Article

Study of Fe₃O₄/PS System in Degrading BPA in Aqueous Solution

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The degradation of bisphenol A (BPA) by Fe₃O₄/persulfate system was investigated in aqueous solution. The influences of the initial concentrations of Fe₃O₄, persulfate (PS) and BPA, pH value, and initial reaction temperature on BPA removal were studied. The radical species was investigated by adding excessive dose of scavenger (methanol (MeOH) and *tert*-butanol (TBA)) into Fe₃O₄/PS system for the purpose of radical scavenging. The degradation products of BPA were detected by gas chromatography-mass spectrometry (GC-MS). The recyclability of Fe₃O₄ was also evaluated. The BPA removal rate of 80.7% was achieved under the following conditions: $[BPA]_0 = 1$ mg L^{-1}, $[PS]_0 = 0.2$ mM, $[Fe_3O_4]_0 = 0.1$ g L^{-1}, $T_0 = 20 \pm 1$ °C, $pH_0 = 6.8 \pm 0.2$. The results confirmed that the main free radicals in the reaction process were sulfate radicals, followed by hydroxyl radicals. Some intermediate products of BPA degradation, such as phenols, benzoquinones and benzoic acid were identified by GC-MS.

Keywords: sulfate radicals, Fe₃O₄, bisphenol A, hydroxyl radicals, advanced oxidation processes

Introduction

Bisphenol A (2,2-bis(4-hydroxyphenyl)propane, BPA), a white solid, has been widely used as a ubiquitous intermediate in manufacturing polycarbonate plastics, epoxy resins and polysulfone.[1,2] Therefore, BPA is present in many daily supplies, such as toys, bottles, food and beverage packaging, water supply pipes, and the polymers used in dental treatment.[3,4] BPA is a well-known and studied endocrine disrupting compound (EDC), which can mimic hormones and cause reproductive damage, cancer and other adverse effects on the human body and the ecological environment.[5,6] Previous studies[7,8] have shown that BPA can interfere with the endocrine system of humans and animals even at concentrations below 1 μg m^{-3}. Due to the discharge of domestic sewage and industrial wastewater, as well as the infiltration of landfill leachate, BPA has frequently been found in surface water and groundwater.[9,10] The study showed that the BPA concentration in some water

environments can be as high as 100 μg L^{-1}.[10] At present, the concentration of BPA in water environment and its harm to aquatic organisms have attracted the attention of researchers who are working on the research of refractory organics removal methods.

Since BPA is a refractory pollutant with two benzene rings, conventional biological processes in wastewater treatment plants are not efficient for complete removal of BPA.[11] There are several alternative approaches that have been used to deal with the BPA over the years, such as adsorption,[12,13] chlorination with sodium hypochlorite,[14] and the advanced oxidation processes (AOPs). The adsorption is restricted owing to the low hydrophobicity ($logK_{ow}$) of BPA that limits the adsorption efficiency,[15] and the chlorinated metabolites formed during chlorination with sodium hypochlorite cause some side effects.[16] In contrast, AOPs are popular due to their ability to decompose refractory organics into biodegradable and benign products by powerful free radicals such as hydroxyl radicals (•OH) or sulfate radicals ($SO_4^{\bullet-}$).[17] In AOPs, ozone (O_3),[18] hydrogen peroxide (H_2O_2), peroxymonosulfate (PMS), and persulfate

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(PS) are commonly used oxidants, which can generate free radicals after being activated by certain ways.[11] For instance, in the UV/O_3, UV/H_2O_2, and Fe^{II}/H_2O_2 processes, O_3 and H_2O_2 can produce •OH due to UV or iron activation; in the UV/PS, Fe^0/PS, Fe^{II}/PS, and Fe_3O_4/PS processes, PS can generate $SO_4^{•-}$ also due to UV or iron activation.[11,18] Although $SO_4^{•-}$ and •OH have close oxidizing potentials (for $SO_4^{•-}$, E_0 = 2.6-3.1 V; for •OH, E_0 = 1.8-2.7 V), the half-life of $SO_4^{•-}$ is longer than that of •OH, and the oxidant PS is more stable than O_3 and H_2O_2. On the one hand, iron is a common material with benign property, which makes it as an activator to show economic and environmental advantages. On the other hand, from the standpoint of stability, ease of storage, and generation of sulfate radicals, PS is considered to be more suitable as an oxidant in AOPs. Therefore, the use of iron to activate PS to generate free radicals in degradation of refractory organics has become one of the research hotspots in AOPs. The mechanisms by which various forms of iron activate PS are attributed to the redox reactions between Fe^{II} and PS. Based on the existence form of iron, iron-based activator can be classified into homogeneous (such as Fe^{II}) and heterogeneous (such as Fe^0 and Fe_3O_4).[19] As a homogeneous activator, Fe^{II} is completely dissolved in the solution, which easily causes excessive Fe^{II}, thereby trapping the generated free radicals and reducing the degradation efficiency of organic matter.[20,21] On the contrary, as heterogeneous activates, Fe^0 and Fe_3O_4 can release Fe^{II} into the water solution at a certain rate to avoid the extinction of free radicals caused by excessive Fe^{II}. Fe_3O_4 is a preferred activator with mixed valence oxide containing Fe^{II} and Fe^{III}, and it is able to constantly produce Fe^{II} to react with PS and generate free radicals. In addition, Fe_3O_4 is the main component of magnetite in nature, so it is easy to obtain. Compared with Fe^{II} and Fe^0, it is easy to recover Fe_3O_4 from wastewater based on its sub-magnetism. Fe_3O_4 can also reduce the cost of large volumes of waste effluent treatment and will not result in secondary pollution.[22]

Some researchers used Fe^{II} and Fe^0 to activate PS for the treatment of BPA,[22,23] and some researchers studied sulfamonomethoxine, ciprofloxacin hydrochloride degradation in Fe_3O_4/PS systems.[22,24,25] However, there are few studies towards BPA removal using Fe_3O_4/PS systems, especially the scavenging experiment of free radicals and the intermediate identification of BPA degradation products still need be further studied. In this paper, Fe_3O_4 magnetic particles have been used as activator to activate PS to produce free radicals for the removal of BPA. The performance of the Fe_3O_4/PS system on the degradation of BPA was systematically investigated, the possible effects of environmental factors on BPA removal, and BPA degradation mechanism were discussed in detail. Moreover, the role of active radical species was also explored using scavenging experiments, and the recycling performance of Fe_3O_4 was evaluated based on Fe_3O_4 reuse experiment.

Experimental

Chemicals and equipment

The main chemicals and equipment used in the experiments are present in Tables 1 and 2, respectively. The content of Fe_3O_4 in the iron oxide material is greater than 99.5%, the particle size of iron oxide is 20 nm, and the specific surface area of iron oxide is 51.46 m^2 g^{-1}.

Batch experiments

A 1000 mg L^{-1} of BPA aqueous stock solution was prepared for dilution into a series of concentrations in the batch experiments. The experiments were conducted in the 500-mL beakers placed on a magnetic heating stirrer with

Table 1. The main experimental chemicals

Chemical	Molecular formula	Purity	Supplier
Bisphenol A	$C_{15}H_{16}O_2$	premium grade	McLean Co., Ltd. (Shanghai, China)
Iron oxide	Fe_3O_4	analytical grade	McLean Co., Ltd. (Shanghai, China)
Sodium persulfate	$Na_2S_2O_8$	analytical grade	Sinopharm Co., Ltd. (Shanghai, China)
Sodium hydroxide	NaOH	analytical grade	Tianjin Chemical Reagent Factory (Tianjin, China)
Sulfuric acid	H_2SO_4	analytical grade	Beijing Chemical Reagent Factory (Beijing, China)
Methanol	CH_3OH	chromatographically grade	Norsch Co., Ltd. (Chengdu, China)
tert-Butanol	$C_4H_{10}O$	chromatographically grade	McLean Co., Ltd. (Shanghai, China)
Hexane	C_6H_{14}	analytical grade	Beijing Chemical Reagent Factory (Beijing, China)
Dichloromethane	CH_2Cl_2	analytical grade	Beijing Chemical Reagent Factory (Beijing, China)
Sodium chloride	NaCl	analytical grade	Beijing Chemical Reagent Factory (Beijing, China)
Anhydrous sodium sulfate	Na_2SO_4	analytical grade	Xilong Science Co., Ltd. (Shantou, China)

Table 2. The main equipment

Equipment	Model	Manufacturer
Ultra pure water machine	Elemental 1810 D	Chongqing Moore Water Treatment Equipment Co., Ltd. (Chongqing, China)
Electronic analytical balance	FA2104A	Shanghai Leigu Instrument Co., Ltd. (Shanghai, China)
Magnetic stirrer	SH-II-4C	Guangdong Foheng Instrument Co., Ltd. (Foshan, China)
pH meter	pHS-3C	Shanghai INESA Scientific Instrument Co., Ltd. (Shanghai, China)
High-phase liquid chromatography (HPLC)	G7121A	Agilent Technologies (China) Co., Ltd. (Shanghai, China)
Nitrogen blowing concentrator	XSF-12	Shanghai Xuansheng Scientific Instrument Co., Ltd. (Shanghai, China)
Gas chromatography mass spectrometry (GC-MS)	7890B-7000C	Agilent Technologies (China) Co., Ltd. (Shanghai, China)
Oven	GHG-9040N	Hangzhou Zhuochi Instrument Co., Ltd. (Hangzhou, China)

the operating speed of 200 rpm. Firstly, the BPA solution (500 mL) with the designed concentration was added to the beaker, then predetermined amount of PS and Fe₃O₄ was quickly plunge into the beaker to trigger the reaction. The reaction temperature was adjusted by the heater, and the pH was adjusted by adding 0.1 M NaOH or H₂SO₄ to the solution. The entire reaction time was set to 60 min. Aliquots (0.5 mL) were taken out of the beaker and put into the sample bottle. Then, 0.5 mL ethanol was immediately added into the sample bottle to stop the reaction. The samples were taken every 10 min from the beaker, and the residual concentration of BPA of the final samples were detected by high-performance liquid chromatography (HPLC). For the scavenging of free radicals generated in the reaction, the experiments were performed by adding methanol (MeOH) and *tert*-butanol (TBA) with preset concentrations in beakers.

Analytical methods

The BPA concentration in samples was examined by a HPLC equipped with a C18 column (4.6 mm × 150 mm, 4 μm) by using a fluorescence detector at 228 nm. The mobile phase was 70% methanol at a flow rate of 0.8 mL min⁻¹. The excitation and emission wavelengths are 228 and 312 nm, respectively. The temperature of the column compartment was 25 °C and the injection volume was 20 μL. The retention time of BPA under above conditions was 3.48 min.

The oxidation products of BPA were carried out by a gas chromatography-mass spectrometry (GC-MS). The chromatographic analysis was performed via injection in splitless mode (split ratio of 10:1, injection volume of 1 μL) at 260 °C using a quartz capillary column (length: 30 m, inner diameter: 0.25 mm, film thickness: 0.25 μm) with a helium flow of 1.0 mL min⁻¹. The qualitative analysis was performed with electron ionization (EI) at 70 eV using the full scan mode in the *m/z* range of 45-280. The ion source and quadrupole temperature were maintained at 230 and 150 °C, respectively.

The removal rate η (%) of BPA is calculated using equation 1, where C_0 is the initial concentration of BPA (mg L⁻¹), C_t is the BPA concentration after t min treatment (mg L⁻¹). The fitting of the kinetic equations in the experiment are based on the first-order reaction kinetic equation, as shown in equation 2, where k is the kinetic constant (min⁻¹), b is the y intercept (no unit).

$$\eta = \frac{C_0 - C_t}{C_0} \times 100 \tag{1}$$

$$\ln\left(\frac{C_t}{C_0}\right) = -kt + b \tag{2}$$

Results and Discussion

The effect of the initial Fe₃O₄ dose

As the activator of PS, Fe₃O₄ plays a very important role in the reaction of Fe₃O₄/PS system. We investigated the effects of six Fe₃O₄ doses used in activating PS on removing BPA. The experimental results are presented in Figure 1. Without adding Fe₃O₄, the BPA removal rate can reach 19.68% by PS alone within 60 min. We speculate that this was due to temperature or light energy, which promote PS to produce $SO_4^{\bullet-}$ (equation 3), thereby removing BPA. A previous research[26] confirmed that PS can be catalyzed by ambient temperature to form $SO_4^{\bullet-}$ to degrade organic matter. As adding Fe₃O₄ to the system, the removal rate of BPA was significantly increased. The Fe^II on the surface of Fe₃O₄ can react with PS to generate $SO_4^{\bullet-}$ (equation 4), and the BPA was removed. As the dose of Fe₃O₄ increased from 0.1 to 0.2 g L⁻¹, the BPA removal rate increased from 41.94 to 56.49% within 60 min. When the dose of Fe₃O₄ was increased to 0.3-0.5 g L⁻¹, the removal rate of BPA did not change much, compared with the BPA removal rate of 0.2 g L⁻¹ of Fe₃O₄. We speculate that there are three possible reasons for this BPA degradation curve. Firstly, due to the increase of Fe₃O₄ dosage, more Fe^II can be produced, and

excessive Fe^{II} will extinguish $SO_4^{\bullet-}$ (equation 5),[27] which will reduce the BPA removal rate. Secondly, the excessive $SO_4^{\bullet-}$ formed can react between themselves and reduce the number of $SO_4^{\bullet-}$ (equation 6).[28] Finally, the increase in the amount of Fe_3O_4 (0.3-0.5 g L^{-1}) causes the consumption of PS to increase. At 40 min, PS is exhausted and the number of free radicals decreases, so the degradation rate of BPA increases slowly.

$$S_2O_8^{2-} \xrightarrow{\text{energy}} 2SO_4^{\bullet-} \tag{3}$$
$$Fe^{II} + S_2O_8^{2-} \rightarrow Fe^{III} + SO_4^{\bullet-} + SO_4^{2-} \tag{4}$$
$$Fe^{II} + SO_4^{\bullet-} \rightarrow Fe^{III} + SO_4^{2-} \tag{5}$$
$$SO_4^{\bullet-} + SO_4^{\bullet-} \rightarrow S_2O_8^{2-} \tag{6}$$
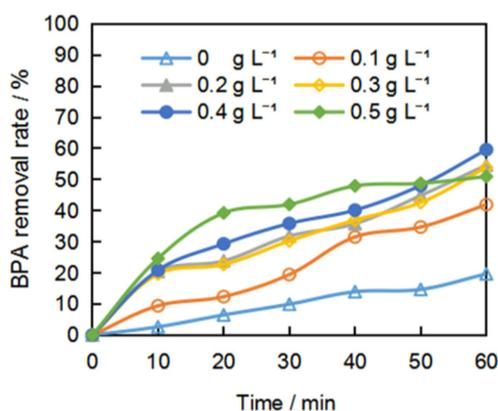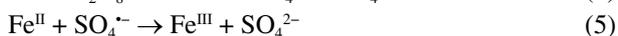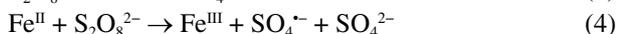
Figure 1. The effect of the initial Fe_3O_4 concentration on BPA removal. $[BPA]_0 = 5$ mg L^{-1}, $[PS]_0 = 0.2$ mM, $[Fe_3O_4]_0 = 0$-0.5 g L^{-1}, $T_0 = 20 \pm 1$ °C, $pH_0 = 6.8 \pm 0.2$.

The effect of the initial PS concentration

The initial concentration of PS is an important factor affecting the BPA removal by Fe_3O_4 activation. Figure 2 gives the effect of the PS initial concentration on BPA degradation by Fe_3O_4 activation. In the absence of PS, it was found that 10.3% of BPA was removed within 60 min, indicating that Fe_3O_4 could adsorb BPA as an adsorbent. Sun *et al.*[29] also found that nano-Fe_3O_4 can adsorb 2,4-dichlorophenol, but the efficiency was very low compared with Fe_3O_4/PS catalytic degradation. With the increase in the PS concentration from 0.1 to 0.3 mM, the BPA removal rate was elevated from 34.3 to 65.2% within 60 min, which could be due to the larger amount of $SO_4^{\bullet-}$ produced by PS/Fe_3O_4 system (equation 4). However, when the initial concentration of PS increased from 0.3 to 0.5 mM, the BPA removal rate increased only by 1.4% within 60 min. We have identified three possible reasons for this result. Firstly, excessive PS (0.4-0.5 mM) slowed down the degradation rate of BPA due to the elimination of $SO_4^{\bullet-}$ by PS (equation 7). Secondly, more $SO_4^{\bullet-}$ could also react with each other and lose their oxidation performance

(equation 6). Finally, the increase in PS concentration causes the continuous consumption of Fe_3O_4, and the amount of Fe^{II} released from Fe_3O_4 cannot meet the demand for high concentrations of PS. Therefore, the relatively insufficient amount of catalyst results in a slower reaction rate of catalyzing PS to $SO_4^{\bullet-}$, and ultimately affects the degradation efficiency of BPA.

$$S_2O_8^{2-} + SO_4^{\bullet-} \rightarrow S_2O_8^{\bullet-} + SO_4^{2-} \tag{7}$$
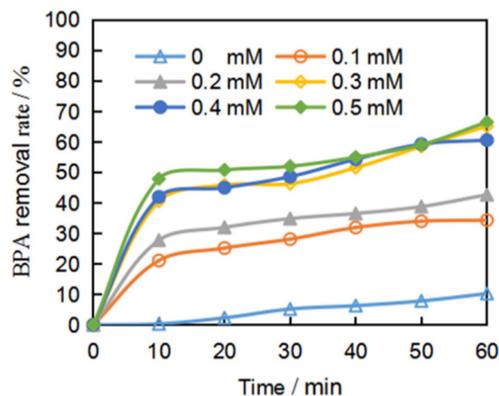
Figure 2. The effect of the initial PS concentration on BPA removal. $[BPA]_0 = 5$ mg L^{-1}, $[PS]_0 = 0$-0.5 mM, $[Fe_3O_4]_0 = 0.1$ g L^{-1}, $T_0 = 20 \pm 1$ °C, $pH_0 = 6.8 \pm 0.2$.

The effect of the initial BPA concentration

The concentration of the substrate is also an important factor determining the degradation efficiency. It can be seen from the Figure 3 that when the initial BPA concentration increased from 1 to 5 mg L^{-1}, after 60 min of reaction, the BPA removal rate dropped from 80.70 to 40.30%. When the initial concentration of BPA is 5 mg L^{-1}, the kinetic constant for BPA removal is 0.00942 min^{-1} ($\ln(C_t/C_0) = -0.00942t + 0.02804$), and the reaction is the slowest. When the initial concentration of BPA was 1 mg L^{-1}, the kinetic constant for BPA increased to 0.02466 min^{-1} ($\ln(C_t/C_0) = -0.02466t + 0.09686$), which was 2.6 times faster than the degradation rate of 5 mg L^{-1} BPA. As the amount of PS and Fe_3O_4 remained unchanged, the number of $SO_4^{\bullet-}$ generated did not increase, and the increase of BPA concentration resulted to a relative shortage of $SO_4^{\bullet-}$, which reduced the BPA removal rate. Therefore, in order to improve the degradation efficiency of BPA, the amount of oxidant and catalyst needs to be increased accordingly.

The effect of the initial pH

It is clear that the advanced oxidation reaction in which PS is activated by transition metals is heavily
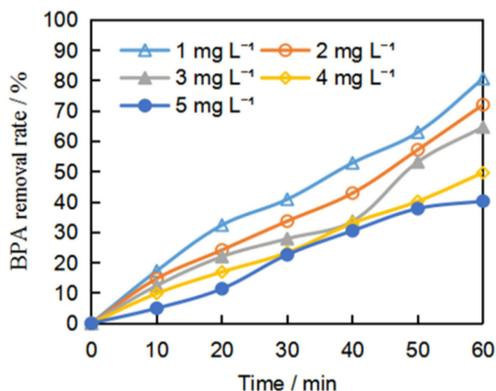
Figure 3. The effect of the initial BPA concentration on BPA removal. [BPA]$_0$ = 1-5 mg L^{-1}, [PS]$_0$ = 0.2 mM, [Fe$_3$O$_4$]$_0$ = 0.1 g L^{-1}, T$_0$ = 20 ± 1 °C, pH$_0$ = 6.8 ± 0.2.

dependent on solution pH. Therefore, we examined the BPA removal in Fe$_3$O$_4$/PS system at different pH of 3, 5, 7 and 9 (Figure 4). According to the BPA removal in descending order, the corresponding pH values were 5, 3, 7, 9, respectively. In other words, the pH value at the maximum BPA removal rate was 5, with the removal rate of 59.2%. Under acidic conditions of pH 3-5, the reaction proceed more efficiently due to the solubilization of the Fe^{II} on the surface of heterogeneous activator Fe$_3$O$_4$. Therefore, the homogeneous activation of Fe^{II} occurs more effectively for generating SO$_4$$^{•-}$ towards removing BPA under acidic conditions. However, under neutral or alkaline conditions, Fe^{II} can hydrolyze to produce the precipitant Fe(OH)$_2$ which forms a passivation layer on the surface of Fe$_3$O$_4$, which hinders the migration of Fe^{II} into water, and ultimately slows down the catalytic reaction. In addition, SO$_4$$^{•-}$ can react with H$_2$O and OH to produce •OH (equation 8) whose oxidizing power is less than SO$_4$$^{•-}$. These reasons resulted in the reduction of BPA oxidation performance under alkaline conditions. This finding was similar to the study of

Liu *et al.*[30] about treatment of landfill leachate biochemical effluent using Fe$_3$O$_4$/PS system.

$$OH^- + SO_4^{•-} \rightarrow •OH + SO_4^{2-} \qquad (8)$$

The effect of the reaction temperature

Temperature is a crucial parameter in the treatment of wastewater as it can affect the rate of chemical reactions. Some scholars have reported experiments that high temperature can activate PS.[31-33] We investigated the removal of BPA under four temperature conditions (20, 35, 50 and 70 °C) in Fe$_3$O$_4$/PS and only PS system. The experimental results with or without Fe$_3$O$_4$ appearing in PS system at different temperatures are shown in Figure 5. In Figure 5, the curve marked with blank is the BPA removal without Fe$_3$O$_4$ (only PS). When only PS was added to the system, the removal rate of BPA increased significantly with the temperature increasing. The highest removal rate occurred at 70 °C and the lowest removal rate occurred at 20 °C. When the temperature was 70 °C, the fastest kinetic constant for BPA removal was 0.00821 min^{-1} (ln(C$_t$/C$_0$) = −0.00821t + 0.01496), which was 2 times faster than the 20 °C rate of 0.00414 min^{-1} (ln(C$_t$/C$_0$) = −0.00414t + 0.00818). Since heat can activate PS to produce SO$_4$$^{•-}$ (equation 3), the increase in temperature was conducive to the degradation of BPA. When both PS and Fe$_3$O$_4$ were added to the system, the removal rate of BPA was significantly increased compared to the system with only PS. At 20 and 70 °C, the removal rate of BPA was 40.46 and 87.10% after 60 min, respectively. This showed high temperature and Fe$_3$O$_4$ have the ability to synergistically catalyze the degradation of BPA by PS. However, the higher the temperature, the more energy is consumed. The actual situation of sewage treatment

Figure 4. The effect of the initial pH concentration on BPA removal. [BPA]$_0$ = 5 mg L^{-1}, [PS]$_0$ = 0.2 mM, [Fe$_3$O$_4$]$_0$ = 0.1 g L^{-1}, T$_0$ = 20 ± 1 °C, pH$_0$ = 3-9.
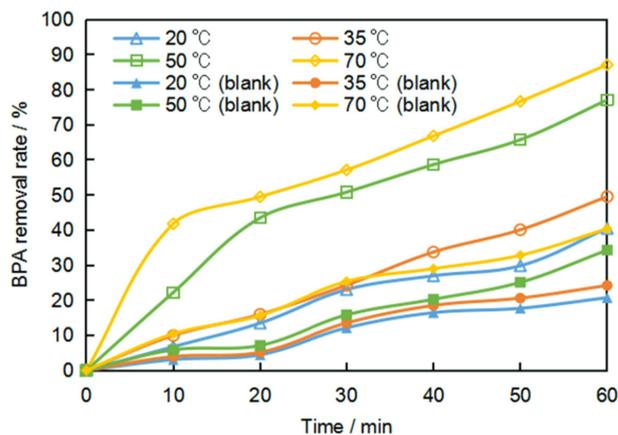
Figure 5. The effect of the reaction temperature on BPA removal. [BPA]$_0$ = 5 mg L^{-1}, [PS]$_0$ = 0.2 mM, [Fe$_3$O$_4$]$_0$ = 0 g L^{-1}, 0.1 g L^{-1}, T$_0$ = 20-70 °C, pH$_0$ = 6.8 ± 0.2.

should be considered to determine the best temperature from the perspective of energy saving. In addition, as the temperature increased from 20 to 70 °C, only adding Fe_3O_4 to the system, the BPA removal rate increased from 10.22 to 12.18% (data not shown). In other words, as the temperature increased, Fe_3O_4 alone cannot improve the efficiency of its adsorption of BPA.

The scavenging of the free radicals

MeOH and TBA are commonly used chemical scavengers to distinguish $SO_4^{\bullet-}$ and $\bullet OH$ as they react with free radicals with different rate constants. MeOH is an effective scavenger for $\bullet OH$ (reaction rate constant, $k = 9.7 \times 10^8$ M^{-1} s^{-1}) and $SO_4^{\bullet-}$ ($k = 1.1 \times 10^7$ M^{-1} s^{-1}), while TBA is an effective scavenger for $\bullet OH$ ($k = 6.0 \times 10^8$ M^{-1} s^{-1}) and not for $SO_4^{\bullet-}$ ($k = 9.1 \times 10^5$ M^{-1} s^{-1}). As observed in Figure 6, without adding the MeOH or TBA, 48.5% of BPA degradation rate was acquired within 60 min. The MeOH and TBA of 80 mM added separately to the system resulted in BPA removal to drop to 25.9 and 45.4%, respectively. As the concentration of MeOH and TBA increased to 800 mM, the degradation rate of BPA further decreased to 12.8 and 39.9%. The addition of MeOH had a more obvious effect on the decrease of BPA degradation rate. Therefore, it was inferred that the $SO_4^{\bullet-}$ generated in the reaction was the main free radical, followed by the $\bullet OH$.
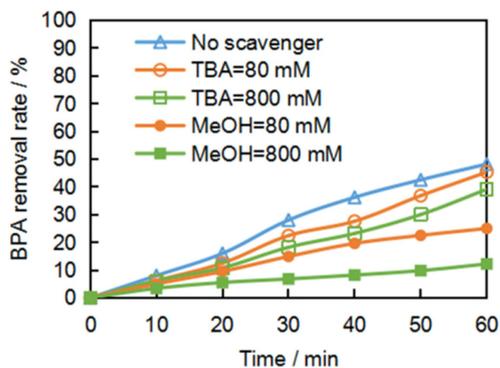
Figure 6. The effect of MeOH and TBA on BPA removal. $[BPA]_0 = 5$ mg L^{-1}, $[PS]_0 = 0.2$ mM, $[Fe_3O_4]_0 = 0.1$ g L^{-1}, $T_0 = 35 \pm 1$ °C, $pH_0 = 6.8 \pm 0.2$.

BPA degradation products and pathways

GC-MS was used to qualitatively analyze the intermediate product of BPA degradation by nano-Fe_3O_4 activated PS. The reaction conditions are as follows: $[BPA]_0 = 5$ mg L^{-1}, $[PS]_0 = 0.2$ mM, $[Fe_3O_4]_0 = 0.4$ g L^{-1}, $T_0 = 35 \pm 1$ °C, $pH_0 = 5.0$. The possible intermediate products of BPA degradation are shown in Table 3. The detected intermediate products were mainly aromatic compounds, including phenol, *p*-benzoquinone,

p-hydroquinone, 4-(2-hydroxypropan-2-yl) phenol, 4-isopropenylphenol, *p*-hydroxybenzene propanoic acid and 4-hydroxybenzoic acid. The possible degradation pathways of BPA are shown in Figure 7. The free radicals generated from nano-Fe_3O_4/PS system attacked the C–C bond between isopropyl and benzene rings of bisphenol A, forming 4-(2-hydroxypropan-2-yl)phenol and phenol.[34] 4-(2-Hydroxypropan-2-yl) phenol was gradually oxidized into 4-isopropenylphenol, *p*-hydroxyphenylpropionic acid, and 4-hydroxybenzoic acid.[35,36] Phenol was gradually oxidized into *p*-hydroquinone and *p*-benzoquinone. Then, all the aromatic compounds produced by two pathways were oxidized into small molecular compounds,[17,37] some of which will be mineralized into CO_2 and H_2O under the conditions set in Fe_3O_4/PS system.
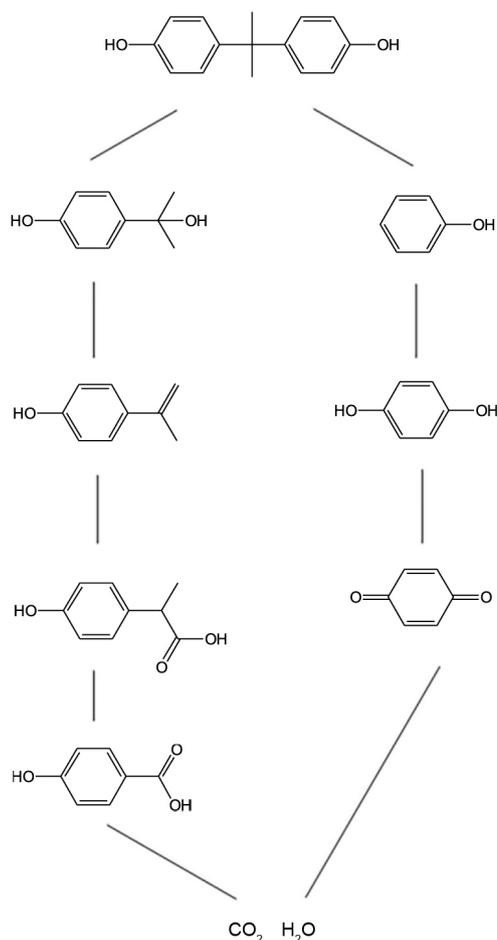
Figure 7. The possible degradation pathways of BPA.

Reusability of Fe_3O_4

In order to investigate the recyclability of Fe_3O_4, a magnet was used to separate Fe_3O_4 from the solution. After separation, the Fe_3O_4 was rinsed with deionized water, and dried indoors with natural ventilation for use in the next

Table 3. The possible intermediates of BPA degradation

Serial number	Chemical name	Molecular formula	Molecular weight / ($g\ mol^{-1}$)	Molecular structure
1	bisphenol A	$C_{15}H_{16}O_2$	228	
2	phenol	C_6H_6O	94	
3	*p*-hydroquinone	$C_6H_6O_2$	110	
4	*p*-benzoquinone	$C_6H_4O_2$	108	
5	4-(2-hydroxypropan-2-yl) phenol	$C_9H_{12}O_2$	152	
6	4-isopropenylphenol	$C_9H_{10}O$	134	
7	*p*-hydroxybenzene propanoic acid	$C_9H_{10}O_3$	166	
8	4-hydroxybenzoic acid	$C_7H_6O_3$	138	
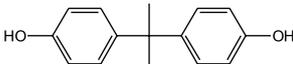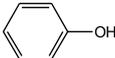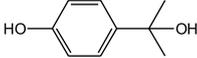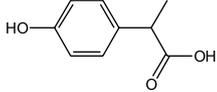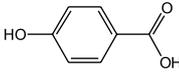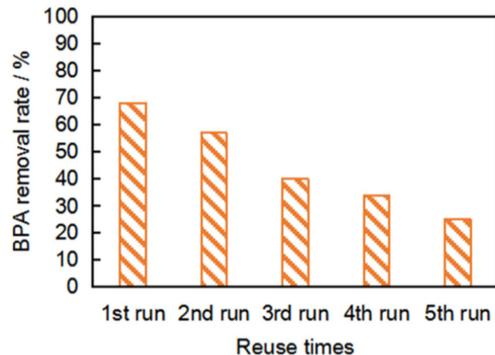
Figure 8. Reuse of Fe₃O₄ and BPA removal rate. $[BPA]_0 = 5\ mg\ L^{-1}$, $[PS]_0 = 0.2\ mM$, $[Fe_3O_4]_0 = 0.2\ g\ L^{-1}$, $T_0 = 35 \pm 1\ °C$, $pH_0 = 5 \pm 0.2$.

experiment. It can be seen from Figure 8 that the removal rate of BPA dropped from 68.0 to 26.9% after five cycles of Fe₃O₄. In the absence of Fe₃O₄, PS alone could remove about 20% of BPA, so it is believed that after five cycles of Fe₃O₄, the catalytic activity of Fe₃O₄ is already very low. It is speculated that the decrease in the activity of Fe₃O₄ is due to the fact that most of the Fe^{II} becomes Fe^{III} that cannot effectively activate PS.[38]

Conclusions

Fe₃O₄/PS performed well as a sulfate radical-based AOP process in degradation of endocrine disruptor BPA. The removal rate of BPA was related to Fe₃O₄ dose, PS concentration, BPA concentration, pH and temperature. The best BPA removal rate of 80.7% could be acquired under the selected conditions of $[BPA]_0 = 1\ mg\ L^{-1}$, $[PS]_0 = 0.2\ mM$, $[Fe_3O_4]_0 = 0.1\ g\ L^{-1}$, $T_0 = 20 \pm 1\ °C$, $pH_0 = 6.8 \pm 0.2$. The oxidation of BPA by Fe₃O₄/PS mainly relies on sulfate radicals generated during the reaction, and hydroxyl radicals play a minor role. The possible intermediates of BPA degradation were determined as phenol, *p*-benzoquinone, *p*-hydroquinone, 4-(2-hydroxypropan-2-yl) phenol, 4-isopropenylphenol, *p*-hydroxybenzene propanoic acid and 4-hydroxybenzoic acid. The performance of Fe₃O₄ was significantly reduced after five times of reuse.

Acknowledgments

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