Microwave-enhanced Mn-Fenton process for the removal of BPA in water

Shuo Li ^a, Guangshan Zhang ^{a,*}, Peng Wang ^{a,*}, Heshan Zheng ^a, Yongjie Zheng ^b

^a *State Key Laboratory of Urban Water Resource and Environment, School of
Municipal and Environmental Engineering, Harbin Institute of Technology, Harbin,
150090, China*

^b *College of Chemistry and Chemical Engineering, Qiqihar University, Qiqihar,
161006, China*

*Corresponding authors. Tel.: 86-451-86283557; Fax: 86-451-86283557.

E-mail addresses: gszhanghit@gmail.com (G.S. Zhang), pwang73@vip.sina.com (P. Wang)

Abstract:

Microwave-enhanced Fenton oxidation process is a promising method to degrade Bisphenol A (BPA) in aqueous solution. In this study, Mn^{2+} ion was introduced into a microwave-enhanced Fenton system for removing BPA in wastewater. The results showed that the BPA removal rate in Microwave-enhanced Mn-Fenton (MW-Mn-Fenton) process was higher than that of in Fenton process or in other Fenton process with inclusion of metal under microwave irradiation. The effects of pH value, H_2O_2 dosage, Fe^{2+} ion dosage, Mn^{2+} ion dosage, initial concentration of BPA, microwave power and irradiation time on the degradation of BPA were investigated in detail. The optimum values of operating parameters were found at a pH value of 4.0, a H_2O_2 concentration of 34.0 mg/L, a Fe^{2+} ion concentration of 2.1 mg/L, a Mn^{2+} ion concentration of 2.7 mg/L, a microwave power of 300.0 W after 6.0 min of irradiation when the initial concentration of BPA was 100.0 mg/L. Under the optimal conditions, the removal efficiency of BPA and Total Organic Carbon (TOC) reached 99.7% and 53.1%, respectively. The BPA can be degraded completely at low initial concentration. The degradation efficiency for the BPA aqueous solution decreased gradually with increasing pH value was from 2.0 to 8.0. Less iron sludge was produced in short time and greater reagent utilization efficiency was achieved in MW-Mn-Fenton process in comparison with normal Fenton process. This study facilitates further research for practical application of the Fenton process in water treatment.

Keywords: Mn-Fenton; microwave irradiation; Manganese; BPA; hydroxyl radical

1. Introduction

Environmental Endocrine Disruptors (EEDs) can cause bioaccumulation and reproductive toxicity which are very harmful to human health and ecological environment [1]. In the early 1930s, synthetic estrogens have been reported to result from the mischief of the EEDs [2,3]. BPA is one of the most common EEDs. Meanwhile it is an important raw material widely used as a monomer for the production of polycarbonates, epoxy resins, plasticizers, flame retardants, paints, and other chemical products [4-7]. Nowadays, more and more people have realized that EEDs such as BPA have estrogenic effect and environmental carcinogenesis. Therefore, finding out some eco-friendly methods to rapidly and efficiently degrade BPA is essential for both human health and environment.

Recently, a number of approaches, such as biodegradation by algae [8], adsorption [9-11], photocatalysis [12,13], and Fenton processes [14-16] have been developed to decompose BPA. Among these methods, there exist some defects including low degradation efficiency, long reaction time and high reaction cost. Therefore, it is imperative to develop a significant degradation method for highly efficient removal of BPA in waste water. Fenton method is considered to be an efficient way to remove refractory organics in wastewater, which has been extensively applied in dyeing wastewater treatment [17-19]. Nevertheless, the traditional Fenton process has two major disadvantages, (1) a limited pH range (2.5-3.5), which led to the increased treatment cost due to pH value adjustment and (2) excessive ions sludge which results in secondary pollution. To overcome these drawbacks, other metal ions

were introduced to the Fenton process as an alternative for degradation of organic pollutants [20]. Moreover, the Fenton process with inclusion of other ions, especially Mn^{2+} ions could avoid these factors which affect the practical application in industry [21,22].

In the early stage, microwave has been used in the military affairs. Recently, due to its special heating mechanism, it has been widely applied to accelerate the heating process, even to catalyze degradation activity [23,24]. Microwave heating has great advantages of rapid and selective heating in comparison with traditional heating techniques. It enhances chemical reactivity and enables the reaction control easily [25]. In addition, non-thermal effect of microwave induces the excitation of reactant molecules to higher vibrational and rotational energy levels [26]. Due to thermal and non-thermal effect, microwave has played an important role in wastewater treatment [27].

As we known, the traditional Fenton-like process for degradation organic pollutants has been applied in industry. However, the reaction time usually lasts too long and costs too much. Moreover, the different processing parameter conditions had an enormous effect on the degradation of pollutants and the cost of the practical application in industry. In order to improve degradation performance and reagent utilization efficiency, as well as reduce reaction time and treatment cost, a MW-Mn-Fenton system was investigated for degradation of BPA. The experimental parameters were studied through the comparison of removal ratio and reaction rate constant (k) of BPA. In addition, the effects of initial pH value, BPA concentration,

H₂O₂, Fe²⁺ ion and Mn²⁺ ion dosage, microwave power and irradiation time on the degradation of BPA were investigated to obtain the optimum conditions. The objective of this research was to develop an advanced and practical technology for waste water treatment.

2. Experimental

2.1. Materials

BPA, Ferrous sulfate (FeSO₄), Ferric chloride (FeCl₃), Nickel Chloride (NiCl₃), Zinc chloride (ZnCl₂), Manganous chloride (MnCl₂), Cobalt chloride (CoCl₂), Cadmium chloride (CdCl₂), Cupric chloride (CuCl₂) were of analytical grade and purchased from Sinopharm Chemical Reagent Co., Ltd., China. BPA was used as received without any further purification. Hydrogen peroxide (30%, w/w), Sodium hydroxide (NaOH), Hydrochloric acid (HCl) were purchased from Tianjin Kermel Chemical Reagent Co., Ltd., China. All solutions were prepared with distilled water.

2.2. Experimental procedure

100 mL BPA solution and Fenton reagents were added into a 500.0 mL beaker. The initial concentrations of BPA, H₂O₂, Fe²⁺ ion, and different ions were 100.0 mg/L, 68.0 mg/L, 5.6 mg/L, and 6.0 mg/L, respectively. The beaker was heated in a domestic microwave oven (Cooplex-E, PreeKem Scientific Instruments Co., Ltd, China) with microwave power of 200.0 W and frequency of 2450.0 MHz for 1.0-6.0 min as illustrated in Fig. S1 in supporting information. The resulting BPA concentrations after microwave treatment were measured immediately by UV-vis spectrophotometer (L5S, Shanghai instrument analysis instrument Co., Ltd, China).

The pH value, concentrations of Fe^{2+} ion, H_2O_2 , different metal ions, initial BPA, microwave power and irradiation time were adjusted to obtain the optimum conditions. The leached metal ions were detected by ICP-OES (Optima 8000, PerkinElmer Co., Ltd, America). The TOC of the sample was measured by a TOC analyzer (Shimadzu, 5000A). All experiments were performed in triplicate to confirm their reproducibility.

2.3. Analytical methods

The UV-Vis spectra of BPA solutions were recorded from 190.0 to 600.0 nm. The concentrations of BPA solutions were calculated from the measured absorbance at 278.0 nm [28-30], which is the wavelength of maximum absorbance (λ_{max}). The removal ratio of BPA was calculated by using the following equation:

$$R(\%) = \frac{C_0 - C}{C_0} \times 100\% \quad (1)$$

Where R is the removal ratio of BPA. C_0 and C are initial and instantaneous concentrations of BPA (mg/L), respectively.

Under different reaction conditions, the amount of $\text{OH}\cdot$ generation was different which were detected by Molecular fluorescence spectrometer (RF-5301PC, Island ferry international trading (Shanghai) Co., Ltd, Japan). During the reaction, terephthalic acid was used as capture agent (100.0 mg/L). We used it replace BPA which the process was the same as MW-Mn-Fenton process. Meanwhile, $\text{OH}\cdot$ was determined by a photoluminescence technique. There was an excitation wavelength that 315.0 nm and strong fluorescence was produced at 425.0 nm. Terephthalic acid solution was prepared according to the method of Yu [31].

3. Results and discussion

3.1. Influence of different metal ions on the degradation of BPA

The effects of Co^{2+} , Cu^{2+} , Ni^{2+} , Mn^{2+} , Cd^{2+} and Zn^{2+} ions on BPA degradation in MW-Fenton process were shown in Fig. 1. On the basis of MW-Fenton process, all the metal ions could react with H_2O_2 under the same conditions. The concentration of different added ions was 6.0 mg/L, and the H_2O_2 dosage was 68.0 mg/L. The experiments without iron ions were reacted which had no obvious effect on degradation BPA, the BPA removal rates were 57.4% and 91.1% in MW-Fenton process and in MW-Mn-Fenton systems, respectively. When Cu^{2+} and Co^{2+} ion were added, the BPA removal rates were 83.1% and 76.4%, respectively. The main reason for higher removal rate of Mn/ H_2O_2 system was due to enhanced catalytic activity which evoked by Mn^{2+} ion. Furthermore, the BPA degradation effect of other ions in MW-Fenton processes were all lower than that of in Mn/ H_2O_2 system. Although the catalytic abilities of other ions were lower than Mn^{2+} ion, the BPA removal rates still exceeded 50.1%. Obviously, the greater BPA degradation rates with addition of different ions than that of Fenton reagent alone were due to higher catalytic efficiency. Comparatively, the BPA degradation was relied on the interaction of different metal ions and iron ions [32]. The interaction reduced the inhibition effect. The BPA removal rates with addition of different ions listed from high to low as $\text{Mn}^{2+} > \text{Cu}^{2+} > \text{Co}^{2+} > \text{Zn}^{2+} > \text{Ni}^{2+} > \text{Cd}^{2+}$. It can be seen that Mn^{2+} ion had the greatest catalytic ability than other ions at the same concentration. Mn^{2+} and Fe^{2+} ion has an interaction effect to improve BPA degradation. Accordingly, Mn^{2+} ion was chosen to be used in

MW-Fenton process due to the great effect of BPA degradation.

3.2. Examination of influence factors in the MW-Mn-Fenton process

3.2.1. Effect of initial pH value

In this part, pH value was studied as a variable on BPA degradation. $\text{OH}\cdot$ was produced by the reaction between Fe^{2+} ion and H_2O_2 [33]. Especially under acidic conditions (pH=3.0), the Fenton reagent exhibits a relatively excellent treatment effect with a large amount of $\text{OH}\cdot$ generated. According to Fig. 2, BPA degradation was observed in the pH range of 2.0 to 8.0. The removal rate of BPA varied dramatically under different pH values. It increased firstly, and then slowly decreased with rising pH value. The degradation rate of BPA reached nearly 99.3% at pH 3.0. At pH 6.0, the BPA removal rate still exceeded 60.5%. These phenomena can be observed since low pH value facilitates the removal of BPA. Large numbers of generated hydroxyl radicals can oxidase most organic compounds simultaneously. By contrast, some inhibitory effect occurred at high pH value. The main factor affecting BPA removal was generation hydroxyl radicals. Thus the removal rate of BPA decreased at high pH value. In general, considering economic factors, the optimal pH was at 4.0 [23]. The pH values of reaction medium after ending of the studied process were 3.5 ± 0.1 .

3.2.2. Effect of initial BPA concentration

In recent years, microwave irradiation has been applied in many environmental remediation projects, such as refractory organic treatment using microwave reinforced Fenton process due to the capability of molecular level heating which leads to homogeneous and quick thermal reactions [34]. Different initial concentrations were

discussed and three kinds of Fenton processes were compared in this part. In addition, BPA degradation effect, TOC removal, first-order rate constants and R^2 were also presented in Fig. 3. Under the same experiment conditions, the initial BPA concentrations were set from 10.0 mg/L to 100.0 mg/L. In Fig. 3(a), when the initial BPA concentration was 10.0 mg/L, 68.4% of BPA was degraded in 6.0 min using Fenton process. Nevertheless, the BPA was degraded rapidly and completely in aqueous solution in the MW-Mn-Fenton process. When the initial BPA concentration was 100.0 mg/L, the BPA degradation decreased from 68.8% to 39.7% in Fenton process. The removal rate of BPA was 80% in MW-Fenton process. However, the removal rate of BPA decreased from 100.0 % to 98.1 % in MW-Mn-Fenton process. This indicates that the combination of H_2O_2 with Fe^{2+} or Mn^{2+} ions could also form Fenton-like reactions to accelerate the production of $OH\cdot$ radicals [21]. The result of BPA mineralization at different initial concentrations were shown in Fig. 3(b). As the initial BPA concentration increased from 10.0 mg/L to 100.0 mg/L, the TOC removal rate fell from 49.6% to 12.6% in Fenton process. The TOC removal rate changed slightly from 72.4% to 53.5% in MW-Mn-Fenton process. The mineralization was 32.6% at 100.0 mg/L BPA level in MW-Fenton process. The results demonstrated that MW-Mn-Fenton process was more effective to degrade and transfer BPA to other products or intermediates than other processes. It was also effective in mineralizing BPA to carbon dioxide [35-38]. In comparison with the high BPA degradation rate constants from 5.8 min^{-1} (BPA 10.0 mg/L) to 4.2 min^{-1} (BPA 100.0 mg/L) in MW-Mn-Fenton process, this constant decreased from 3.6 min^{-1} (BPA 10.0 mg/L) to

2.2 min⁻¹ (BPA 100.0 mg/L) in Fenton process. After 6.0 min treatment, the reaction rate constant decreased to only 0.006 min⁻¹ for BPA of initial concentration at 100.0 mg/L in the Fenton process. Therefore, MW-Mn-Fenton process exhibits a significant effect on BPA degradation.

3.2.3. Effect of H₂O₂ concentration

H₂O₂ plays an important role in oxidizing process. It is used as a source to provide OH[·]. As seen in Fig. 4(a), with increasing concentration of H₂O₂, the ratio of BPA degradation increased significantly. The BPA removal rate accelerated at 34.0 mg/L of H₂O₂ dosage and reached 90.5% in 6.0 min. The increased degradation efficiency can be attributed to the production of additional OH[·] radicals through H₂O₂ decomposition [39]. On one side, when H₂O₂ dosage was inadequate 34.0 mg/L, there were not enough OH[·] generated to degrade BPA and the removal rate was only 25.6%. On the other side, when the H₂O₂ concentration was exceeded 34.0 mg/L, the exceeded H₂O₂ acted as a scavenger of OH[·] which indicated that there were insufficient OH[·] generated to degrade BPA, thus the removal efficiency was changed obvious [40-42]. According to Eq. (4) and (5), the exceeded H₂O₂ had a negative effect on the degradation of BPA [32]. Therefore, it is necessary to choose an appropriate dosage to remove BPA and the optimum H₂O₂ dosage was selected at 34.0 mg/L for the following treatment to degrade BPA. As seen in Fig. 4 (b), in general the reaction rate constantan proved by the three kinds of Fenton process.

At the H₂O₂ concentration of 34.0 mg/L, the reaction rate constant reached 3.3 min⁻¹ in MW-Mn-Fenton process, and the reaction rate constant was 1.9 min⁻¹ in

MW-Fenton process, whereas it was only 0.6 min^{-1} in Fenton process. These demonstrated that MW-Mn-Fenton process has a significant impact on BPA.

3.2.4. Effect of ferrous ions concentration

Fe^{2+} ion has significant effects on degradation of BPA whatever in Fenton or in MW-Fenton/Mn-Fenton process. Thus, Fe^{2+} dosage was used as a control variable in this part. As shown in Fig. 5(a), when Fe^{2+} dosage increased from 0.6 to 2.1 mg/L, the BPA removal rate increased significantly from 56.5% to 93.8%. Moreover, with the increasing Fe^{2+} dosage up to 1.6 mg/L, the removal rate of BPA reached nearly 80% in 6.0 min. When the Fe^{2+} dosage was 2.1 mg/L, the removal rate of BPA reached nearly 90%. However, when the Fe^{2+} dosage exceeded 2.1 mg/L, the degradation of BPA had inconspicuous effect. When Fe^{2+} dosage was less than 2.1 mg/L, it would lead to insufficient production of $\text{OH}\cdot$ which degrades BPA. Fe^{2+} could not completely react with H_2O_2 to generate $\text{OH}\cdot$ by reactions (4) and (5). The removal rate of BPA was attributed to the generation dosage of $\text{OH}\cdot$. As seen in Fig. 5(b), the reaction rate constants increased from 0.10 to 3.2 min^{-1} in 6.0 min through MW-Mn-Fenton process. The reaction rate constant was 1.6 min^{-1} in MW-Fenton process, which was thirty times faster than that in Fenton system. The Fe^{2+} dosage showed significant effect on degradation of BPA in the MW-Mn-Fenton process. In comparison with the different Fenton processes under the same conditions, MW-Mn-Fenton process has shown the greatest superiority. Accordingly, the optimal

Fe²⁺ dosage was chosen at 2.1 mg/L.

3.2.5. Effect of Mn²⁺ concentration

MW-Fenton process which was different from typical Fenton processes, has a great superiority on degrading pollution. As shown in Fig. 6(a), with the increasing concentration of Mn²⁺ ion, the BPA removal rate was higher than that without any Mn²⁺ ion. When the concentration of Mn²⁺ ion reached 2.7 mg/L, the BPA was completely degraded. This is a result of highly effective utilization of added OH[·]. On one hand, when the concentration of Mn²⁺ ion exceeded 2.7 mg/L, the remained Mn²⁺ ion in the uncompleted reaction was still in the solution. The reason was that the amount of H₂O₂ to react with the redundant Mn²⁺ ion was inadequate to generate OH[·]. In addition, it may result in secondary pollution. On the other hand, when the concentration of Mn²⁺ ion was less than 2.7 mg/L, the BPA degradation rate was only 62.3%. The reason was that an adequate OH[·] concentration could not be generated because of an inadequate Mn²⁺ concentration. In comparison with the three kinds of Fenton processes in Fig. 6(b), MW-Mn-Fenton process has the greatest superiority on reaction rate constants. Accordingly, the optimum Mn²⁺ ions dosage was 2.7 mg/L.

UV-vis absorption spectrum has been widely used as a rapid and comprehensive detection method to explain the degradation path or the change of regular material [43,44]. As seen in Fig. 7, the absorbance of BPA in MW-Mn-Fenton process was 0.9 in 6.0 min, however, it reached 1.43 in MW-Fenton process in 6.0 min. The

degradation rate of MW-Fenton process was 1.1 times higher than that of MW-Mn-Fenton process. The BPA removal rate increased from 0.0 to 100.0 % in 6.0 min. When the absorbance of BPA was low, the BPA removal rate was high. However, the degradation of BPA was only 50.1% in MW-Fenton process in 6.0 min. The absorption peaks decreased to the minimum value at the maximum wavelength (278.0 nm) which indicated that BPA absorbance in MW-Mn-Fenton process is more effective than that in MW-Fenton process since BPA has been completely degraded in MW-Mn-Fenton process [45-47]. The maximum absorption of BPA showed an obvious red shift compared to the ones with more time. The decrease of the absorption and intensities of the BPA indicated that BPA has been degraded by MW-Mn-Fenton process and probably some new intermediate products generated in this process. In brief, the above reasons made us select MW-Mn-Fenton process as the optimal method.

3.2.6. Effect of microwave power

In the microwave degradation process, the reaction temperature and rate were related to the microwave power. Thus, the effect of different microwave power on BPA degradation has been examined. As seen in Fig. 8(a), the removal rate of BPA gradually increased with the increasing energy which was brought by microwave irradiation power [45-46]. Meanwhile, both the BPA removal rate and the H_2O_2 decomposing rate also increased [39]. The heat produced by microwave improved the rapid molecular motion and $OH\cdot$ production which determined the BPA removal rate [48]. In Fig. 8(b), in order to obtain the same BPA removal rate, apparent differences

on the reaction time were found when using different microwave power. For instance, at 90% of the BPA removal rate, the reaction needed 12.0 min to complete at 100 W. However, it only cost 4.0 min at 300.0 W. When the microwave power was greater than 300.0 W, no significant difference was observed for BPA removal rates. The tests were conducted at the microwave power of 300.0 W or 500.0 W. The main reason was that no $\text{OH}\cdot$ remained can be effectively utilized with the energy continue added over a numerical value [40-43,49]. Therefore, 300.0 W was considered to be the optimal irradiation power.

3.2.7. Effect of microwave irradiation time

When the microwave power was confirmed, the degree of refractory organics degradation was different with microwave irradiation time. In Fig. 9, different time significantly affected the BPA removal rate and mineralization. For example, at 1.0 min the BPA removal rate was 60.5% and the TOC removal efficiency was 95.1%. Furthermore, when the irradiation time increased, both the removal rate and TOC removal efficiency of BPA changed more effective than that at 1.0 min. When the microwave irradiation time increased from 3.0 min to 5.0 min, the removal rate of BPA increased from 84.7% to 95.7%. Extend the irradiation time to 6.0 min, the BPA removal rate reached nearly 100.0% and the mineralization was 50.5%. Increasing microwave irradiation time clearly enhanced the H_2O_2 reaction to increase $\text{OH}\cdot$ production and BPA oxidation [49]. If the time was extended to 7.0 min or even longer, more generated energy was needed. However, it costs too much energy on the inconspicuous BPA degradation. Therefore, the optimal microwave reaction time was

considered to be 6.0 min.

3.3. Performance of different processes

In this part, six kinds of methods were conducted to compare the efficiency of BPA degradation including Fenton process (which was heated to 80.0°C), microwave (MW) process, MW-H₂O₂ process, Fenton process, MW-Fenton process and MW-Mn-Fenton process were carried out. As shown in Fig. 10, the BPA removal rate was 53.4% in the heated Fenton process. This was hardly observed by microwave process alone, indicating that the energy of microwave irradiation was too weak to break down the bonds of BPA hence the volatilization of BPA in our experiments could be ignored [42]. The BPA removal rate in MW-H₂O₂ process was only 18.2%. In contrast, the BPA removal efficiency reached 80.8% in MW-Fenton process, which was almost 40.2% higher than that of in Fenton process. The BPA removal rate significantly increased and exceeded 90.3% by MW-Mn-Fenton process. The order of BPA removal efficiency was MW-Mn-Fenton process > MW-Fenton process > Fenton process (heated) > Fenton process > MW-H₂O₂ process > microwave (MW) process. The above results indicated that temperature has a significant impact on improving the degradation reaction. Besides thermal effect, non-thermal effect by microwave irradiation also increases BPA degradation. Moreover, in MW-Mn-Fenton process, Fe²⁺ and Mn²⁺ ion has a synergistic effect on degrading BPA [21]. Consequently, MW-Mn-Fenton process was adopted as a convenient method to degrade BPA in this study.

The difference of peak intensity of 2-hydroxyterephthalic acid in heated and

unheated Fenton process, microwave alone process, MW-H₂O₂ process, Fenton process and Mn-Fenton process under microwave irradiation were compared in this work. As shown in Fig. 11, the fluorescence intensity of 2-hydroxyterephthalic acid in MW-Mn-Fenton process was the highest in degrading BPA. The lowest value was observed in microwave process without any addition of reagent. Furthermore, the removal rate of MW-Fenton process was higher than that of Fenton process whatever under heating or not. Overall temperature accelerates the reaction rate and the OH· generation.

In addition, the fluorescence intensity in MW-Fenton process was 492.8 at 6.0 min, 2.0 times higher than that of in Fenton heating process (232.6). This was much higher than that of in unheated Fenton process (123.9). However, it was 1.3 times lower than that of in MW-Mn-Fenton process (381.1). This indicates that the proportional relationship between Mn²⁺ and Fe²⁺ ion was also affected by OH· generation and the intensity of 2-hydroxyterephthalic acid. Therefore, it could be speculated that the Mn²⁺ ion has an obvious promotion effect on the generation rate and accumulation amount of OH· in MW-Mn-Fenton process since the OH· generation path could be alternated. Obviously, both heating and microwave irradiation improve the generation rate of OH· which enhances the degradation of BPA.

3.4. Comparison with other results

Many pollution degradation methods have been reported in recent years. In this part, the literatures related to different processes on BPA degradation are summarized

in Tab. 1. The methods name, initial concentration of BPA, the factors, BPA removal rate and first-order reaction kinetics were given. Some methods were given in Tab.1 such as photo-degradation process, ozonation process, ultrasonic degradation process, which were combined with the traditional process to remove refractory organics in aqueous solution [50]. These methods have been used as effective treatments to degrade pollution in industry. However, some issues still exist and need to solve urgently. These problems limit the application of traditional processes in industry application. Comparing the advantages and disadvantages of different methods, BPA removal rate and first-order reaction kinetics were used as evaluating indicators to identify the optimal methods [44]. In Tab. 1, MW-Mn-Fenton process had a significant BPA degradation at high BPA concentration. It takes shorter reaction time and little Fenton reagent than other processes. Moreover, MW-Mn-Fenton process has a great ascendancy with the maximum reaction kinetics. The advantages of MW-Mn-Fenton process were embodied obviously. It indicated that MW-Mn-Fenton process effectively enhanced the BPA removal efficiency and the rate constants [51]. The leached Fe^{2+} was 0.08 mg/L and Mn^{2+} was 0.10 mg/L which were both much less than the initial concentrations. It indicated that Mn^{2+} and Fe^{2+} ions were coexisted, participated and could improve the BPA degradation in MW-Mn-Fenton process. In other words, microwave could facilitate the removal rate of pollution compounds from aqueous solution in a short time. In general, the MW-Mn-Fenton process has dramatic advantages on BPA degradation.

4. Conclusions

In order to enhance the MW-Fenton process, to reduce the reagent dose, and to exploit the pH range, a MW-Mn-Fenton process was invested in this work. It was a very new method for the oxidation of refractory organic pollutants. By adding Mn^{2+} ion, the BPA degradation effect was found to be accelerated in a wide pH range from 2.0 to 8.0. Among the experiment, Mn^{2+} ion was used at the homogeneous system for improving BPA degradation effect. Furthermore, the effects of the pH value (4.0), H_2O_2 dosage (34.0 mg/L), Fe^{2+} ion dosage (2.1 mg/L), Mn^{2+} ion dosage (2.7 mg/L), microwave power (300.0 W), and irradiation time (6.0 min) on the degradation of BPA were investigated in detail. Under the same reaction conditions, the removal rate of BPA reached 99.7% at 2.7 mg/L Mn^{2+} ion concentration, and the TOC removal rate was 53.1%. The addition of Mn^{2+} ion also strongly influenced $\text{OH}\cdot$ generation as well as the first-order reaction kinetics (k/min^{-1}). MW-Mn-Fenton process probably changed the initial generation path of $\text{OH}\cdot$ since the possible generation of complicated multi-nuclear metal complexes. In general, this paper examined the homogeneous Fenton process with the combination of Mn^{2+} ion under microwave irradiation preliminarily. The results provided fundamental basis and technology for further practical application.

Acknowledgments

The work was supported by State Key Laboratory of Urban Water Resource and Environment (Harbin Institute of Technology) (2015DX03), the Fundamental Research Funds for the Central Universities (HIT. NSRIF. 201671) and the National Science Foundation for Post-doctoral Scientists of China (2014M561356).

References

- [1] N. Bolong, A.F. Ismail, M.R. Salim, D. Rana, T. Matsuura, A. Tabe-Mohammadi, Negatively charged polyethersulfone hollow fiber nanofiltration membrane for the removal of bisphenol A from wastewater, *Sep. Purif. Technol.* 73 (2010) 92-99.
- [2] J.W. Cook, E.C. Dodds, C.L. Hewett, A synthetic oestrus-exciting compound, *Nature*. 131 (1933) 56-57.
- [3] E.C. Dodds, W. Lawson, Synthetic estrogenic agents without the phenanthrene nucleus, *Nature*. 137 (1936) 996.
- [4] N. Lu, Y. Lu, F. Y. Liu, $H_3PW_{12}O_{40}/TiO_2$ catalyst-induced photodegradation of bisphenol A (BPA): Kinetics, toxicity and degradation pathways, *Chemosphere*. 91 (2013) 1266-1272.
- [5] Q. Han, H. Wang, W. Dong, T. Liu, Y. Yin, H. Fan, Degradation of bisphenol A by ferrate(VI) oxidation: Kinetics, products and toxicity assessment, *Chem. Eng. J.* 262 (2015) 34-40.
- [6] X. Yang, P. Tian, C. Zhang, Y. Deng, J. Xu, J. Gong, Y. Han, Au/carbon as Fenton-like catalysts for the oxidative degradation of bisphenol A, *Appl. Cal. B.* 134 (2013) 145-152.
- [7] H. Zhang, Controlled/"living" radical precipitation polymerization: A versatile polymerization technique for advanced functional polymers, *Eur. Polym. J.* 49 (2013) 579-600.
- [8] S. Saiyood, A.S. Vangnai, P. Thiravetyan, D. Inthorn, Bisphenol A removal by the *Dracaena* plant and the role of plant-associating bacteria, *J. Hazard. Mater.* 178 (2010) 777-785.
- [9] J. Li, B. Zhou, Y. Liu, Q. Yang, W. Cai, Influence of the coexisting contaminants on bisphenol A sorption and desorption in soil, *J. Hazard. Mater.* 151 (2008) 389-393.
- [10] I. Bautista-Toledo, M.A. Ferro-Garcia, J. Rivera-Utrilla, C. Moreno-Castilla, F.J. Vegas Fern A Ndez, Bisphenol A removal from water by activated carbon. Effects of carbon characteristics and solution chemistry, *Environ. Sci. Technol.* 39 (2005) 6246-6250.
- [11] S. Y U Ksel, N. Kabay, M. Y U Ksel, Removal of bisphenol A (BPA) from water by various nanofiltration (NF) and reverse osmosis (RO) membranes, *J. Hazard. Mater.* 263 (2013) 307-310.
- [12] R. Doong, S. Chang, C. Tsai, Enhanced photoactivity of Cu-deposited titanate nanotubes for removal of bisphenol A, *Appl. Cal. B.* 129 (2013) 48-55.
- [13] C. Jia, Y. Wang, C. Zhang, Q. Qin, S. Kong, S. Kouakou Yao, Photocatalytic degradation of bisphenol A in aqueous suspensions of titanium dioxide, *Environ. Eng. Sci.* 29 (2012) 630-637.
- [14] E. Kusvuran, D. Yildirim, Degradation of bisphenol A by ozonation and determination of degradation intermediates by gas chromatography-mass spectrometry and liquid chromatography--mass spectrometry, *Chem. Eng. J.* 220 (2013) 6-14.
- [15] F.J. Rivas, A.N. Encinas, B. Acedo, F.J. Beltr A N, Mineralization of bisphenol A by advanced oxidation processes, *J. Chem. Technol. Biot.* 84 (2009) 589-594.
- [16] X. Yang, P. Tian, C. Zhang, Y. Deng, J. Xu, J. Gong, Y. Han, Au/carbon as Fenton-like catalysts for the oxidative degradation of bisphenol A, *Appl. Cal. B.* 134 (2013) 145-152.
- [17] J. Sun, S. Sun, G. Wang, L. Qiao, Degradation of azo dye Amido black 10B in aqueous solution by Fenton oxidation process, *Dyes Pigments.* 74 (2007) 647-652.
- [18] M.S. Lucas, J.A. Peres, Decolorization of the azo dye Reactive Black 5 by Fenton and photo-Fenton oxidation, *Dyes Pigments.* 71 (2006) 236-244.
- [19] M. Neamtu, A. Yediler, I. Siminiceanu, A. Kettrup, Oxidation of commercial reactive azo dye aqueous solutions by the photo-Fenton and Fenton-like processes, *J. Photoch. Photobio. A.* 161 (2003) 87-93.
- [20] N. Wang, T. Zheng, J. Jiang, P. Wang, $Cu(II)-Fe(II)-H_2O_2$ oxidative removal of 3-nitroaniline in water under microwave irradiation, *Chem. Eng. J.* 260 (2015) 386-392.

- [21] C. Su, W. Li, X. Liu, X. Huang, X. Yu, Fe-Mn-sepiolite as an effective heterogeneous Fenton-like catalyst for the decolorization of reactive brilliant blue, *Front. Environ. Sci. Eng.* (2014) 1-9.
- [22] J. Zhang, W. Zhu, H. Li, W. Jiang, Y. Jiang, W. Huang, Y. Yan, Deep oxidative desulfurization of fuels by Fenton-like reagent in ionic liquids, *Green Chem.* 11 (2009) 1801-1807.
- [23] D.A. Jones, T.P. Lelyveld, S.D. Mavrofidis, S.W. Kingman, N.J. Miles, Microwave heating applications in environmental engineering—a review, *Resour. Conserv. Recy.* 34 (2002) 75-90.
- [24] S. Deng, G. Zhang, X. Wang, Preparation and performance of polyacrylonitrile fiber functionalized with iminodiacetic acid under microwave irradiation for adsorption of Cu(II) and Hg(II). *Chem. Eng. J.* 276 (2015) 349-357.
- [25] S.W. Kingman, N.A. Rowson, Microwave treatment of minerals-a review, *Miner. Eng.* 11 (1998) 1081-1087.
- [26] J. Sanz, J.I. Lombrana, A.M. De Luis, M. Ortueta, F. Varona, Microwave and Fenton's reagent oxidation of wastewater, *Environ. Chem. Let.* 1 (2003) 45-50.
- [27] N. Wang, T. Zheng, J. Jiang, P. Wang, Cu(II)-Fe(II)-H₂O₂ oxidative removal of 3-nitroaniline in water under microwave irradiation, *Chem. Eng. J.* 260 (2015) 386-392.
- [28] C. Li, X. Li, Degradation of endocrine disrupting chemicals in aqueous solution by interaction of photocatalytic oxidation and ferrate (VI) oxidation, *Water Sci. Technol.* 55 (2007) 217-223.
- [29] S. Poorahong, C. Thammakhet, P. Thavarungkul, P. Kanatharana, Online in-tube microextractor coupled with UV-Vis spectrophotometer for bisphenol A detection, *J. Environ. Sci. Health. A.* 48 (2013) 242-250.
- [30] S. Fukahori, H. Ichiura, T. Kitaoka, H. Tanaka, Capturing of bisphenol A photodecomposition intermediates by composite TiO₂-zeolite sheets, *Appl. Cal. B.* 46 (2003) 453-462.
- [31] J. Yu, W. Wang, B. Cheng, B. Su, Enhancement of photocatalytic activity of mesoporous TiO₂ powders by hydrothermal surface fluorination treatment, *J. Phys. Chem. C.* 113 (2009) 6743-6750.
- [32] G. Zhu, J. Yin, P. Wan, H. Zheng, B. Deng, Fe (III)/H₂O₂-like system for removal of azo dye from aqueous solution, *Sep. Sci. Technol.* 50 (2015) 2220-2229.
- [33] D. Vujević, S. Papić, N. Koprivanac, A.L.V.C. Bo V Z I C, Decolorization and mineralization of reactive dye by UV/Fenton Process, *Sep. Sci. Technol.* 45 (2010) 1637-1643.
- [34] X. Liu, X. Quan, L. Bo, S. Chen, Y. Zhao, Simultaneous pentachlorophenol decomposition and granular activated carbon regeneration assisted by microwave irradiation, *Carbon.* 42 (2004) 415-422.
- [35] E.C. Catalkaya, F. Kargi, Effects of operating parameters on advanced oxidation of diuron by the Fenton's reagent: a statistical design approach, *Chemosphere.* 69 (2007) 485-492.
- [36] M. Silva, A.G. Trov O, R. Nogueira, Degradation of the herbicide tebuthiuron using solar photo-Fenton process and ferric citrate complex at circumneutral pH, *J. J. Photoch. Photobio. A.* 191 (2007) 187-192.
- [37] M. Perez, F. Torrades, J.E.A. Garc I A-Hortal, X. Dom E Nech, J.E. Peral, Removal of organic contaminants in paper pulp treatment effluents under Fenton and photo-Fenton conditions, *Appl. Cal. B.* 36 (2002) 63-74.
- [38] Y. Segura, R. Molina, F. Martinez, J.A. Melero, Integrated heterogeneous sono--photo Fenton processes for the degradation of phenolic aqueous solutions, *Ultrason. Sonochem.* 16 (2009) 417-424.
- [39] G. Cheng, J. Lin, J. Lu, X. Zhao, Z. Cai, J. Fu, Advanced Treatment of Pesticide-Containing

- Wastewater Using Fenton Reagent Enhanced by Microwave Electrodeless Ultraviolet, *Biomed. Res. Int.* 2015 (2015)1-8.
- [40] C. Bradu, L. Frunza, N. Mihalche, S. Avramescu, M. NeaCTUA, I. Udrea, Removal of Reactive Black 5 azo dye from aqueous solutions by catalytic oxidation using CuO/Al₂O₃ and NiO/Al₂O₃, *Appl. Cal. B.* 96 (2010) 548-556.
- [41] S.G. Kumar, L.G. Devi, Review on modified TiO₂ photocatalysis under UV/visible light: selected results and related mechanisms on interfacial charge carrier transfer dynamics, *J. Photoch. Photobio. A.* 115 (2011) 13211-13241.
- [42] W. Pan, G. Zhang, T. Zheng, P. Wang, Degradation of p-nitrophenol using CuO/Al₂O₃ as a Fenton-like catalyst under microwave irradiation, *RSC Advances.* 5 (2015) 27043-27051.
- [43] Y.A. Shaban, M.A. El Sayed, A.A. El Maradny, R.K. Al Farawati, M.I. Al Zobidi, Photocatalytic degradation of phenol in natural seawater using visible light active carbon modified (CM)-n-TiO₂ nanoparticles under UV light and natural sunlight illuminations, *Chemosphere.* 91 (2013) 307-313.
- [44] V. Eskizeybek, F. Sarı, H. Gülce, A. Gülce, A. Avcı, Preparation of the new polyaniline/ZnO nanocomposite and its photocatalytic activity for degradation of methylene blue and malachite green dyes under UV and natural sun lights irradiations, *Appl. Cal. B.* 119-120 (2012) 197-206.
- [45] C. Li, X.Z. Li, Degradation of endocrine disrupting chemicals in aqueous solution by interaction of photocatalytic oxidation and ferrate (VI) oxidation, *Water Sci. Technol.* 55 (2007) 217-223.
- [46] S. Fukahori, H. Ichiura, T. Kitaoka, H. Tanaka, Capturing of bisphenol A photodecomposition intermediates by composite TiO₂-zeolite sheets, *Appl. Cal. B.* 46 (2003) 453-462.
- [47] W. Zhao, N. Sheng, R. Zhu, F. Wei, Z. Cai, M. Zhai, S. Du, Q. Hu, Preparation of dummy template imprinted polymers at surface of silica microparticles for the selective extraction of trace bisphenol A from water samples, *J. Hazard. Mater.* 179 (2010) 223-229.
- [48] E. Kan, S.G. Huling, Effects of temperature and acidic pre-treatment on Fenton-driven oxidation of MTBE-spent granular activated carbon, *Environ. Sci. Technol.* 43 (2009) 1493-1499.
- [49] J.R. Kim, S.G. Huling, E. Kan, Effects of temperature on adsorption and oxidative degradation of bisphenol A in an acid-treated iron-amended granular activated carbon, *Chem. Eng. J.* 262 (2015) 1260-1267.
- [50] H. Katsumata, S. Kawabe, S. Kaneco, T. Suzuki, K. Ohta, Degradation of bisphenol A in water by the photo-Fenton reaction, *J. Photoch. Photobio. A.* 162 (2004) 297-305.
- [51] C. Zhang, G. Zeng, L. Yuan, J. Yu, J. Li, G. Huang, B. Xi, H. Liu, Aerobic degradation of bisphenol A by *Achromobacter xylosoxidans* strain B-16 isolated from compost leachate of municipal solid waste, *Chemosphere.* 68 (2007) 181-190.
- [52] E. Kusvuran, D. Yildirim, Degradation of bisphenol A by ozonation and determination of degradation intermediates by gas chromatography-mass spectrometry and liquid chromatography-mass spectrometry, *Chem. Eng. J.* 220 (2013) 6-14.
- [53] R. Wang, D. Ren, S. Xia, Y. Zhang, J. Zhao, Photocatalytic degradation of Bisphenol A (BPA) using immobilized TiO₂ and UV illumination in a horizontal circulating bed photocatalytic reactor (HCBPR), *J. Hazard. Mater.* 169 (2009) 926-932.
- [54] Y. Ding, X. Xia, Y. Ruan, H. Tang, In situ H⁺-mediated formation of singlet oxygen from NaBiO₃ for oxidative degradation of bisphenol A without light irradiation: Efficiency, kinetics, and mechanism, *Chemosphere.* 141 (2015) 80-86.
- [55] F.H.F. Mariana Neamțu, Degradation of endocrine disrupting bisphenol A by 254 nm irradiation

545 in different water matrices and effect on yeast cells, Water Res. 40 (2006) 203745-203750.
546 [56] J. Zhang, B. Sun, X. Guan, Oxidative removal of bisphenol A by permanganate: Kinetics,
547 pathways and influences of co-existing chemicals, Sep. Purif. Technol. 107 (2013) 48-53.
548 [57] K. Zhang, N. Gao, Y. Deng, T.F. Lin, Y. Ma, L. Li, M. Sui, Degradation of bisphenol-A using
549 ultrasonic irradiation assisted by low-concentration hydrogen peroxide, J Environ Sci (China). 23
550 (2011) 31-36.
551

Fig. 1. The effect of different ions on removal rate of BPA. (BPA initial concentration = 100.0 mg/L, pH = 3.0, microwave power = 200.0 W, microwave irradiation time = 6.0 min, H₂O₂ dosage = 68.0 mg/L, Fe²⁺ dosage = 5.6 mg/L, other metal ions dosage = 6.0 mg/L).

Fig. 2. Effect of pH on removal rate of BPA. (BPA initial concentration = 100.0 mg/L, pH = 3.0, microwave power = 200.0 W, microwave irradiation time = 6.0 min, H₂O₂ dosage = 68.0 mg/L, Fe²⁺ dosage = 5.6 mg/L, Mn²⁺ dosage = 5.5 mg/L).

Fig. 3. (a) BPA degradation and (b) TOC removal in the degradation of BPA by the Fenton processes for different BPA concentrations. (pH = 4.0, microwave power = 200.0 W, microwave irradiation time = 6.0 min, H₂O₂ dosage = 68.0 mg/L, Fe²⁺ dosage = 5.6 mg/L, Mn²⁺ dosage = 5.5 mg/L).

Fig. 4. (a) Effect of different H₂O₂ dosage on removal rate of BPA in MW-Mn-Fenton process and (b) comparison with Fenton and MW-Fenton. (BPA initial concentration = 100.0 mg/L, pH = 4.0, microwave power = 200.0 W, irradiation time = 6.0 min, Fe²⁺ dosage = 5.6 mg/L, Mn²⁺ dosage = 5.5 mg/L).

Fig. 5. (a) Effect of different Fe²⁺ dosage on removal rate of BPA in MW-Mn-Fenton process and (b) comparison with Fenton and MW-Fenton. (BPA initial concentration = 100 mg/L, pH = 4.0, microwave power = 200.0 W, irradiation time = 6.0 min, H₂O₂ dosage = 34.0 mg/L, Mn²⁺ dosage = 5.5 mg/L).

Fig. 6. (a) Effect of Mn²⁺ dosage on removal rate of BPA in MW-Mn-Fenton process and (b) comparison with Fenton and MW-Fenton.

(BPA initial concentration = 100.0 mg/L, pH = 4.0, microwave power = 200.0 W, irradiation time = 6.0 min, H₂O₂ dosage = 34.0 mg/L, Fe²⁺ dosage = 2.1 mg/L).

Fig. 7. (a) The UV-vis absorption spectra of BPA with the reaction time and (b) comparison with MW-Fenton.

Fig. 8. (a) Effect of microwave power on removal of BPA and (b) First-order kinetics curves in MW-Mn-Fenton process. (BPA initial concentration = 100.0 mg/L, pH = 4.0, irradiation time = 6 min, H₂O₂ dosage = 34.0 mg/L, Fe²⁺ dosage = 2.1 mg/L, Mn²⁺ dosage = 2.7 mg/L).

Fig. 9. Effect of reaction time on removal rate of BPA and mineralization. (BPA initial concentration = 100.0 mg/L, pH = 4.0, microwave power = 300.0 W, H₂O₂ dosage = 34.0 mg/L, Fe²⁺ dosage = 2.1 mg/L, Mn²⁺ dosage = 2.7 mg/L).

582 Fig. 10. The effect of different processes on removal rate of BPA. (BPA initial concentration =
583 100.0 mg/L, pH = 4.0, microwave power = 300.0 W, microwave irradiation time = 6.0 min, H₂O₂
584 dosage = 34.0 mg/L, Fe²⁺ dosage = 2.1 mg/L, Mn²⁺ dosage = 2.7 mg/L).

585 Fig. 11. OH· generated in different processes. (BPA initial concentration = 100mg/L, pH = 4.0,
586 microwave power = 300.0 W, microwave irradiation time = 6.0 min, H₂O₂ dosage = 34.0 mg/L,
587 Fe²⁺ dosage = 2.1 mg/L, Mn²⁺ dosage = 2.7 mg/L).

588

Table 1

Results of BPA degradation and first-order reaction kinetics by different processes.

Num.	Methods	Initial concentration of BPA	Factors	BPA removal (%)	First-order reaction kinetics (k/min ⁻¹)	Ref.
1	photo-Fenton	10.0 mg/L	Fe ²⁺ 0.4 mmol/L H ₂ O ₂ 4 mmol/L Reaction time 36 h	93%	0.87	[50]
2	Achromobacter xylosoxidans strain B-16	10.0 mg/L	Inoculation 0.5 mL Reaction time 7 d pH 7.0	86.83%	0.0498	[51]
3	Photo-degradation	5 mg/L	pH 8.2 Reaction time 30 min H ₃ PW ₁₂ O ₄₀ 6.3%	86.9%	3.7	[4]
4	ozonation	0.509 mmol/L	pH 3.0 ozonation time 20 min	100.0%	2.11	[52]
5	photocatalytic	10 ppm	pH 7.4 TiO ₂ dosage (R) 1% Reaction time 6 h	97%	0.5506	[53]
6	NaBiO ₃ for oxidative degradation	0.1 mmol/L	NaBiO ₃ 1 g/L pH 5.0 Reaction time 60 min	97.3%	1	[54]
7	Photodegradation by yeast cells	520 µM	Reaction time 120 min pH 6.7 H ₂ O ₂ 500 mmol/L	70%	0.05	[55]
8	Permanganate	5 µM	pH 7.0 Reaction time 15 min Permanganate 100 µmol/L	99%	0.94	[56]
9	ultrasonic degradation	1 mg/L	Reaction time 120 min Ultrasonic frequency 800 kHz Power intensity 3.0 W/cm ² humic acid 2.5 mg/L	99%	0.0567	[57]
10	MW-Mn-Fenton	100mg/L	Reaction time 6min Fe ²⁺ 2.1 mg/L Mn ²⁺ 2.7 mg/L H ₂ O ₂ 34.0 mg/L	99.7%	4.67	Present study

Fig. 1. The effect of different ions on removal rate of BPA.

(BPA initial concentration = 100.0 mg/L, pH = 3.0, microwave power = 200.0 W, microwave irradiation time = 6.0 min, H₂O₂ dosage = 68.0 mg/L, Fe²⁺ dosage = 5.6 mg/L, other metal ions dosage = 6.0 mg/L).

Fig. 2. Effect of pH on removal rate of BPA.

(BPA initial concentration = 100.0 mg/L, pH = 3.0, microwave power = 200.0 W, microwave irradiation time = 6.0 min, H_2O_2 dosage = 68.0 mg/L, Fe^{2+} dosage = 5.6 mg/L, Mn^{2+} dosage = 5.5 mg/L).

Fig. 3. (a) BPA degradation and (b) TOC removal in the degradation of BPA by the Fenton processes for different BPA concentrations.

(pH = 4.0, microwave power = 200.0 W, microwave irradiation time = 6.0 min, H₂O₂ dosage = 68.0 mg/L, Fe²⁺ dosage = 5.6 mg/L, Mn²⁺ dosage = 5.5 mg/L).

Fig. 4. (a) Effect of different H_2O_2 dosage on removal rate of BPA in MW-Mn-Fenton process and (b) comparison with Fenton and MW-Fenton. (BPA initial concentration = 100.0 mg/L, pH = 4.0, microwave power = 200.0 W, irradiation time = 6.0 min, Fe^{2+} dosage = 5.6 mg/L, Mn^{2+} dosage = 5.5 mg/L).

Fig. 5. (a) Effect of different Fe^{2+} dosage on removal rate of BPA in MW-Mn-Fenton process and (b) comparison with Fenton and MW-Fenton. (BPA initial concentration = 100.0 mg/L, pH = 4.0, microwave power = 200.0 W, irradiation time = 6.0 min, H_2O_2 dosage = 34.0 mg/L, Mn^{2+} dosage = 5.5 mg/L).

Fig. 6. (a) Effect of Mn^{2+} dosage on removal rate of BPA in MW-Mn-Fenton process and (b) comparison with Fenton and MW-Fenton.
 (BPA initial concentration = 100.0 mg/L, pH = 4.0, microwave power = 200.0 W, irradiation time = 6.0 min, H_2O_2 dosage = 34.0 mg/L, Fe^{2+} dosage = 2.1 mg/L).

Fig. 7. (a) The UV-vis absorption spectra of BPA with the reaction time and (b) comparison with MW-Fenton.

Fig. 8. (a) Effect of microwave power on removal of BPA and (b) First-order kinetics curves in MW-Mn-Fenton process.
 (BPA initial concentration = 100.0 mg/L, pH = 4.0, irradiation time = 6.0 min, H₂O₂ dosage = 34.0 mg/L, Fe²⁺ dosage = 2.1 mg/L, Mn²⁺ dosage = 2.7 mg/L).

Fig. 9. Effect of reaction time on removal rate of BPA and mineralization.

(BPA initial concentration = 100.0 mg/L, pH = 4.0, microwave power = 300.0 W, H₂O₂ dosage = 34.0 mg/L, Fe²⁺ dosage = 2.1 mg/L, Mn²⁺ dosage = 2.7 mg/L).

Fig. 10. The effect of different processes on removal rate of BPA.

(BPA initial concentration = 100.0 mg/L, pH = 4.0, microwave power = 300.0 W, microwave irradiation time = 6.0 min, H₂O₂ dosage = 34.0 mg/L, Fe²⁺ dosage = 2.1 mg/L, Mn²⁺ dosage = 2.7 mg/L).

Fig. 11. OH· generated in different processes.

(BPA initial concentration = 100.0 mg/L, pH = 4.0, microwave power = 300.0 W, microwave irradiation time = 6.0 min, H₂O₂ dosage = 34.0 mg/L, Fe²⁺ dosage = 2.1 mg/L, Mn²⁺ dosage = 2.7 mg/L).