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# Simultaneous removal of bisphenol A and phosphate in zero-valent iron activated persulfate oxidation process

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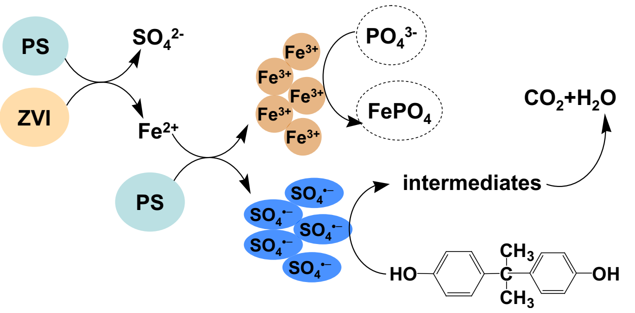
## HIGHLIGHTS

- Simultaneous removal of BPA and phosphate was achieved in ZVI/PS process.
- Increasing the concentration of ZVI or PS accelerated the removal of BPA.
- Sulfate radical attacked BPA through electrons transfer and hydrogen abstraction.
- NOM showed inhibitory effect on BPA removal but not phosphate.

## GRAPHICAL ABSTRACT



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## ABSTRACT

In this study, the removal of bisphenol A (BPA) and phosphate in zero-valent iron activated persulfate (ZVI/PS) oxidation process was investigated. Activation of PS by ZVI mainly produces strong oxidizing sulfate radicals ($SO_4^{\bullet-}$) which can efficiently degrade organic contaminants. ZVI is ultimately transformed to ferric iron ($Fe^{3+}$) which works as a coagulant to remove phosphate. It was demonstrated that BPA and phosphate could be simultaneously removed in this system. The oxidation of BPA in ZVI/PS process followed pseudo-first-order kinetics. The reaction rate increased with increased PS and ZVI dosage. Eight transformation products were identified using gas chromatography–mass spectrometry (GC–MS) technique. $SO_4^{\bullet-}$-induced oxidative transformation of BPA included electron transfer and hydrogen abstraction mechanisms. Carbonate exhibited no obvious influence on the removal both of phosphate and BPA. Natural organic matter (NOM) showed inhibitory effect on BPA degradation but had no appreciable negative effect on phosphate removal. Simultaneous removal of BPA and phosphate was also observed in wastewater treatment plant effluent with relatively high efficiency. The results of this work indicate that ZVI/PS process could serve as a novel treatment technique for removal of trance organic contaminants and phosphate simultaneously.

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*Abbreviations:* AOPs, advanced oxidation processes; BOD, biological oxygen demand; BPA, bisphenol A; COD, chemical oxygen demand; DCM, dichloromethane; DNPH, 2,4-dinitrophenylhydrazine; DNT, 2,4-dinitrotoluene; EDC, endocrine disrupting chemical; EI, electron impact; GC–MS, gas chromatography–mass spectrometry; HA, humic acid; HPLC, high performance liquid chromatography; IPP, isopropenylphenol; MeOH, methanol; NOM, natural organic matter; PES, polyethersulfone; Ph, phenol; PhO, phenoxy; PhxBPA, phenoxyl BPA; PMS, peroxymonosulfate; PS, persulfate; TFAA, trifluoroacetic anhydride; TOC, total organic carbon; WWTP, wastewater treatment plant; ZVI, zero-valent iron.

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## 1. Introduction

Bisphenol A (BPA) is widely used in the synthesis of polymers including phenol resins, epoxy resins, polycarbonates, polyesters and polyacrylates [1]. BPA-based polymers are important raw materials to manufacture various daily consumer products such as water bottles, coatings of food containers, sport equipments, etc. BPA can be leached from these products and end up in sewage. Because it can interfere with the endocrine system by disturbing the synthesis, release, transport and metabolism of hormones, BPA is recognized as an endocrine disrupting chemical (EDC) [2]. BPA can cause adverse health effects such as liver damage, estrogenic potency and thyroid hormone disruption to human and animals [3,4]. Thus, the presence of BPA in the environment has raised great concern to the public and regulatory agencies.

Conventional municipal water treatment includes primary, secondary and tertiary treatment processes. Primary treatment is basically a physical process to separate insoluble particles. Secondary treatment relies on aerobic sludge process to remove biological oxygen demand (BOD). Tertiary treatment process is designed to remove nutrients such as nitrogen and phosphate. In principle, conventional municipal water treatment processes are not designed for the removal of hydrophilic micropollutants such as EDCs [5–8]. Previous studies have demonstrated that BPA was poorly removed in conventional wastewater treatment processes. Its half-life time in aerobic sludge system was reported from days to weeks [9]. As a result, BPA is discharged to the environment with wastewater treatment plant effluents in a continuous manner. Removal of trace BPA contamination has become an emerging challenge to municipal water treatment industry. It should be noted that many water treatment plants, especially in rural areas of China, are only equipped with primary and secondary treatment processes. Tertiary treatment process is in fact not popular due to the shortage of management capability and capital investment. Consequently, nutrients are poorly removed in the absence of tertiary treatment process. On the other hand, discharge of nutrients has caused serious eutrophication of natural water bodies. In China, phosphate is generally the limiting nutrient for algae growth in fresh waters [10,11]. Thus, it is of key importance to control phosphate in wastewater.

In recent years, sulfate radical ($SO_4^{\cdot-}$) based advanced oxidation processes (SR-AOPs) were found to be effective for decomposition of refractory organic contaminants in contaminated soils and ground waters [12–15]. $SO_4^{\cdot-}$ has a standard redox potential of 2.5–3.1 V (depending on pH) [16,17], making it one of the strongest oxidants in nature. It reacts with organic compounds primarily through electron transfer mechanism with a second-order rate constant of $10^6$–$10^9\ M^{-1}\ s^{-1}$ [17]. $SO_4^{\cdot-}$ can be *in situ* generated by activating persulfate (PS) or peroxymonosulfate (PMS) by UV [18–20], heat [21–24], transit metals ($Co^{2+}$, $Fe^{2+}$, $Ag^{+}$) [25–27], or base [28,29]. Among the activation methods for $SO_4^{\cdot-}$ generation, transient metal activation has the advantage of high efficiency and low energy demand [16,30]. Of a variety of transient metals that can activate PS, iron is of particular interest due to its nontoxic nature and abundance. PS can be effectively activated by $Fe^{2+}$ to generate $SO_4^{\cdot-}$ [16,30]. The $Fe^{2+}$ activated PS reaction requires activation energy of 12 kcal $mol^{-1}$, which is significantly lower than the value of 33.5 kcal $mol^{-1}$ required for thermal rupture of the O—O bond [31]. Reactions involving in $Fe^{2+}$/PS process are illustrated in Eqs. (1) and (2).

$$S_2O_8^{2-} + Fe^{2+} \rightarrow Fe^{3+} + SO_4^{\cdot-} + SO_4^{2-} \tag{1}$$

$$SO_4^{\cdot-} + Fe^{2+} \rightarrow Fe^{3+} + SO_4^{2-} \tag{2}$$

$$Fe^0 + H_2O + 0.5O_2 \rightarrow Fe^{2+} + 2OH^- \quad (oxicconditions) \tag{3}$$

$$Fe^0 + 2H_2O \rightarrow Fe^{2+} + 2OH^- + H_2 \quad (anoxicconditions) \tag{4}$$

$$S_2O_8^{2-} + Fe^0 \rightarrow Fe^{2+} + 2SO_4^{2-} \tag{5}$$

$$Fe^0 + 2Fe^{3+} \rightarrow 3Fe^{2+} \tag{6}$$

However, some intrinsic drawbacks of $Fe^{2+}$/PS system may restrict its practical application. For example, $Fe^{2+}$/PS system can only maintain high efficiency at acidic conditions [16]. In addition, $SO_4^{\cdot-}$ can be consumed by reacting with excessive $Fe^{2+}$ in water (Eq. (2)), which results in reduced degradation efficiency of target contaminants [32].

Zero-valent iron (ZVI) can serve as an alternative source of $Fe^{2+}$. In ZVI/PS system, $Fe^{2+}$ is produced by ZVI corrosion under oxic/anoxic condition and/or oxidation by PS (Eqs. (3)–(5)) [33–36]. Unlike homogeneous $Fe^{2+}$ activation, $Fe^{2+}$ is gradually released into the aqueous solution in ZVI/PS system. In this way, accumulation of excessive $Fe^{2+}$ and the subsequent quenching of $SO_4^{\cdot-}$ (Eq. (2)) can be minimized [33–36]. In addition, $Fe^{2+}$ can be regenerated by recycling $Fe^{3+}$ at the surface of ZVI through Eq. (6). Thus, utilization efficiency of PS is greatly improved [33–36]. These advantages of ZVI/PS process have been well demonstrated in previous studies. For example, Oh et al. found that the degradation process of 2,4-dinitrotoluene (DNT) in $Fe^{2+}$/PS system lasted only for a short period and only 20% of the DNT was removed because of the consumption of $SO_4^{\cdot-}$ by reacting with excessive $Fe^{2+}$ [36]. In comparison, the removal of DNT proceeded for a longer time and approximately 90% of the DNT was eliminated in ZVI/PS system because $Fe^{2+}$ was gradually released [36].

Degradation of BPA in $SO_4^{\cdot-}$-based oxidation processes has been studied previously [37–42], and examples include UV/PMS, ultrasound/PS, heat/PS, and $Co^{2+}$/PMS processes. Table S1 in the Supplementary data summarizes the optimum removal rates and kinetics of BPA from these studies [37–42]. However, limited information is available on the removal efficiency of BPA by ZVI/PS process. In the present study, the feasibility of simultaneous removal of BPA and phosphate by ZVI activated PS oxidation (ZVI/PS) was investigated. In this process, BPA is destructed by $SO_4^{\cdot-}$. Meanwhile, in the presence of excess PS, ZVI is oxidized to form ferric iron ($Fe^{3+}$) ultimately, which can potentially serve as a coagulant to remove phosphate. This technique can be applied as an advanced treatment process to remove emerging organic contaminants and phosphate residues escaped from conventional water treatment processes.

## 2. Materials and methods

### 2.1. Chemicals and materials

Zero valent iron (ZVI, 99.5% purity, particle size smaller than 150 μm), sodium persulfate ($Na_2S_2O_8$, ⩾98%), potassium dihydrogen phosphate ($KH_2PO_4$, ⩾99.5%), trifluoroacetic anhydride (TFAA, 99%), 2,4-dinitrophenylhydrazine (DNPH, 98%) were obtained from Aladdin Chemistry Co., Ltd. (Shanghai, China). HPLC grade methanol (MeOH) and dichloromethane (DCM) were purchased from Tedia (Fairfield, OH). BPA ($C_{15}H_{16}O_2$, 99%) and Natural organic matter (NOM) was purchased from International Humic Substance Society. Other reagents were at least of analytical grade and used as received. All the stock solutions were prepared by dissolving the reagents in Milli-Q water (>18 MΩ cm) prepared from a Millipore system (Bedford, USA) and used within a week. Total organic carbon (TOC) of the NOM stock solution was determined using a TOC-5050A analyzer (Shimadzu, Japan). Solution pH was measured by an E-201-C combined glass electrode (Leici, Shanghai) connected to a PHS-3E microprocessor pH/mV meter