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Degradation of Bisphenol A from aqueous solutions using Fe_3O_4 as a persulfate activator

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ABSTRACT

The present study investigated the degradation of bisphenol A (BPA) from aqueous solution using Fe_3O_4/persulfate process. The effects of pH (3, 5, 7 and 11), persulfate (PS) concentrations (1, 2, 5 and 10 mM), Fe_3O_4 magnetic nanoparticle doses (0.5, 1, 1.5 and 2 g/L), and contact time (5, 10, 20 and 30 min) on BPA removal were examined. The effect of all factors was significant ($p < 0.05$), and the optimal conditions were: pH value of 3, Fe_3O_4 dose of 2 g/L, BPA concentration of 0.1 mg/L, and contact time of 30 min. The BPA removal efficiency under optimal conditions was 98%. The results of this work indicate that Fe_3O_4 nanoparticles can be used as an effective catalyst and adsorbent for the removal of BPA from water and industrial wastewater. Analysis of by-products of BPA using GC-MS detected the presence of compounds with lower molecular weights (4-hydroxyacetophenone, 4-isopropenylphenol, benzoquinone and succinic acid) relative to BPA.

Keywords: Bisphenol A; Fe_3O_4; Persulfate; Advanced oxidation process; Wastewater treatment

1. Introduction

The increasing environmental concentration of phenolic endocrine disrupting chemicals such as Bisphenol A [2,2-bis(4-hdydroxyphenyl) propane] has raised considerable global attention. BPA is a carbon-based synthetic compound, which has broad industrial applications in manufacturing flame retardants, pesticides, antioxidants, epoxy resins and polycarbonate plastics [2,3]. The polycarbonate plastics with high stability and elasticity are extensively used for the production of plastic containers, bottles and water supply pipes. The primary sources of BPA to water system are the effluents from industries manufacturing epoxy and plastics, and leaching from the products containing this synthetic chemical. Annual discharge of about 1 million pounds of BPA is a serious health and environmental concern [4,5]. BPA can pose severe health consequences including disruption of hormone function, impairment of reproductive system, deformities of the genetic tract and breast cancer. Such adverse health effects can occur at a very low dose because of its estrogenic activity [3]. However, the Environmental Protection Agency (EPA) has announced the standard BPA concentration in drinking water as less than 1 ppb [6]. BPA also causes environmental health problems, which are intensified by physicochemical properties of this compound including low solubility and high hydrophobicity [7]. These properties lead to its low biodegradability and accumulation in living organisms [8]. Therefore, its removal from polluted water system is necessary [7].

Various physical, chemical and biological methods have been proposed to remove BPA from aqueous solutions. These methods include adsorption, biodegradation,

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filtration and sonolysis but most of these methods have drawbacks and are not suitable for low concentrations and require a long time and high cost [9,10]. Among different approaches, advanced oxidation processes (AOPs) are commonly used as they are simple, rapid and economic [11]. AOPs can be done with various oxidants such as Ozone, hydrogen peroxide (Fenton process) or persulfate (Fenton-like process) for degradation of pollutants from the environment. Utilization of hydroxyl radical ($^{\bullet}OH$) based AOPs are decreasing due to corrosive properties of peroxides, formed $^{\bullet}OH$ and ozone instability. Recently, sulfate radical ($SO_4^{-\bullet}$) based AOPs has been developed because of their oxidants stability, longer lifetime and high reactivity [12]. Sulfate radical has a high redox potential (2.5–3.1 V). Compared to other oxidants, PS can increase the reaction time between generated sulfate radicals and pollutants and hence can complete oxidation reaction [13].

To generate $SO_4^{-\bullet}$ radicals, PS can be activated using various processes such as thermal, UV, ultrasound, electro chemistry, and metal ions. Among these activators, nanostructured Fe_3O_4 received more attention for their strong magnetic properties and low toxicity [14]. A number of functionalized Fe_3O_4 nanoparticles (NPs) have been applied, and immobilization of catalysts on silica-coated iron oxide nanoparticles have been reported [15]. Fe_3O_4 nano-magnetic (NM) particles have been extensively used as adsorbents and offer advantages such as high surface area and strong magnetic properties. Fe_3O_4 is a rich source of dissolved iron ions and can increase the generation of oxidant ions [14]. The reaction of Fe^{n+} and PS during activation shown in Eq. (1) [12].

$$S_2O_8^{\ 2-} + Fe^{n+} \rightarrow SO_4^{\ -\bullet} + Fe^{n+(n+1)+} + SO_4^{\ 2-} \tag{1}$$

The present study investigated the effectiveness of PS activated with Fe_3O_4 with regard to the removal of BPA from water. The effects of the operating parameters including pH, catalyst dose, contact time, concentrations of PS and BPA were evaluated systematically.

2. Materials and methods

2.1. Materials

Fe_3O_4 Nanoparticles (20–30 nm average particle size, 98 % purity, ≥ 40 $m^2 \cdot g^{-1}$ specific surface area, stock #2650TR, CAS #1317-61-9, and lot #2650-031010) of analytical grade were purchased from the Sigma Co. Ltd., USA. The Fe_3O_4 particles were crystalline. The particle size and shape of iron oxide was determined using transmission electron microscopy (Philips; CM10) at 100 kV.

BPA of 99% purity was obtained from Sigma-Aldrich (USA). Methanol (high purity for GC analysis) and HCl 96% (wt) were purchased from Merck (Germany). NaOH (99% purity; Mallinckrodt Chemical; USA) was used to adjust the initial pH of the aqueous solution. Solid-phase extraction (SPE) cartridges (3 ml/500 mg) were purchased from Macherey-Nagel (Germany).

A stock solution was prepared by adding 100 mg of BPA into deionized water, which was stored in a refrigerator until use. Before each experiment, the pH of the aqueous solution was adjusted using 0.1 M HCl or 0.1 M NaOH. Other diluted solutions were prepared from this stock solution.

2.2. Experimental condition

This study was based on the one-factor-at-a-time method. Several experiments were conducted to evaluate the effect of the parameters by changing one variable while holding the other parameters constant. Batch experiments were conducted using 100 ml brown bottles to which different doses of catalyst (0.5, 1, 1.5 and 2 g/L) were added at an initial BPA concentration (C_0) of 0.1–10 mg/L. The pH was varied from 3 to 11. The glass bottles from the batch experiments were placed on a shaker (Orbital Shaker, model OS625) and stirred at 300 rpm at room temperature for different lengths of time (5, 10, 20, 30 min). Sodium persulfate solution was prepared freshly and before starting the tests at the initial concentrations of 1–10 mM.

After degradation, the solution samples were allowed to settle for 1 min. The Fe_3O_4 was then separated from the suspensions using a magnet. The BPA concentration in the liquid phase was determined using gas chromatography-flame ionization detection (GC-FID) method (6890N model, HP-PLOT Al_2O_3, USA) with a UV detector at 280 nm. The degradation byproducts of BPA were detected using GC-MS (6890N-5973 model, HP-5ms, USA).

All experiments were repeated twice. Blank experiments without the addition of catalyst and PS were also conducted to ensure that the decrease in BPA concentration was not caused by adsorption onto the wall of the glass bottle or volatilization. The solution pH was measured at the beginning of each experiment using a pH meter (Cyberscan H1500; Thermo Fisher Scientific; The Netherlands). The level of BPA in the aqueous solution was determined using standard curves (R^2 = 0.99) by injecting known amounts of standard solution (10, 4, 1, 0.1 mg/L) and measuring the areas under the peaks. The amount of BPA removed (q_e; mg/g), and the percentage of removal (R) was calculated as follows:

$$R = \left(\frac{C_o - C_t}{C_o}\right) \times 100 \tag{2}$$

$$q_e = \frac{(C_o - C_t) \times v}{m} \tag{3}$$

where C_o and C_t (mg/L) are the BPA concentrations at the start and end of each run, respectively; V (L) is the initial solution volume; and m (g) is the adsorbent weight.

2.3. Analysis

Samples were extracted using an SPE C18 cartridge. The SPE cartridges were initially conditioned with 5 ml methanol and 10 ml milli-Q water. Then samples were passed through the wet cartridges at a flow rate of 20 ml/min. First, 2 ml of methanol was passed through the cartridge. Then, sample was evaporated to dryness under gentle nitrogen gas, 100 µl of MTBE was added to the tube, and 3 µl was injected into the GC system (GC-FID 5975B; Agilent Technologies; USA). An HP-5ms fused silica column (30 m × 0.25 mm ID, 0.25 μm) was employed with helium (99.995% purity) as the carrier gas at a flow rate of 1 ml/ min. The injector temperature was set at 250°C, and the sample was injected in splitless mode. The column temperature was set at 100°C for 2 min, increased to 230°C at a rate of 10°C/min and then to 280°C at 5°C/min for a total runtime of 25 min.

GC-MS was used to detect BPA byproducts. Briefly, oxidation byproducts were extracted with dichromate, then dehydrated with anhydrous sodium sulfate and concentrated using a stream of N_2 gas. At GC, the temperature was set at 80°C for 1 min and then at 300°C for 1 min. The mass spectra were recorded with 70 eV electron impact (EI) mode at an ion source temperature of 230°C. The MS detector was operated in a full scan mode (m/z 50–500) for qualitative analysis. The detected peaks were identified according to the library of Agilent Technologies and NIST data. Design Expert 6 (Stat-Ease; USA) was used to ascertain the individual effects of pH, magnetic NPs dose, the initial concentration of BPA, and contact time on the removal of BPA.

3. Results and discussion

3.1. Characterization of Fe_3O_4 nanoparticles

Transmission electron microscopy (TEM) was used to determine the size and morphology of magnetic NPs. Fig. 1 shows that Fe_3O_4 NPs had the size of about 50 nm and they were spherical and interconnected like beads chain. This homogeneous and non-discrete structure may improve the removal efficiency of BPA.

3.2. Effect of pH on the removal of BPA

Studies have shown that the efficiency of the AOPs based on Fe_3O_4/PS system depends strongly on the solution pH. Therefore, we investigated the decomposition of BPA by Fe_3O_4/PS system at adjusted pH values of 3, 5, 7 and 11 (Fig. 2). The highest percentage of BPA (~ 98%) removed at pH 3 and the removal percentage decreased with increasing pH, which indicates that acidic conditions were appropriate for BPA degradation. This reduction in BPA removal efficiency with an increase of pH is possibly due to the transformation of easily oxidizing Fe^{2+} to Fe^{3+} by air under progressive alkaline condition [10]. Acidic condition is favorable for Fe^{2+} induced activation of persulfate to $SO_4^{-\bullet}$, which has a high potential of BPA degradation. While in alkaline conditions, BPA oxidation is reduced due to the presence of $OH^{\bullet}$ as main radical, but the lack of $SO_4^{-\bullet}$ [16]. In other words, under alkaline conditions, hydroxyl ions (OH^-) lead to the rapid formation and precipitation of Fe^{3+} as Fe^{3+} hydroxide [$Fe(OH)_3$] [9]. Therefore, the deficiency of Fe^{2+} in the system lowers the formation of sulfate radicals from PS activation and ultimately reduces BPA removal efficiency. The pH of a solution can change the surface charge of the catalyst, the degree of ionization of its molecules, and the extent of dissociation of functional groups on the active sites of the adsorbent. Zhu et al. [11] showed an increased release of Fe^{2+} from Fe_3O_4 under acidic conditions, leading to a formation of $SO_4^{-\bullet}$ via reacting to PS. Kang et al. [12] in their study on bisphenol removal also reported that the pH of the solution influences the activation of PS with Fe^{2+}. They explained that most activation methods operate under acidic or neutral conditions. Thakur et al. [16] recorded that the reduction of BPA oxidation in alkaline conditions was due to the decrease in the redox potential of OH/H_2O.

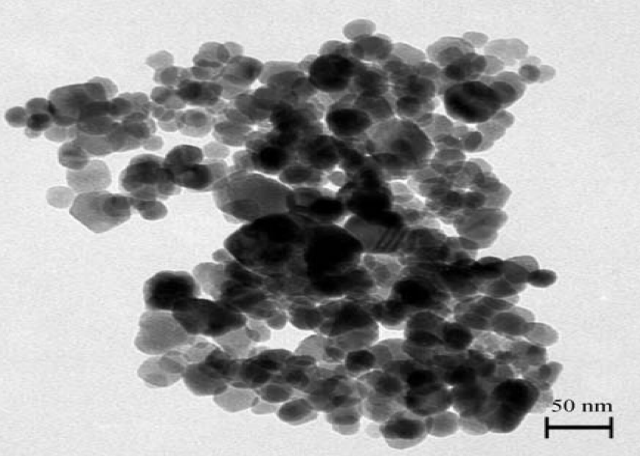


Fig. 1. TEM monograph of Fe_3O_4

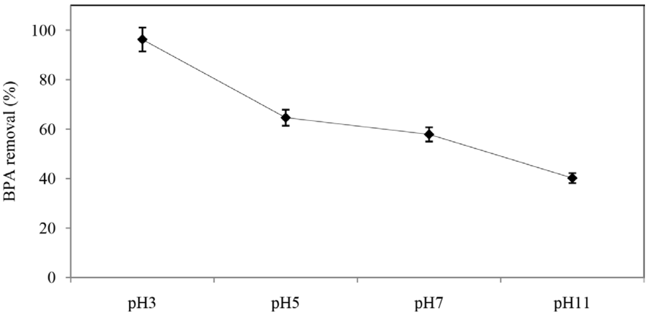


Fig. 2. Effect of pH on the BPA removal for experimental conditions – [BPA] = 1 mg/L, [Fe_3O_4 = 1.5 g/L, [PS] = 5 mM, reaction time = 30 min).

3.3. Effect of time on the removal of BPA

Fig. 3 shows the effect of time on BPA removal by Fe_3O_4/PS at optimum pH 3. The adsorption and degrada-

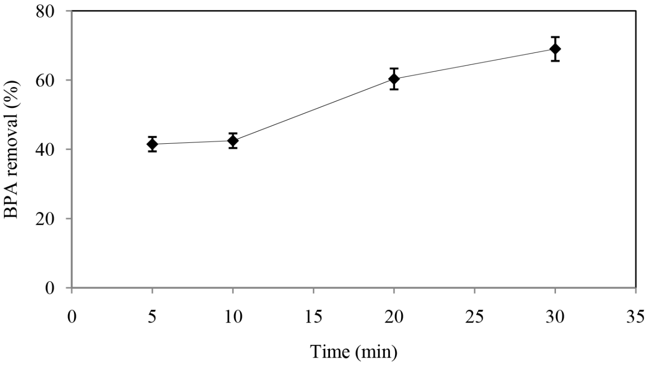


Fig. 3. Effect of reaction time on the BPA removal for experimental conditions: [BPA] = 1 mg/l, [Fe_3O_4 = 1.5 g/L, [PS] = 5 mM, reaction pH = 3.

tion of BPA increased continuously over time. The maximum removal of BPA was 68.5% at 30 min in the system. Such removal of BPA with time is possibly due to the combined effect of attachment of BPA at the sorbent surface and degradation of BPA by $SO_4^{-\bullet}$ radicals generated by Fe_3O_4-induced activation of PS over time [14]. The concentration of released iron ions in the aquatic solution is a function of reaction time. It has been reported that Fe^{2+} slowly releases in solution and hence the initial low removal efficiency is likely due to lack of iron ions at initial times [17].

3.4. Comparison of the effects of PS, Fe_3O_4 and Fe_3O_4/PS on the removal of BPA

In order to evaluate the performance of different systems in the BPA removal, separate experiments (only 5 mM PS without Fe_3O_4, only 1 g/L Fe_3O_4 without PS, and both 5 mM PS and 1 g/L Fe_3O_4) were performed at pH 3.0 with an initial BPA concentration of 1 mg/L. PS or Fe_3O_4 alone has no significant effect on BPA removal, but their cumulative effect (Fe_3O_4 + PS) is significant (Fig. 4). The removal of BPA in the systems with Fe_3O_4 NPs or PS alone was ~ 27% and ~10%, respectively after 30 min of experimental duration. BPA removal by Fe_3O_4 NPs can be attributed to its adsorption on the active sites of NPs surface due to opposite charges between the sorbent and the benzene ring. Minor removal of BPA (~10%) in presence of solely PS suggests minimal decomposition of PS to $SO_4^{-\bullet}$ in the absence of an activator. In contrast, removal of phenol in the compound system (Fe_3O_4 + PS) increased significantly (~80%) due to the activation of PS by Fe^{2+} [12–15]. This indicates that the BPA removal directly depends on the amount of the $SO_4^{-\bullet}$ radicals generated by the catalytic break drown of PS [18].

3.5. Effect of PS concentration and catalyst dose on the removal of BPA

To examine the effect of PS concentration, four individual experiments with PS concentrations of 1, 2, 5 and 10 mM were performed at pH 3 over 30 min reaction period in a system with fixed initial BPA concentration of 1 mg/L and Fe_3O_4 of 1.5 g/L (Fig. 5a). Increase in solution PS concentration has a positive impact on BPA degradation (Fig. 5a) due to increased supply of $SO_4^{-\bullet}$ in the system. However, the efficiency of BPA degradation over 30 min of reaction has significantly increased when PS concentration increased from 1 mM (~20%) to 5 mM (~75%) and further increase of PS concentration to 10 mM (~80%) has little effect (only ~10% increases for 5 mM PS concentration increase) on the removal efficiency. Diao et al. [14] reported that the self-sufficiency of $SO_4^{-\bullet}$ produced at high concentrations of PS could cause a slight change in the removal efficiency. At high concentrations of PS, there is probably a strong competition between BPA and PS for the available $SO_4^{-\bullet}$ and consumption of $SO_4^{-\bullet}$ by PS [Eq. (4)] may reduce BPA removal efficiency.

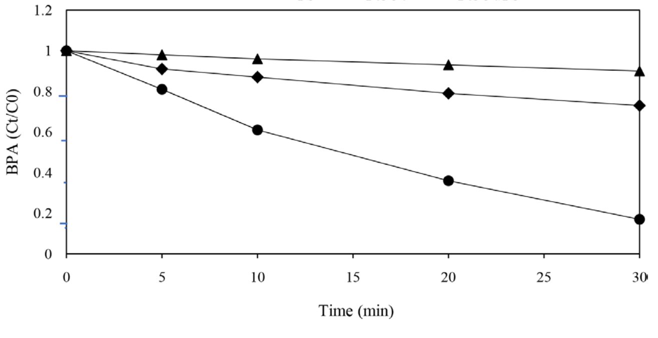


Fig. 4. Removal of BPA in three different systems including (1) PS (2) Fe_3O_4 and (3) PS and Fe_3O_4. Conditions: BPA= 1 mg/L, PS= 5 mM, Fe_3O_4= 1.5 g/L, pH = 3)

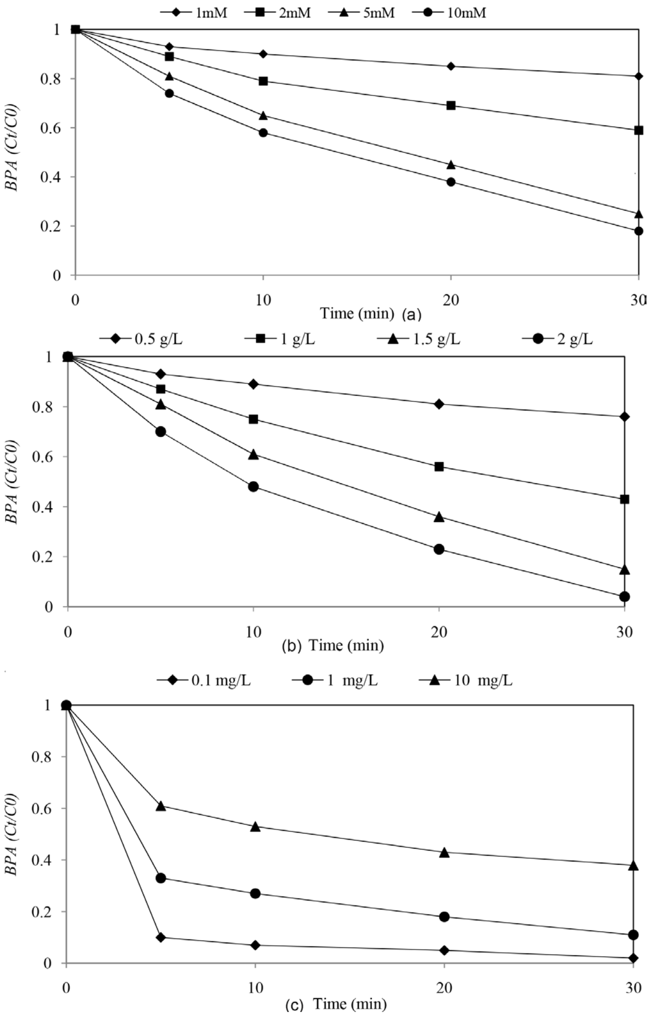


Fig. 5. The effect of different factors on BPA degradation: (a) PS concentration (b) Fe_3O_4 dose (c) BPA concentration.

$$SO_4^{-\bullet} + S_2O_8^{2-} \rightarrow SO_4^{2-} + S_2O_8^{-\bullet} \tag{4}$$

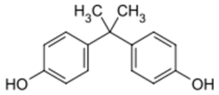
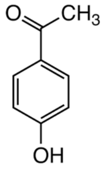
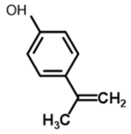
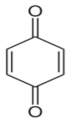
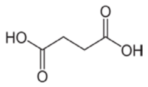
To evaluate the effect of different doses (0.5, 1.0, 1.5 and 2.0 g/L) of Fe_3O_4 NPs on BPA removal efficiency at pH 3 over 30 min reaction period, four separate experiments with fixed initial concentrations of BPA and PS at 1 mg/L and 5 mM, respectively, were performed (Fig. 5b). The BPA removal efficiency increased with increasing Fe_3O_4 dose due to the production of increased Fe^{2+} in an aqueous solution that acts as persulfate activator to generate more sulfate radicals (Fig. 5b). In addition to being used as a catalyst for PS, Fe_3O_4 NPs also can act as a sorbent in the system. The presence of high surface area in NPs results in absorption of pollutants in their surface active sites. Therefore, increasing dose of Fe_3O_4 NPs provides higher surfaces for BPA uptake. On the other hand, Fe_3O_4 NPs produces iron ions in aqueous solution that act as a persulfate activator. Therefore, at higher NPs dosages, increasing amount of Fe ions can break up persulfate to produce more $SO_4^{-\bullet}$ radicals [17]. Zhang et al. [15] showed that an increase in Fe_3O_4 particle dose slowly increased the removal efficiency of phenolic and aniline compounds. Amin et al. [19] showed that the rapid removal of benzene by magnetic nanoparticles occurred through adsorption on the external surface and micro-pores. They also found that benzene removal efficiency increased as the nanoparticle dose increased. The results of the present study showed statistical differences ($p < 0.05$) between the different doses of nanoparticle for BPA removal ($p < 0.05$).

The removal efficiency of variable initial BPA concentrations (0.1, 1, 10 mg/L) at pH 3 in a system with 1.5 g/L Fe_3O_4 and 5 mM PS over 30 min reaction time is shown in Fig. 5c. The degradation of BPA reduced from 98% to 62% when the initial BPA concentration increased from 0.1 to 10 mg/L. This can be attributed to the reduction of active sites (which are constant for 1.5 g/L Fe_3O_4) on the Fe_3O_4 NPs surface, as well as the deficiency of $SO_4^{-\bullet}$ to degrade additional BPA. This also indicates that PS concentration and Fe_3O_4 NPs dose may need to increase to maintain sufficient supply of sulfate radicals and Fe_3O_4 if the concentration of BPA in waste solution increases [20–22].

3.6. BPA degraded by-products and its degradation mechanism

Identification of by-products during the degradation of BPA (under optimal conditions) in the Fe_3O_4/PS system after 20 min and 30 min was performed using GC-MS. The results of the BPA removal efficiency indicate that a large amount of BPA was decomposed to intermediate. After degradation, four main by-products (4-isopropylenecatechol, 4-hydroxyacetophenone, benzoquinone, and succinic acid) were detected (Table 1). In comparison to BPA, the molecular weight of by-products decreased over time, indicating the effectiveness of Fe_3O_4/PS system on the degradation of BPA. During the reaction, $SO_4^{-\bullet}$ radical led to the breakdown of aromatic rings and created aliphatic compounds (i.e., succinic acid) with simpler structure [23–25]. The breakdown of the aromatic ring of BPA and its complete mineralization is time-dependent [26]. Guo et al. [20] reported that with an increase in reaction time of up to 120 min, complete mineralization occurs and the BPA is completely converted to CO_2 and H_2O. The initial by-products of BPA degradation may be more toxic than BPA, but sequential oxidation reactions eliminate dangerous intermediates and reduce their toxicity [26]. The BPA degradation process introduced by Fe_3O_4/PS can be described as follows [27]. One of the mechanisms for BPA removal is its absorption on the surface of the magnetic nanoparticles and their deposition. Another mechanism that causes BPA degradation is the oxidation of NPs under acidic conditions, which leads to the production of Fe ions. Some of these released ions react with dissolved oxygen in the water and produce reactive radicals such as $OH^{\bullet}$ and $H_2O_2^{\bullet}$ that can destroy BPA. Another part of iron ions decomposes persulfate to $SO_4^{-\bullet}$. Thus BPA destruction

Table 1
BPA by products formed in Fe_3O_4/PS system and detected using GC-MS

Reaction time (min)	Intermediate products	Molecular formula	Structural formula	Molar mass
0	BPA	$C_{15}H_{16}O_2$		228
20	4-hydroxyacetophenone	$C_8H_8O_2$		136
20	4-isopropenylphenol	$C_9H_{10}O$		134
30	benzoquinone	$C_6H_4O_2$		108
30	succinic acid	$C_4H_6O_4$		118

begins with $SO_4^{-\bullet}$ and $OH^\bullet$ radicals attack [15,20]. In the persulfate based AOPs, $SO_4^{-\bullet}$ attacks the BPA and breaks C=C bond. Bisphenol A is converted into a lower molecular weight compound by transferring an electron from its ring structure to $SO_4^{-\bullet}$. This new compound has a cationic structure and can react with H_2O to form more stable crystalline compounds. Chain reactions during the oxidation process lead to the breakdown of more aromatic rings to less toxic aliphatic compounds. The succinic acid is one of the compounds that formed from the conversion of the ring chain into the straight chain, was detected in our samples [27,28].

4. Conclusions

In this study, utilizes advanced oxidation process to generate sulfate radicals through activation of PS by Fe_3O_4 NPs for degradation of BPA. Effect of various parameters such as pH, PS concentration, Fe_3O_4 NPs dose, and reaction time was investigated to optimize the removal of BPA. The BPA removal efficiency decreased with increasing pH, and optimal BPA removal was achieved at initial pH 3. The BPA degradation percentage increased significantly when PS concentration and Fe_3O_4 dose increased from 1 to 5 mM and 0.5 to 1.5 g/L, respectively and subsequent increase of these two parameters to 10 mM and 2 g/L, respectively, resulted in minor changes in removal efficiency. Either PS or Fe_3O_4 alone showed minor contribution on BPA degradation. An investigation of by-products derived from degradation of BPA in the Fe_3O_4/PS system confirms the presence of compounds with lower molecular weight and simpler structure (e.g., succinic acid).

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