heating methods, i.e. thermostatic and microwave were 51.92, 0.18, 47.90 and 26.74, 0.65, 72.61%, respectively. It clearly indicated that at the same temperature, the amount of Fe(c) generated under the force of microwave was pronouncedly higher than that of thermostatic, which indicated that microwave was able to promote the formation of hydroxyl-ferric and mononuclear or multinuclear hydrolysates. To some extent, this result confirmed the non-thermal effect of microwave. Comparing with the treatment of wastewater [12], it could be inferred that the higher amount of Fe(c) would result in higher coagulation efficiency, as well as higher removal efficiency of whole system.

Under the same reaction condition, the result of FL-M system was compared with that of thermostatic Fenton-like reaction (FL-T). As for the conventional heating experiment, its reaction temperature was identical to that of effluent of FL-M system. The comparison is listed in Table 4 [12]. From this table, one can see that the biodegradability (B/C was 0.470) of effluent of FL-M was superior to that of FL-T. In addition, on the basis of the results shown in Fig. 9 and Table 1, it could be concluded that the increase of reaction temperature was beneficial for the formation of high polymeric species Fe(c), while microwave was able to generate more Fe(c) than that of thermostatic at the same temperature. Fe(c) was capable of facilitating the net rolling-sweeping action, which enhanced the removal efficiency of macromolecular organics in coagulation system.

Furthermore, as reported in literature [30], microwave was able to promote the generation of hydroxyl radicals via H_2O_2 decomposition, leading to improve the oxidative capacity of system. Comparing with the result obtained from thermostatic heating, the removal efficiency of phenol by microwave was as higher as 20%. Therefore, microwave was much more suitable for Fenton reaction to oxidize refractory organic compounds and improved the biodegradability of effluent.

With regard to the above-mentioned results, microwave not only promoted the formation of high polymeric ferric species to enhance the coagulation of system, but also improved the oxidation capacity of system. Consequently, it could proclaim that microwave was in favor of improving degradation efficiency of Fenton-like

reaction comparing with Fenton-like reaction performed at ambient temperature and conventional heating.

4. Conclusions

In the present work, the effect of microwave on species distribution of ferric hydrolysates, as well as the effect of the hydrolysates on the treatment efficiency of high concentration pharmaceutical wastewater in a microwave enhanced Fenton-like reaction system was intensively investigated. A ferron-complexation timed spectrophotometric method was used to classify the Fe(III) speciation under different reaction conditions. Effects of microwave power, initial pH and reaction temperature on species distribution were intensively investigated. When microwave power was set at 300 W, the amount of high polymeric ferric species Fe(c) achieved its summit. The difference of species distribution was significant at different pH. In strong acidic condition, hydrolysates were mainly consisted of monomeric or oligomeric species, and Fe(a) accounted for 62.7%. As the increase of pH, the amount of high polymeric ferric species increased. When pH was more than 5, the amount of Fe(c) reached its maximum, accounting for 64%. The increment of reaction temperature resulted in an increasing formation of Fe(c) and more importantly microwave was able to generate more Fe(c) than that of thermostatic at the same temperature. Comparing with the treatment of pharmaceutical wastewater, it could be inferred that the formation of high polymeric ferric species Fe(c) facilitated the net rolling-sweep action in coagulation process, which enhanced the removal efficiency of entire reaction system.

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