

## Article

# The Kinetic Simulation of Persulfate Activation by Nano-Ferrosferric Oxide

Tiehong Song <sup>1,\*</sup>, Yanjiao Gao <sup>2</sup>, Guanqiao Li <sup>1</sup>, Yaxin Chen <sup>1</sup> and Qiang Li <sup>1</sup>

<sup>1</sup> Key Laboratory of Songliao Aquatic Environment, Ministry of Education, Jilin Jianzhu University, Changchun 130118, China

<sup>2</sup> College of Civil Engineering and Architecture, Liaoning University of Technology, Jinzhou 121001, China

\* Correspondence: songtiehong2002@163.com

**Abstract:** Nano-ferrosferric-oxide ( $n\text{Fe}_3\text{O}_4$ )-activated persulfate (PS) technology was used to remove pollutant bisphenol A (BPA) in water. The effects of  $n\text{Fe}_3\text{O}_4$  concentration, PS concentration, BPA concentration, temperature, and pH were investigated in terms of the degradation effect of BPA. The results showed that more PS dosage and lower BPA concentration could improve the degradation rate of BPA. When other conditions were constant, the degradation rate of BPA increased with the increase of temperature. When pH was 5, the degradation rate of BPA was the highest. When the initial PS concentration and pH were changed, the degradation rate of BPA was consistent with the pseudo-secondary kinetic model. Under other conditions, the degradation rate of BPA was consistent with the pseudo-first-order kinetic model. Sulfate radical ( $\text{SO}_4^{\bullet-}$ ) produced by  $n\text{Fe}_3\text{O}_4$ /PS system was mainly responsible for the degradation of BPA.

**Keywords:** nano-ferrosferric oxide; bisphenol A; sulfate free radical; kinetics



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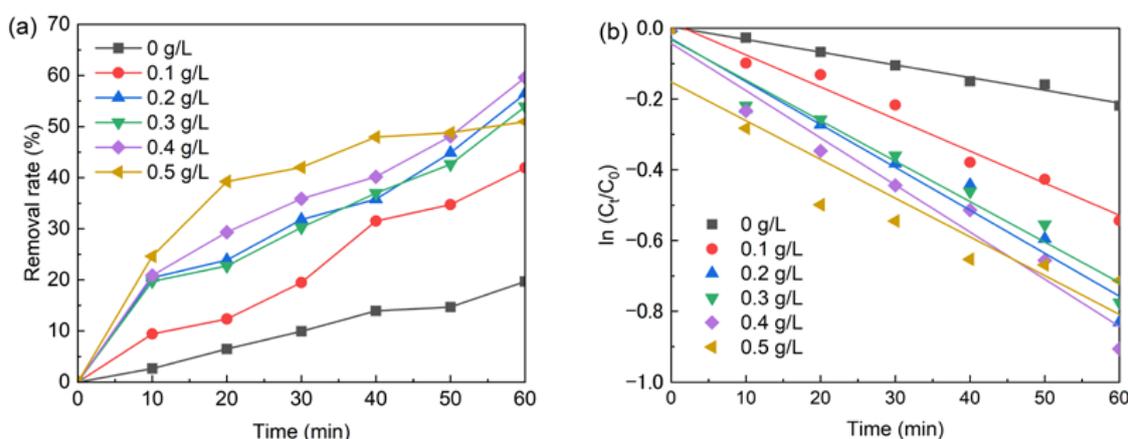
## 1. Introduction

In the decades, due to the increasing use of synthetic chemicals, people have paid great attention to environmental pollution caused by emerging pollutants [1], especially water pollution. Emerging pollutants are toxic and persistent. They are widely detected in water bodies [2,3], and are difficult to remove using traditional methods [4,5]. In the advanced oxidation process, the application of sulfate radicals ( $\text{SO}_4^{\bullet-}$ ) to the oxidative degradation of emerging pollutants has shown a good ability [6]. Nisreen Sabti [7] used  $\text{Fe}_3\text{O}_4/\text{SiO}_2$  to adsorb low initial concentration of Methyl Bromide (MB) and reached better MB removal rate. In addition to being an adsorbent,  $\text{Fe}_3\text{O}_4$  can also be used as an activator of persulfate (PS) to produce  $\text{SO}_4^{\bullet-}$  in water treatment due to its advantages such as easy recovery, large surface area, and high catalytic activity. In this paper, nano-ferrosferric-oxide ( $n\text{Fe}_3\text{O}_4$ ) was used as an activator to catalyze PS to degrade bisphenol A (BPA). The effects of  $\text{SO}_4^{\bullet-}$  on the degradation of BPA were studied by adjusting the five influencing factors: nano-ferrosferric-oxide dosage, persulfate dosage, initial substrate concentration (BPA), temperature, and initial pH. The degradation effect of BPA was simulated and analyzed from the point of view of kinetics.

## 2. Results

### 2.1. $n\text{Fe}_3\text{O}_4$ Dosage

It was to take 500 mL of 5 mg/L BPA in 6 beakers at a temperature of 20 °C and add 0.2 mM sodium persulfate and 0, 0.1, 0.2, 0.3, 0.4, 0.5  $n\text{Fe}_3\text{O}_4$  solution, respectively. The test results are shown in Figure 1a, and the fitted curve is shown in Figure 1b. The fitted curve equations and parameters are shown in Table 1.



**Figure 1.** (a) The effect of nFe<sub>3</sub>O<sub>4</sub> dosage on BPA removal; (b) The kinetic of BPA degradation by nFe<sub>3</sub>O<sub>4</sub> dosage. Conditions: [nFe<sub>3</sub>O<sub>4</sub>] = 0.1–0.5 g/L, T = 20 °C, pH = 6.8, [PS] = 0.2 mM, [BPA] = 5 mg/L.

**Table 1.** The kinetic parameters of BPA degradation by nFe<sub>3</sub>O<sub>4</sub> dosage.

Nano-Ferrosferric-Oxide/gL <sup>-1</sup>	ln (C <sub>t</sub> /C <sub>0</sub> )	R <sup>2</sup>
0	−(−0.00371 + 0.00359t)	0.984
0.1	−(−0.01475 + 0.00905t)	0.975
0.2	−(0.02968 + 0.01212t)	0.946
0.3	−(0.03261 + 0.01143t)	0.959
0.4	−(0.04346 + 0.01332t)	0.960
0.5	−(0.15189 + 0.01095t)	0.823

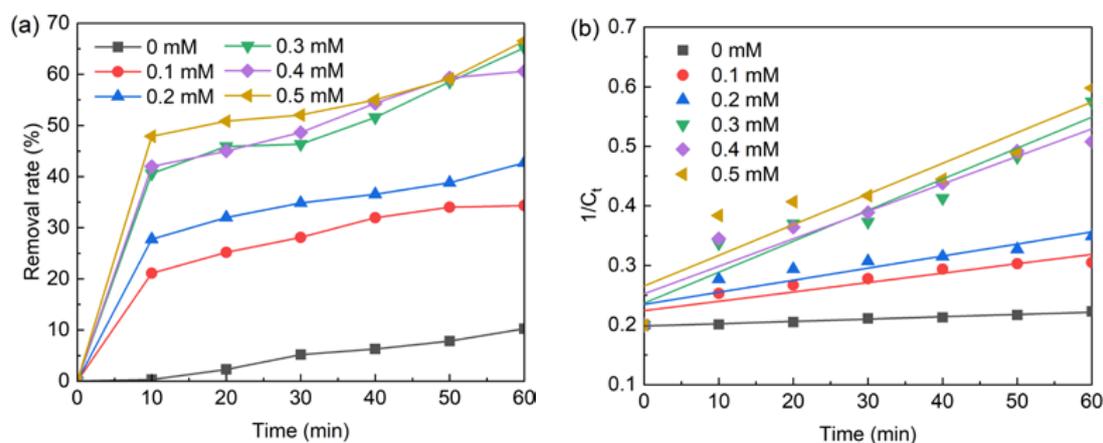
It can be seen from Figure 1 that, without nFe<sub>3</sub>O<sub>4</sub>, the removal rate of BPA can reach 19.68% after 60 min of reaction. The reason for this is that temperature and light can activate PS to produce SO<sub>4</sub><sup>•−</sup>, which can remove BPA. It was significant to add nFe<sub>3</sub>O<sub>4</sub> to the system for increasing the removal rate of BPA; this was due to the formation of Fe<sup>2+</sup> on the surface of nFe<sub>3</sub>O<sub>4</sub> activated PS to produce SO<sub>4</sub><sup>•−</sup>, which led to the removal of BPA.

It is shown from Table 1 that the dosage of nFe<sub>3</sub>O<sub>4</sub> has a significant impact on the BPA degradation rate. When nFe<sub>3</sub>O<sub>4</sub> is not in the system, the BPA degradation rate is only 0.00359 min<sup>−1</sup>. With the increase in nFe<sub>3</sub>O<sub>4</sub> dosage, the degradation rate of BPA is accelerated firstly, and then slowly lowered. The analysis is due to the increase in nFe<sub>3</sub>O<sub>4</sub> dosage, which leads to the increase in Fe<sup>2+</sup>, and the generation of more SO<sub>4</sub><sup>•−</sup>, which leads the accelerated degradation rate of BPA. On the one hand, the excessive Fe<sup>2+</sup> can result in a quenching reaction with SO<sub>4</sub><sup>•−</sup>. On the other hand, the excessive SO<sub>4</sub><sup>•−</sup> also leads to a mutual quenching reaction between SO<sub>4</sub><sup>•−</sup> and other free radicals, which will reduce SO<sub>4</sub><sup>•−</sup> in the system, thus slowing down the degradation rate of BPA.

## 2.2. Dosage of Sodium Persulfate

Six parts of nFe<sub>3</sub>O<sub>4</sub> (each 0.1 g/L) were added to the six beakers (each 500 mL) containing BPA (5 mg/L), then different concentrations of PS (0 mM, 0.1 mM, 0.2 mM, 0.3 mM, 0.4 mM, 0.5 mM) were put respectively into the six beakers to initiate chemical reactions. The test results are shown in Figure 2a and the fitted curve is shown in Figure 2b. The fitted curve equations and parameters are shown in Table 2. It can be seen from Table 2 that the amount of PS has a significant impact on the degradation rate of BPA. When the amount of PS increased from 0.1 mM to 0.3 mM, the degradation rate of BPA was accelerated. The degradation of BPA was the slowest when the PS dosage was 0.1 mM. The results showed that sodium persulfate could accelerate the degradation rate of BPA. Because it can produce more SO<sub>4</sub><sup>•−</sup>, it accelerates the degradation of BPA. However, excessive sodium persulfate can cause the degradation rate of BPA to slow down, because excessive sodium persulfate can also become the quenching agent of SO<sub>4</sub><sup>•−</sup> [8,9]. This

indicates that sodium persulfate has an appropriate concentration, and so the optimal dosage of sodium persulfate is 0.3 mM.



**Figure 2.** (a) The effect of PS dose on BPA removal; (b) The kinetic of BPA degradation by PS dosage. Conditions: [PS] = 0.1–0.5 mM, T = 20 °C, pH = 6.8, [nFe<sub>3</sub>O<sub>4</sub>] = 0.1 g/L, [BPA] = 5 mg/L.

**Table 2.** The kinetic parameters of BPA degradation by PS dosage.

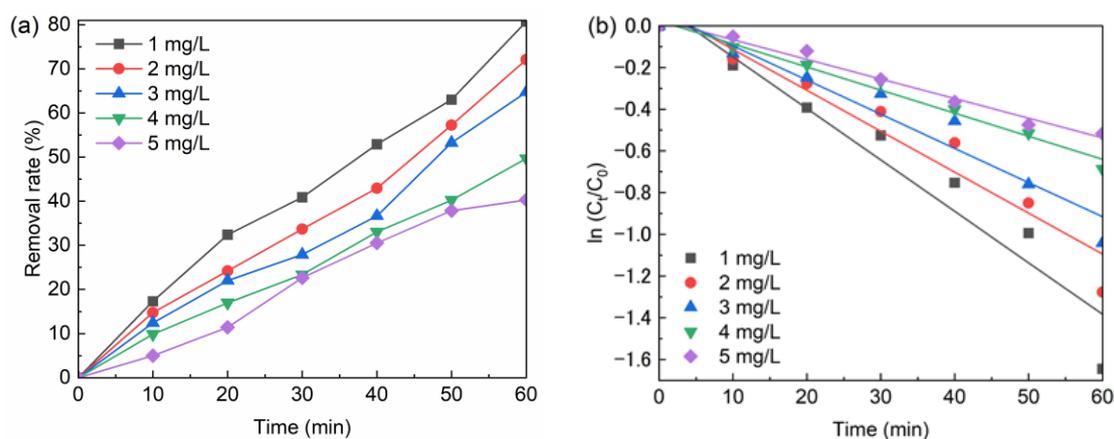
Initial Substrate Concentration (mM)	Pseudo-First-Order Reaction Kinetics Mode	R <sup>2</sup>
0	$1/C_t = 0.19832 + 0.000389t$	0.973
0.1	$1/C_t = 0.22407 + 0.00158t$	0.839
0.2	$1/C_t = 0.23471 + 0.00203t$	0.800
0.3	$1/C_t = 0.23664 + 0.00521t$	0.901
0.4	$1/C_t = 0.25243 + 0.00461t$	0.893
0.5	$1/C_t = 0.2655 + 0.00515t$	0.825

### 2.3. Initial Substrate Concentration

The experiment required 500 mL of 1 mg/L, 2 mg/L, 3 mg/L, 4 mg/L, 5 mg/L BPA solution in 6 beakers, at a temperature 20 °C, with the addition of 0.1 g/L nFe<sub>3</sub>O<sub>4</sub>, 0.2 mM sodium persulfate. The test results are shown in Figure 3a and the fitted curve is shown in Figure 3b. The fitted curve equations and parameters are shown in Table 3. According to Figure 3, with the increase in initial BPA concentration, the amount of BPA removal increased, but the removal rate of BPA decreased. In this analysis, the amount of BPA removed raise because the initial BPA concentration increased the amount of BPA per unit volume, which in turn increased the probability of collision between them. However, as the concentration of nFe<sub>3</sub>O<sub>4</sub> and sodium persulfate remained unchanged and only a certain amount of SO<sub>4</sub><sup>•−</sup> was able to be produced, so the removal rate of BPA was reduced [10,11]. It can be seen from Table 3 that the initial BPA concentration has a significant impact on the degradation rate of BPA. With the increase in the initial BPA concentration, the degradation rate of BPA gradually slows down. When the initial concentration of BPA was 5 mg/L, the degradation rate of BPA was 0.00942 min<sup>−1</sup>, and the reaction was the slowest.

**Table 3.** The kinetic parameters of BPA degradation.

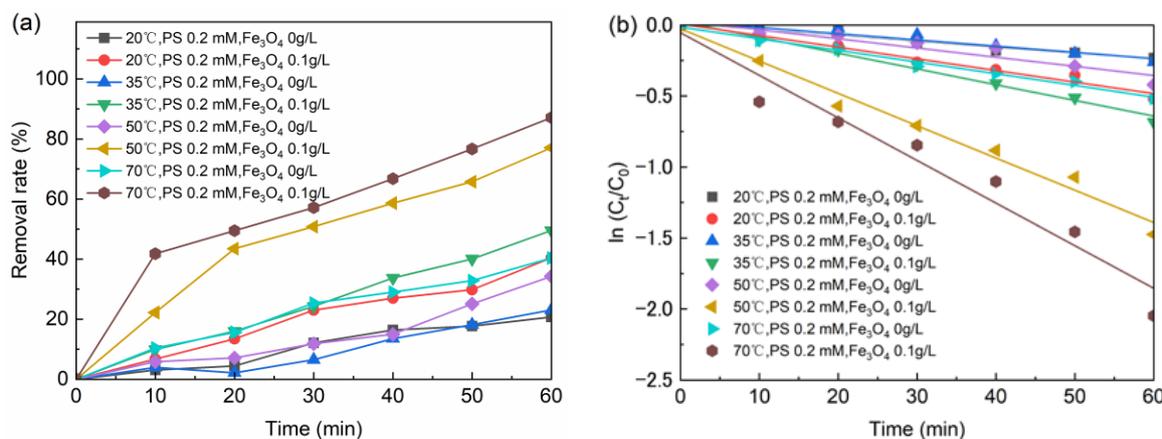
BPA Initial Concentration (mg/L)	Pseudo-First-Order Reaction Kinetics Mode	R <sup>2</sup>
1	$\ln(C_t/C_0) = -(-0.09686 + 0.02466t)$	0.913
2	$\ln(C_t/C_0) = -(-0.08361 + 0.01963t)$	0.922
3	$\ln(C_t/C_0) = -(-0.06782 + 0.01639t)$	0.927
4	$\ln(C_t/C_0) = -(-0.0235 + 0.01106t)$	0.981
5	$\ln(C_t/C_0) = -(-0.02804 + 0.00942t)$	0.980



**Figure 3.** (a) The effect of BPA concentration on BPA removal; (b) The kinetic of BPA degradation by BPA concentration. Conditions:  $[n\text{Fe}_3\text{O}_4] = 0.1 \text{ g/L}$ ,  $T = 20 \text{ }^\circ\text{C}$ ,  $\text{pH} = 6.8$ ,  $[\text{PS}] = 0.2 \text{ mM}$ ,  $[\text{BPA}] = 1\text{--}5 \text{ mg/L}$ .

#### 2.4. Temperature

When the temperature was  $20 \text{ }^\circ\text{C}$ ,  $35 \text{ }^\circ\text{C}$ ,  $50 \text{ }^\circ\text{C}$ ,  $70 \text{ }^\circ\text{C}$  and bisphenol A was  $5 \text{ mg/L}$ , the removal rate of BPA increased from 20.72% to 40.36%. One experiment was to add  $0.2 \text{ mM}$  sodium persulfate and  $0.1 \text{ g/L}$   $n\text{Fe}_3\text{O}_4$ , and the other experiment was to add  $0.2 \text{ mM}$  sodium persulfate without  $n\text{Fe}_3\text{O}_4$ . The test results are shown in Figure 4a, and the fitted curve is shown in Figure 4b. The kinetic equations of BPA degradation at different initial reaction temperature could be expressed by the pseudo-first-order reaction kinetic equation (Table 4).



**Figure 4.** (a) The effect of temperature on BPA removal; (b) The kinetic of BPA degradation at different temperature. Conditions:  $\text{pH} = 6.8$ ,  $[\text{BPA}] = 5 \text{ mg/L}$ .

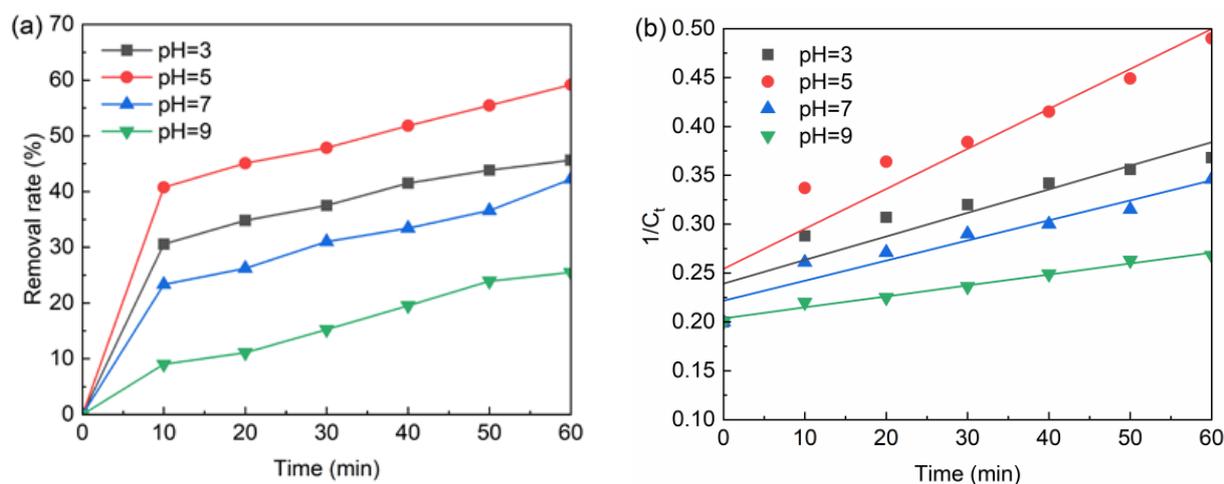
**Table 4.** The kinetic parameters of BPA degradation at different temperatures.

Dosage	Temperature ( $^\circ\text{C}$ )	Pseudo-First-Order Reaction Kinetics Mode	$R^2$
PS: 0.2 mM $n\text{Fe}_3\text{O}_4$ : 0 g/L	20	$\ln(C_t/C_0) = -(-0.00818 + 0.00414t)$	0.959
	35	$\ln(C_t/C_0) = -(-0.02654 + 0.00439t)$	0.900
	50	$\ln(C_t/C_0) = -(-0.03193 + 0.00645t)$	0.889
	70	$\ln(C_t/C_0) = -(0.01496 + 0.00821t)$	0.986
PS: 0.2 mM $n\text{Fe}_3\text{O}_4$ : 0.1 g/L	20	$\ln(C_t/C_0) = -(0.00807 + 0.00819t)$	0.973
	35	$\ln(C_t/C_0) = -(0.02368 + 0.01109t)$	0.984
	50	$\ln(C_t/C_0) = -(0.02543 + 0.02277t)$	0.978
	70	$\ln(C_t/C_0) = -(0.05465 + 0.02998t)$	0.945

When the temperature was 20 °C, the degradation of BPA was the slowest. When the temperature elevated to 70 °C, the degradation rate of BPA increased to 2.4 times faster than the rate at 20 °C. Considering the actual situation of sewage treatment, the optimal temperature is 35 °C from the perspective of energy saving.

### 2.5. pH

When the pH was 3, 5, 7, 9, the method required the addition of 0.2 mM sodium persulfate and 0.1 g/L nFe<sub>3</sub>O<sub>4</sub> at the temperature 20 °C. The BPA concentration was 5 mg/L. The test results are shown in Figure 5a, and the fitted curve is shown in Figure 5b. The fitted curve equations and parameters are shown in Table 5.



**Figure 5.** (a) The effect of pH on BPA removal; (b) The kinetic of of BPA degradation at different pH. Conditions: [nFe<sub>3</sub>O<sub>4</sub>] = 0.1 g/L, T = 20 °C, pH = 3–9, [PS] = 0.2 mM, [BPA] = 5 mg/L.

**Table 5.** The kinetic parameters of BPA degradation at different pH.

Initial pH	Pseudo-Second-Order Reaction Kinetics Mode	R <sup>2</sup>
3	1/C <sub>t</sub> = 0.23925 + 0.00241t	0.818
5	1/C <sub>t</sub> = 0.25432 + 0.00409t	0.869
7	1/C <sub>t</sub> = 0.22168 + 0.00205t	0.903
9	1/C <sub>t</sub> = 0.20364 + 0.00112t	0.979

As shown in Figure 5, with the increase in pH, the removal of BPA increased firstly and then decreased. After the reaction for 60 min, the removal rate of BPA was the highest at pH 5 and the lowest at pH 9, with the removal rates of 59.16% and 25.5%, respectively.

Table 5 shows that pH has a significant effect on the degradation rate of BPA. With the gradual increase in pH, the reaction speed was accelerated at first and then slowed down. The degradation rate of BPA under acidic conditions was much higher than that under alkaline conditions. When pH and acidity conditions are more favorable for the formation of SO<sub>4</sub><sup>•−</sup>, the degradation rate of BPA is faster. Thus, the optimal pH is 5.

## 3. Materials and Methods

### 3.1. Experimental Reagent

The main reagents used in the experiment are superior purity bisphenol A (McLean Biochemical Technology Co., Ltd., Shanghai, China), analytical purity nano-ferrosoferric-oxide (McLean Biochemical Technology Co., Ltd., Shanghai, China), analytical purity sodium persulfate (National Pharmaceutical Group Chemical Reagent Co., Ltd., Shanghai, China), sodium hydroxide and sulfuric acid (Jindong Tianzheng Fine Chemical Reagent Factory, Tianjin, China).

The freshly made ultrapure water was used to analyze and prepare experimental reagents in the entire experimental process. The test samples were filtered through a 0.22  $\mu\text{m}$  filter membrane, and 0.5 mL of methanol was added to terminate the reaction.

### 3.2. Experimental Instruments

Moore ultrapure water machine (Xuyuan Medical Equipment Co., Ltd., Shanghai, China), electronic analytical balance (Leigu Instrument Co., Ltd., Shanghai, China), pH meter (Yidian Scientific Instrument Co., Ltd., Shanghai, China), high-phase liquid chromatography (HPLC) (Agilent G7121A, Santa Clara, CA, USA) were used. Bisphenol A concentration was determined by the use of a high-performance liquid chromatography (HPLC) with fluorescence detector. The HPLC conditions were: C18 (4.6 mm  $\times$  150 mm, 4  $\mu\text{m}$ ) was selected for the column, the volume ratio of methanol/water was 70/30 in the mobile phase, the injection volume was 20 mL, and the flow rate was 0.8 mL/min. The column temperature is 25  $^{\circ}\text{C}$  and the excitation and emission wavelengths are 228 nm and 312 nm. Under these conditions, the retention time of bisphenol A is 3.48 min.

### 3.3. Analysis Method

The first-order reaction equation is [12]:

$$dC/dt = kC, \quad (1)$$

C—the concentration of residual bisphenol A at the time of degradation t/mg L<sup>-1</sup>.

k—reaction rate constant/min.

The second-order reaction equation is [12]:

$$dC/dt = kC^2, \quad (2)$$

C—the concentration of residual bisphenol A at the time of degradation t/mg L<sup>-1</sup>.

k—reaction rate constant/min.

## 4. Conclusions

(1) The use of nFe<sub>3</sub>O<sub>4</sub>-activated PS to treat refractory organics is an effective advanced oxidation method. In the nFe<sub>3</sub>O<sub>4</sub>/PS system, the factors affecting the removal rate of bisphenol A include the dosage of nFe<sub>3</sub>O<sub>4</sub>, the dosage of PS, pH and temperature. (2) When the nFe<sub>3</sub>O<sub>4</sub> dosage was 0 ~ 0.5 g/L, the removal rate of BPA decreased with the increase in the initial PS concentration and BPA. However, the removal rate of bisphenol A increased obviously with the increase in temperature. As such we conclude that the higher the temperature, the faster the reaction speed. Considering energy conservation, the optimal temperature is 35  $^{\circ}\text{C}$ , and the best pH is 5. (3) When the initial PS concentration and pH were changed, the degradation rate of BPA was consistent with the pseudo-secondary kinetic model. Under other conditions, the degradation rate of BPA was consistent with the pseudo-first-order kinetic model. (4) The experimental conclusion can provide technical support for the removal of BPA in water by using nFe<sub>3</sub>O<sub>4</sub> to activate the PS.

**Author Contributions:** Conceptualization, T.S. and Y.G.; methodology, G.L.; software, Q.L.; validation, T.S. and Q.L. formal analysis, G.L.; investigation, Y.C.; data curation, Y.G.; writing—original draft preparation, T.S.; writing—review and editing, Y.G.; visualization, Y.C.; supervision, T.S.; project administration, T.S.; funding acquisition, T.S. All authors have read and agreed to the published version of the manuscript.

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**Conflicts of Interest:** The authors declare no conflict to any personal circumstances.

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