



## Enhanced degradation of 4-nitrophenol by microwave assisted Fe/EDTA process

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### ABSTRACT

A microwave assisted zero-valent iron oxidation process was studied in order to investigate the synergetic effects of MW irradiation on Fe/EDTA system (Fe/EDTA/MW) treated 4-nitrophenol (4-NP) from aqueous solution. The results indicated that the thermal effect of microwave improved the removal effect of 4-NP and TOC through raising the temperature of the system, as well as the non-thermal effect generated by the interaction between the microwave and the Fe resulting in an increase in the hydrophobic character of Fe surface. During the degradation of 4-NP in Fe/EDTA/MW system, the optimum value for MW power, Fe, EDTA dosage was 400 W, 2 g and 0.4 mM, respectively. The possible pathway for degrading the 4-NP was proposed based on GC/MS and HPLC analysis of the degradation intermediates. The concentration change course of the main bio-refractory by-products, the aminophenol formed in the degradation of 4-NP suggested a more efficient degradation and mineralization in Fe/EDTA/MW system. Finally, BOD<sub>5</sub>/COD<sub>Cr</sub> of the solution increased from 0.237 to 0.635 after reaction for 18 min, indicating that the biodegradability of wastewater was greatly improved by Fe/EDTA/MW system and would benefit to further treatment by biochemical methods.

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### 1. Introduction

The corrosion of zero-valent iron by oxygen could produce reactive oxidants capable of oxidizing pesticides, aromatic compounds, and chelating agents [1,2]. However, the oxidant yield was too low to degrade effectively those pollutants [3]. Several investigators had reported that the addition of EDTA to oxygen-containing solutions of zero-valent iron increased oxidant yield [4,5]. It was not a very effective mean for practical application yet [6]. Fortunately, the use of MW for assisting and strengthening oxidation of many recalcitrant organic compounds was extensively investigated [7]. Microwave (MW) was a part of the electromagnetic spectrum and occurs in wavelengths of 1 mm to 1 m at corresponding frequencies of 300 GHz to 300 MHz and could provide rapid heating of material. The characteristic of MW effect capable of enhancement of reaction rate via selective heating resulted from internal molecule vibration had attracted wide attention from many researchers, who had tried to modify conventional chemical to improve the degradation efficiency of pollutant by using MW assisted method [8].

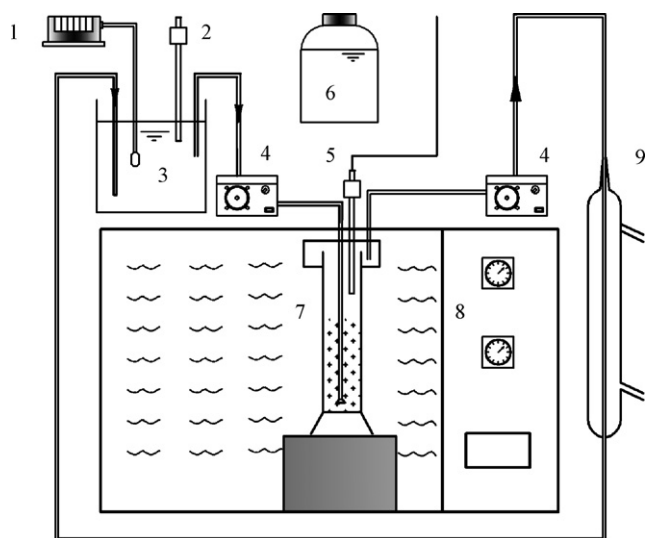
For example, when microwave and Fenton reagent were combined to degrade the organic pollutant, the thermal effect of the microwave could improve significantly the reaction rate of Fenton and raise the degradation efficiency of the organic pollutant [9]. Hence, a novel combined system of zero-valent iron irradiation by microwave worthy paid our attention, which could be used to efficiently destroy the organic via thermal effect from MW accelerate the reaction rates of zero-valent iron with EDTA to significantly increase oxidant yield.

At the same time, microwave was not merely a heat source. Some studies have assumed an additional effect termed a non-thermal effect resulted from polarizing parts of macromolecules aligning with the poles of the electromagnetic field leading to possible breakage of hydrogen bonds bring about denaturation and death [10]. For example, Horikoshi et al. [11] suggested that non-thermal effect from the microwave radiation also played a significant role in degrading organic through contrast experiments. Therefore, this study would also examine microwave's non-thermal effect on the degradation of organic by zero-valent iron system.

Accordingly, the present study focused on (1) examining the influence of microwave radiation on zero-valent iron oxidation system's capacity to degrade the organic matter; (2) delineating the difference in the heating effect between microwave and traditional methods by comparing the impact on the oxidation process of zero-valent iron with EDTA; (3) studying the effect of initial condition,

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**Fig. 1.** Schematic diagram of experimental setup (1) aeration device; (2) pH controller; (3) 4-NP solution container; (4) metrical pump; (5) thermometer; (6) acid solution bottle; (7) reactor; (8) microwave oven; (9) condenser tube.

such as MW power, iron and EDTA dosage as well as pH on the degradation of pollutant.

In this study, typical organic contaminant, such as 4-NP, was chosen as simulating pollutants. Several types of industrial and agricultural wastewaters containing 4-NP, were very harmful and highly toxic towards microorganisms [12,13]. It is therefore important to assess the fate of this pollutant in the environment and develop effective methods to remove them from water.

## 2. Materials and methods

### 2.1. Materials

Analytical grade 4-NP, ethylene diamine tetraacetic acid disodium dehydrate salt (EDTA), was purchased from School of Chemistry and Chemical Engineering, Nanjing University. Fe (diameters between 0.2 and 0.3 mm) and normal hexane (HPLC grade) were obtained from Nanjing Zhongdong Chemical Glass Instrument Co. Ltd., China, and other chemical (such as HCl and H<sub>2</sub>SO<sub>4</sub>) were of analytical grade.

### 2.2. Apparatus

As shown in Fig. 1, a modified household microwave oven (frequency 2.45 GHz, max power 750 W) was used to supply the microwave energy, inside which was an organic glass reactor ( $\varphi$  4 cm  $\times$  15 cm, Nanjing Pmma factory, China). Experiments were performed in this reactor. Temperature measurer (TM902C, Zhejiang, China) was used to detect the temperature of the solution in the reactor. 4-NP solution container was used to adjust the initial reaction condition. pH controller (Mettler Toledo FE20, Shanghai, China) and acid solution bottle were used to regulate the initial pH of the solution. The aeration device (SB-2800, Nanjing, China) supplied the solution with continuous oxygen needed for reaction. 4-NP was pumped into the reactor through digital display constant current pump (HL-6B, Shanghai, China) and degradation occurred under the MW irradiation. The effluent went through the condenser tube so that the temperature of the solution in the reactor was controlled at  $80 \pm 5^\circ\text{C}$ . The effluent then flowed back to 4-NP solution container, forming a closed cycling reaction system. The total amount of water processed by the system was 200 ml. The flow rate of the pump was controlled at the constant 200 ml/min.

The processes of Fe/EDTA method, MW assisted Fe/EDTA method (Fe/EDTA/MW), conventional thermally assisted Fe/EDTA method (Fe/EDTA/TH), MW alone method were operated in this apparatus, but Fe/EDTA/TH process had the organic reactor installed in the constant temperature oscillator (THZ-98, Taicang, China) maintaining the same temperature with that in the Fe/EDTA/MW process.

### 2.3. Analysis

All samples were immediately analyzed to avoid further reaction. The determination of 4-NP and *p*-aminophenol was carried out on a high-performance liquid chromatography (HPLC, Gilson, France) equipped with UV detector (UV-1575, Jasco Co. Ltd., Japan) and C<sub>18</sub> reverse-phase column (250 mm  $\times$  4.6 mm, 5- $\mu\text{m}$  ODS, Kromasil, China) [14]. Aliquots of 25  $\mu\text{l}$  were injected to HPLC to determine the concentration of 4-NP, running with mobile phase of acetonitrile/water/concentrated H<sub>3</sub>PO<sub>4</sub> (v/v/v) at 58/42/0.2. The separation was performed using an ODS-18 reversed phase column at a flow rate of 1.5 ml min<sup>-1</sup>, column temperature of 25  $^\circ\text{C}$ , and wavelength set of 254 nm. Analyses of COD<sub>Cr</sub> and BOD<sub>5</sub> were measured in parallel to investigate biodegradability of the 4-NP effluents after treatment [15]. Total organic carbon (TOC) analyzer was used to investigate the mineralization of 4-NP after the reaction. The intermediates were identified by GC-MS: typically a 10 ml sample from the reactor was acidified to pH < 2 with H<sub>2</sub>SO<sub>4</sub>. Then it was extracted from dehydrated with anhydrous sodium sulfate and 2 ml extract of it was took and stored in the fridge until analysis within 4 h [16].

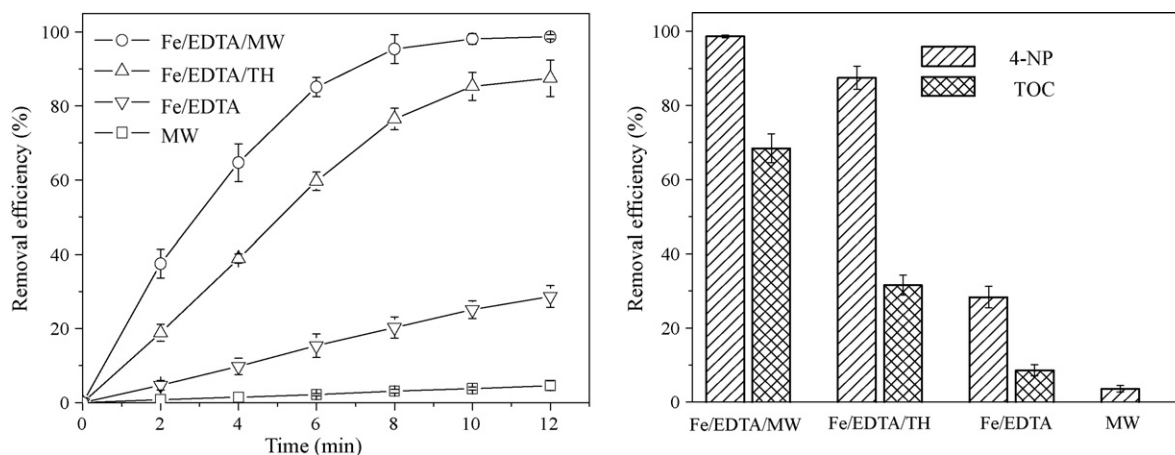
The same experiments were carried out in duplicate to check the reproducibility of results and standard deviation of each experiment was within  $\pm 5\%$ , which showed that the match between successive experiments was excellent. The data reported in the paper are the arithmetic average of the results derived from repeated MW assisted oxidation experiments.

## 3. Results and discussion

### 3.1. Comparison of 4-NP degradation in different systems

In order to assess the effect of MW in the degradation of 4-NP, and simultaneously investigate the non-thermal effect of MW on the organic degradation, comparative experiments were carried out in MW, Fe/EDTA, Fe/EDTA/MW and Fe/EDTA/TH system, respectively. These experiments were operated under the same conditions of pH, MW power, reaction time, iron addition and EDTA concentration.

The corresponding temporal decreases of the concentration of the 4-NP and TOC during the degradation are showed in Fig. 2a. MW radiation alone for 12 min had nearly no degradation of the organic pollutants. In contrast, in Fe/EDTA system, 28.7% 4-NP decomposition was found after 12 min operation, correspondingly 9.8% TOC was removed. Contrary to the Fe/EDTA system, during the same reaction time, the 4-NP removal in the Fe/EDTA/TH system reached 87.5%, indicating the thermal effect on the degradation of 4-NP could improve the removing efficiency of the organic. Interestingly, complete degradation of 4-NP was almost achieved after the introduction of MW into the Fe/EDTA system, which showed that MW assisted oxidation process was effective to promote the degradation of the 4-NP. Meanwhile, the differences of the degradation results among the Fe/EDTA/MW, Fe/EDTA and Fe/EDTA/TH system indicated that MW irradiation could cause thermal effect to induce the temperature of the degradation process to increase and additional non-thermal effect to play a significant role in the degradation of 4-NP. This result was similar to the degradation of RhB in other studies [11].



**Fig. 2.** (a) Degradation of 4-NP in different comparison experiments; (b) TOC and 4-NP removal of different comparison blank experiments. (Initial condition was iron 4 g; EDTA 0.2 mM; initial 4-NP 1000 mg/L; MW power 350 W; pH 3;  $T 80 \pm 5^\circ\text{C}$ ; reaction time 12 min.)

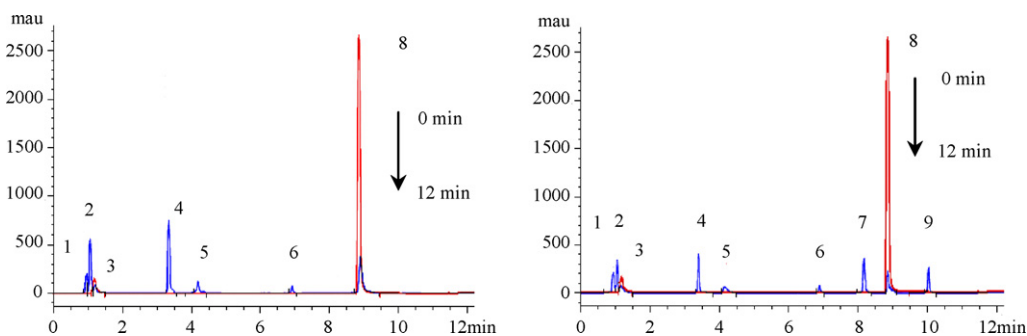
As shown in Fig. 2b, the removal rates of 4-NP of Fe/EDTA/MW and Fe/EDTA/TH were 98.7% and 87.5%, respectively, while the removals of TOC were 68.4% and 31.6%, respectively, indicating that 4-NP was more easily mineralized in Fe/EDTA/MW system. However, as for the Fe/EDTA/TH system, 4-NP was degraded effectively but complete mineralization was hard to achieve. Fig. 3 shows the comparison of the HPLC spectrum before and after treatment of 4-NP solution by these different systems. After treatment for 12 min, the peaks for 4-NP, hydroquinone, benzoquinone, nitrobenzene, phenol, 4-aminophenol and low molecule acid were found in Fe/EDTA/MW system, while in the Fe/EDTA/TH system, the peaks of nitrobenzene and phenol were not found. Due to the same temperature in these two systems, it could be inferred that MW could cause additional non-thermal effect to play an important role in the degradation of 4-NP. Meanwhile, the obvious “arc light” phenomenon was found among the Fe surface during the experiment of Fe/EDTA/MW system. Magnetic transition metal enjoys high capacity for MW absorption, and metal potential on Fe surface could interact fiercely with the MW to induce the high-energy electron irradiation and non-equilibrium plasma in this system [17], leading the iron surface to be more hydrophobic, which was easier to be oxidized by  $\text{O}_2$  to generate  $\cdot\text{OH}$  or easier to chelate with EDTA and cause chain reactions to generate  $\cdot\text{OH}$ . Therefore, the amount of  $\cdot\text{OH}$  increased [18].

### 3.2. Influencing factors on the degradation of 4-NP in Fe/EDTA/MW system

The effect of different initial conditions, such as MW power, Fe addition, EDTA dose and pH value was investigated.

MW power is a crucial factor for the investigation of the thermal effect and non-thermal effect of MW on assisting and enhancing oxidation of the organic pollutant. Comparative experiments were carried out in four MW powers, such as 300, 350, 400 and 450 W. Other parameters remained constant, namely, EDTA 0.2 mM, Fe addition 2 g and pH value 3. As shown in Fig. 4a, a stepwise increase of removal rate of 4-NP was observed with the increase of MW power from 300 to 450 W, and the improvement of MW power had a positive effect on the degradation of 4-NP. It was widely accepted that chemical reaction would be affected remarkably by temperature, which would accelerate the reaction rates. Generally, the more improvement input MW power, the higher temperature increase. That is to say, the MW power was improved in order that the system temperature would be raised to accelerate the reaction rate and promote the degradation of the organic pollutants in the system. However, the increased removal rate became less obvious when the input power increased from 400 to 450 W. Furthermore, high input power also means high electricity consumption and results in the rapid increase of system temperature, posing stricter requirement for heat-resistance of the apparatus.

As described above, EDTA played an important role in the oxidation of 4-NP because EDTA acted as chelating agent to supply coordination orbit and induce chain reaction to generate active free radical [19]. Accordingly, the comparative experiments with different initial EDTA dosages were conducted to investigate the effect of the amount of EDTA on the 4-NP degradation. EDTA dosages were set as 0, 0.1, 0.2, 0.4, 0.8 and 2 mM. Fig. 4b shows that the removal efficiency of 4-NP was very low (only 35.6%) in the absence of EDTA after reaction for 12 min. However, the removal efficiency of 4-NP was improved rapidly to 72.5% when 0.1 mM EDTA was introduced into the electrolytic system, and a successive addition of EDTA up



**Fig. 3.** HPLC chromatograms of the 4-NP intermediates in different systems. (1. RT = 0.96, oxalic; 2. RT = 1.036, 4-aminophenol; 3. RT = 1.201, EDTA; 4. RT = 3.418, hydroquinone; 5. RT = 4.146, propionate; 6. RT = 6.705, benzoquinone; 7. RT = 8.181, phenol; 8. RT = 8.876, 4-NP; 9. RT = 10.032, nitrobenzene).

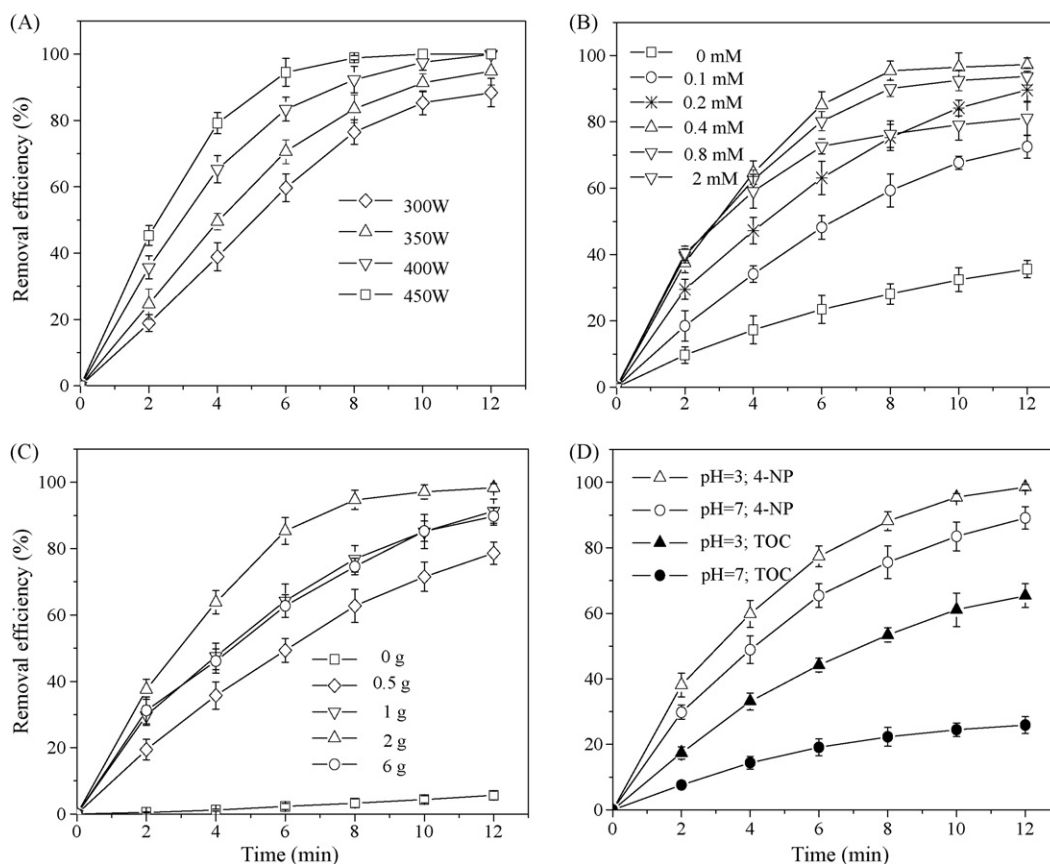


Fig. 4. Different influencing factors on the removal of 4-NP: (a) MW power; (b) EDTA dose; (c) Fe dose; (d) pH value.

to 0.4 mM brought about continuous increase in the 4-NP removal efficiency. However, further increase of EDTA addition from 0.4 to 2 mM led to a slight decrease of removal rate, which indicated that EDTA of excessive amount would have adverse effect on the 4-NP degradation in the Fe/EDTA/MW system. Because EDTA had great influence on the generation of the free radical as chelating agent, while it was also belong to organic and would compete for the free radical generated in the 4-NP system to have degrading reaction between the target substrate. Meanwhile, excessive EDTA might inhibit the formation of  $[\text{Fe}^{\text{II}}(\text{EDTA})(\text{O}_2)]^{2-}$ , which was indispensable for the production of active oxidants [20].

Fe, as the source of active oxidants, had great effect on the degradation rate, and Fig. 4c illustrates the degradation of 4-NP under different initial Fe dosages. Almost no effect of 4-NP degradation was observed after the reaction for 12 min in the absence of Fe addition. However, obvious 4-NP degradation was found after the Fe was added into the reactor, and 4-NP removal was much lower with 0.5 g Fe, indicating this dose was insufficient for effective 4-NP degradation. When the Fe dosage amount was increased from 0.5 to 2 g, the 4-NP removal efficiency rose continuously. Obviously, Fe addition could accelerate the decomposition of 4-NP, as more  $\text{Fe}^{2+}$  ions were generated which further simultaneously accelerated the formation of organic ligand and the production of active oxidants [21]. However, it was worthwhile to note the difference between the significant increase of removal rate with raising initial Fe dose from 0.5 to 2 g and the slight increase of removal rate observed when the initial Fe dose was further increase from 2 to 6 g. It could be explained that the more Fe dosage, the more  $\text{Fe}^{2+}$  ions, which would result in rapid consumption of  $\cdot\text{OH}$  or other active oxidants. Simultaneously, excessive Fe would also lead to an environmental concern.

pH is also a crucial factor for Fe/EDTA/MW to degrade the organic pollutants as it can influence the existing state of the Fe in the solution, as well as the characteristics and activity of the free radical generated in the system [22,23]. Fig. 4d shows the effect of the solution's acidity on the removal of 4-NP and TOC by Fe/EDTA/MW, only two levels of value 3 and 7 were investigated here. In the presence of 300 W MW, both the 4-NP removal rates showed slight difference at pH 3 and pH 7, while the TOC removal rate appeared to be significantly different. In the Fe/EDTA/MW, the MW improved dynamic rate of the reaction and reduced the activation energy of the reactant [24], facilitating the occurrence of 4-NP degradation. In acidic condition much hydroxyl radicals were generated to improve the TOC removal effect in Fe/EDTA/MW system, in contrast, it was most likely to produce a different oxidant at natural pH values, such as ferryl ion, which had a weak oxidation capacity and was unable to oxidize aromatic compounds, leading to low TOC removal rate [25].

### 3.3. Reaction intermediates and the possible mechanistic pathway

To investigate the pathway of 4-NP degradation, the intermediates in the treatment of 4-NP by Fe/EDTA/MW process were identified by GC/MS analysis and the results are shown in Fig. 5. Furthermore, based on the products determined by the HPLC chromatogram (Fig. 3), the main degradation pathway was proposed in Fig. 6. 4-NP was firstly reduced to 4-aminophenol by Fe in the system and was further degraded to nitrobenzene, phenol and other chemicals as a result of the MW effect. The products were then oxidized by the free radical such as hydroxyl radical to hydroquinone and benzoquinone, which were further oxidized to ring opening compounds, generating low molecular acid, even  $\text{H}_2\text{O}$  and  $\text{CO}_2$ .

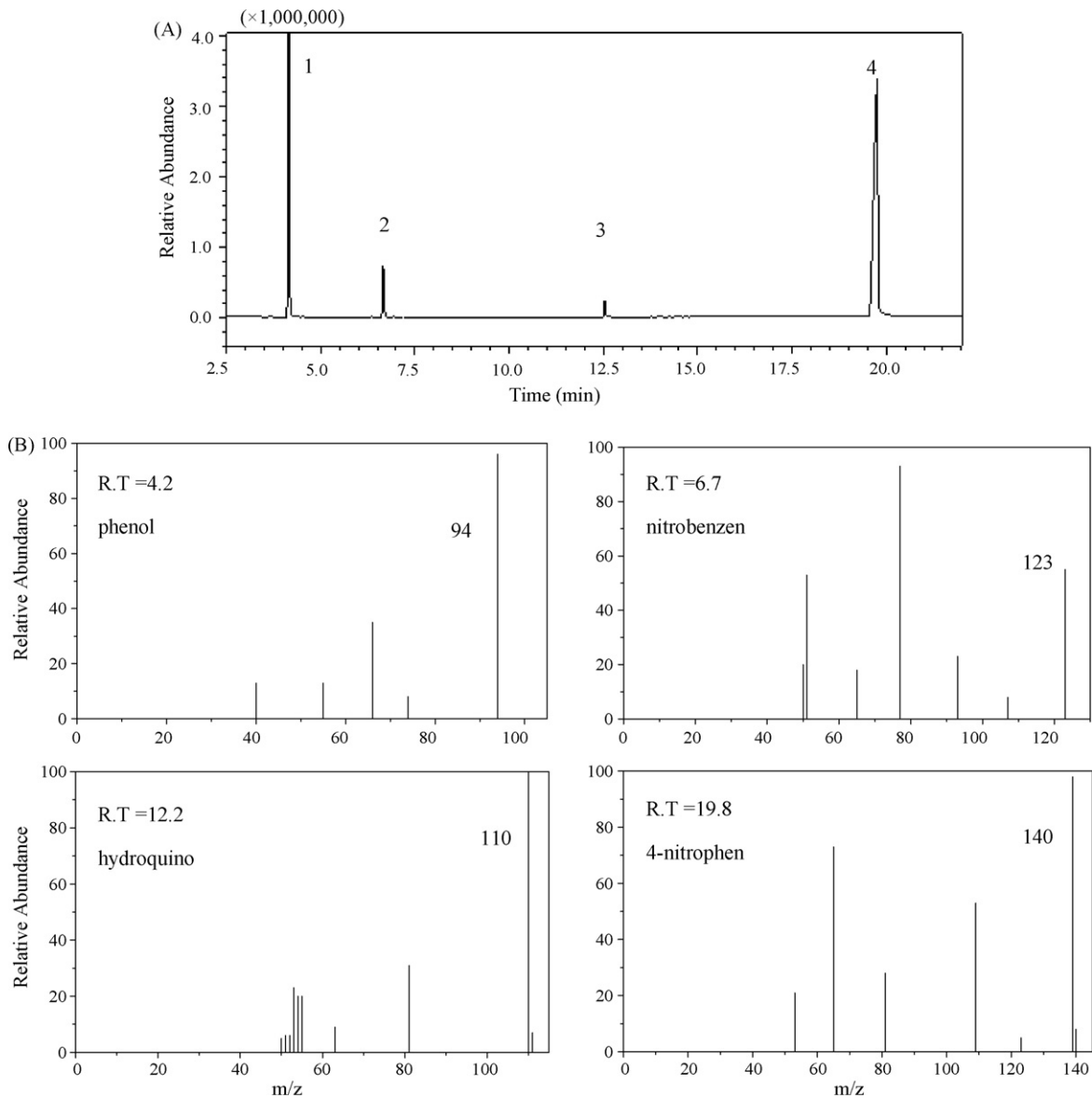


Fig. 5. GC/MS analysis of intermediates of 4-NP after 12 min of degradation by Fe/EDTA/MW system.

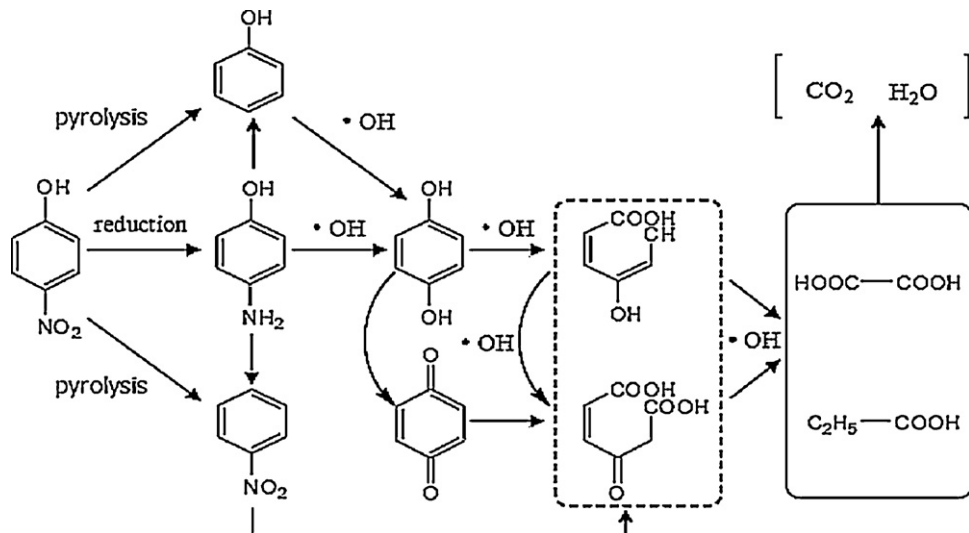


Fig. 6. General reaction pathway proposed for 4-NP degradation in Fe/EDTA/MW system (organic compounds inside dashed panel should be intermediate opening of the ring reported by other related literature, which could not be determined in this paper yet).

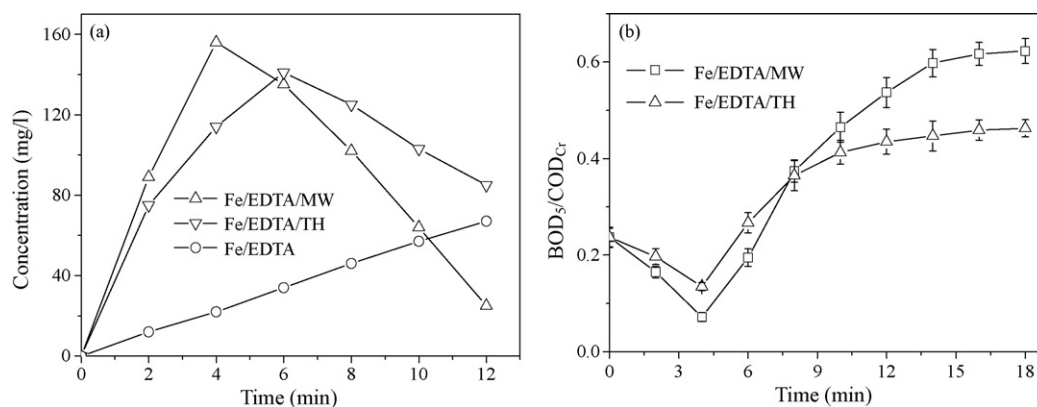


Fig. 7. (a) Variation of AP against time in different systems; (b) biodegradability of the outflow in different systems (condition as in Fig. 2).

One concern in these systems was the formation of undesirable degradation intermediate, such as toxic, recalcitrant compounds. In view of these, 4-aminophenol (AP) evolutions against time in these processes were compared because it was hard to be biologically degraded [26,27], and the change in AP concentration could indicate the strength of oxidation capacity of these reaction systems. The objective of this section was to demonstrate that MW assisted oxidation process would also benefit intermediates evolution compared with the individual Fe/EDTA and Fe/EDTA/TH.

The variation of AP against time under these processes is shown in Fig. 7a. It was observed that AP increased as soon as the reaction started, then decreased after reaching a peak concentration, and after a reaction for 12 min, its concentration turned to be very low in Fe/EDTA/MW system. In Fe/EDTA/TH system, AP was produced very quickly, exactly the same as that in Fe/EDTA/MW system, but began to decrease after it reached the maximum amount at about 6 min. However, what differed from the degradation of Fe/EDTA/MW system was that AP was degraded extremely slowly, showing that it was difficult to degrade to other organic or acids. While in Fe/EDTA system, the formation rate of AP was very slow, indicating that the degradation capability of organic was very weak. So, based on the changing trend of these three systems in accordance with aminophenol, it can be inferred that MW assistance oxidation process can generate more active radicals with strong oxidation capacity to promote the organic degradation.

### 3.4. Investment of biodegradability

The ratio BOD<sub>5</sub>/COD<sub>Cr</sub> is an important biochemical index, wastewater is considered with high biodegradability as the ratio is higher than 0.4 [28]. Fig. 7b shows the biodegradability of the effluent processed by Fe/EDTA/MW system in terms of BOD<sub>5</sub>/COD<sub>Cr</sub>. The initial value of BOD<sub>5</sub>/COD<sub>Cr</sub> of 4-NP waste water was 0.237. It was surprising that the ratio went down continuously along with the reaction, after the reaction for 4 min, it reached the minimum 0.07. A possible explanation was that some toxic intermediates with low biodegradability were generated during the reaction, for example, AP and benzoquinones. Afterwards, the ratio went up continuously with the reaction and reached 0.635 at the end of the experiment. Because Fe/EDTA/MW could obviously improve the biodegradability of the wastewater, it indicated that this process could be applied to treat those wastewaters containing recalcitrant aromatic substances.

## 4. Conclusions

In Fe/EDTA/MW system, MW could effectively enhance degradation of 4-NP in Fe/EDTA system. As for the 4-NP of 200 ml with

the initial concentration of 1000 mg/l, after the reaction for 12 min, the TOC and 4-NP removal efficiency is significantly higher than those in Fe/EDTA, Fe/EDTA/TH system.

Through the single factor experimental analysis of 4-NP degradation by Fe/EDTA/MW, the best value which values 400 W, 2 g, 0.4 mM, respectively, and shows that MW power, Fe, EDTA dosage have a positive effect on the removal of 4-NP and TOC, while excess Fe and EDTA dose will lead to a slight decrease of TOC and 4-NP remove rates, and acidic condition is benefit to the removal organic.

The intermediates generated by 4-NP degradation in the Fe/EDTA/MW system were analyzed qualitatively by GC/MS and HPLC chromatogram to infer the degradation pathway of 4-NP. The biodegradability of the wastewater was improved through the system, beneficial to the following biological treatment.

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