Activated persulfate by iron-based materials used for refractory organics degradation: a review

Yanjiao Gao, Pascale Champagne, David Blair, Ouwen He and Tiehong Song

ABSTRACT

Recently, the advanced oxidation processes (AOPs) based on sulfate radicals (SRs) for organics degradation have become the focus of water treatment research as the oxidation ability of SRs are higher than that of hydroxyl radicals (HRs). Since the AOP-SRs can effectively mineralize organics into carbon dioxide and water under the optimized operating conditions, they are used in the degradation of refractory organics such as dyes, pesticides, pharmaceuticals, and industrial additives. SRs can be produced by activating persulfate (PS) with ultraviolet, heat, ultrasound, microwave, transition metals, and carbon. The activation of PS in iron-based transition metals is widely studied because iron is an environmentally friendly and inexpensive material. This article reviews the mechanism and application of several iron-based materials, including ferrous iron (Fe^{2+}), ferric iron (Fe^{3+}), zero-valent iron (Fe^0), nano-sized zero-valent iron (nFe^0), materials-supported nFe^0, and iron-containing compounds for PS activation to degrade refractory organics. In addition, the current challenges and perspectives of the practical application of PS activated by iron-based systems in wastewater treatment are analyzed and prospected.

Key words | advanced oxidation process, iron-based materials, persulfate, refractory organics, sulfate radicals

INTRODUCTION

In recent decades, with the increasing manufacture and the use of synthetic chemicals, a lot of wastewater containing some refractory organics is produced. Wastewater carrying these organics is usually collected by pipelines and sent to centralized wastewater treatment plants (WWTPs) for processing. However, the removal of refractory organics in the WWTPs is not complete by the biological treatment-based secondary treatment processes. It is necessary to further treat refractory organics in a more efficient way after secondary treatment processes in order to reduce the organic pollution load of the receiving water bodies.

The advanced oxidation processes (AOPs) are currently considered to be the best processes to remove refractory organics because of their strong ability to break chemical bonds of refractory organics (Fast et al. 2017). The AOPs initially investigated were based on hydroxyl radicals (HRs, HO·) produced in situ to degrade organic compounds. Two oxidants, hydrogen peroxide (H_2O_2) and ozone (O_3)
are activated by ultraviolet (UV) or ferrous ions (Fe$^{2+}$) to produce HRs (Deng & Zhao 2015). The main processes consisting of H$_2$O$_2$ or O$_3$ are H$_2$O$_2$/UV, O$_3$/UV, O$_3$/H$_2$O$_2$/UV, and Fe$^{2+}$/H$_2$O$_2$ which often called the Fenton process (Csay et al. 2014; Ghatak 2014). Based on Fenton process, photo-Fenton (Klamperth et al. 2013; Pouran et al. 2015), electro-Fenton (Nidheesh & Gandhimathi 2012; Yahya et al. 2014), sono-Fenton (Ioan et al. 2007; Ghauch et al. 2016), and sono-photo-Fenton (Babuponthusami & Muthukumar 2011) have also been extensively studied. However, the Fenton-based processes have several defects: Both H$_2$O$_2$ and O$_3$ are unstable, difficult to store and transport, and used in large quantities; the optimal pH value is around 3.0, which will increase pH regulating agents (Neyens & Baeyens 2005).

In recent years, the AOPs based on sulfate radicals (SRs, SO$_4$$^{2-}$) are widely studied in degradation of organic pollutants because they overcome some shortcomings of AOPs-HRs. For instance, SRs have higher oxidation potential (E$_0$ = 2.5–3.1 V) and longer half-life (t$_{1/2}$ = 30–40 μs) than that of HRs (E$_0$ = 1.7–2.8 V, t$_{1/2}$ ≤ 1 μs), and can selectively react with unsaturated or aromatic compounds under a wide pH range of 2.0–8.0 (Olmez-Hanci & Arslan-Alaton 2013; Ike et al. 2018). PS (E$_0$ = 2.01 V) can be activated to produce SRs in the presence of energy (UV, ultrasonic, and heat) (Guo et al. 2014; Darsinou et al. 2015; Ji et al. 2015), transition metals (Fe, Co, Ni, Cu, Ag, and Mn) (Liu et al. 2014; Rodríguez et al. 2014; Zhang et al. 2015a, 2015b; Kang et al. 2018), and carbon (Cheng et al. 2017). Among these activators, iron has been extensively studied in activating PS to generate SRs. Usually ferrous sulfate (FeSO$_4$) and ferrous chloride (FeCl$_2$) are employed as activators to produce Fe$^{2+}$ in solution. Naim & Ghauch (2009, 2010a, 2010b, 2011a). However, high concentrations of iron and iron-based materials were needed creating additional sludge formation. Therefore, researchers proposed iron use at trace level in combination with chemicals able to produce fugitive reactive oxygen species (ROS) (Ghauch 2015). Advantages of PS include chemical stability, ease of storage and transport, high solubility in water, and low cost, which broaden the application of PS in wastewater treatment (Tsitonaki et al. 2010). In addition, Sodium PS (Na$_2$S$_2$O$_8$) and potassium PS (K$_2$S$_2$O$_8$) are commonly used in research and pilot projects because they produce no secondary pollutants to water. Although high concentrations of sulfate species could be considered at risk which is not the case for PS concentration in the range of 0.1–20 mM (Liu & Wu 2018).

From the published literature available, some scholars have given an overview of the activated methods of sulfate radicals and their application in wastewater treatment (Zhang et al. 2015a, 2015b; Matzek & Carter 2016; Oh et al. 2016; Brenzia & Katsoyiannis 2017; Waclawek et al. 2017; Guerra-Rodríguez et al. 2018; Xiao et al. 2018, 2019; Oh & Lim 2019). However, a detailed review about activated persulfate by iron-based materials used for refractory organics degradation has not been reported yet. Therefore, a specific and deep review on the PS activated by iron-based materials can provide state-of-the-art information for the future research of the AOPs-SRs. This paper reviews the recent advances of mechanism and application of some iron-based materials in activating PS for refractory organics degradation, and the insights towards future application of these activating methods of PS for efficient degradation of refractory organics is summarized and discussed as well.

CHARACTERIZATION METHODS OF IRON-BASED MATERIALS

In order to better understand the physicochemical properties of iron-based materials and analyze the morphology and structure of the materials, some methods of characterizing materials are necessary. There are several analytical methods such as SEM (scanning electron microscopy), TEM (transmission electron microscopy), EDS (energy dispersive system), XRD (X-ray diffraction), XPS (X-ray photoelectron spectroscopy), FTIR (Fourier transform infrared spectrometry), TGA (thermo gravimetric analysis) and BET (Brunauer-Emmett-Teller) method. The detection objects of these analysis methods are shown in Table 1.

FERROUS ION (Fe$^{2+}$) AS ACTIVATOR

Mechanism of homogeneous activation

Ferrous ion is widely used as a homogeneous activator to react with PS to generate SRs. Usually ferrous sulfate (FeSO$_4$) and ferrous chloride (FeCl$_2$) are employed as activators to produce Fe$^{2+}$ in solution. Naim & Ghauch (2016) demonstrated that chloride salt was more efficient toward PS activation than sulfate salt because of common ion effect on hand and because of the generation of chlorine
radicals on the second hand responsible for additional ranitidine degradation. Table 2 lists some parameters and removal rates of refractory organics treated by Fe$^{2+}$/PS system based on recent publications. The reaction mechanism of ferrous ion with PS to generate SRs is presented in Equation (1) (Jiang et al. 2015). The O–O bond of S$_2$O$_8^{2-}$ is cleaved to form main product SO$_4^{2-}$ and byproduct SO$_2^{4-}$ by accepting the electrons provided by Fe$^{2+}$, while Fe$^{2+}$ is oxidized by the S$_2$O$_8^{2-}$ to become Fe$^{3+}$. As described in Equation (2), Fe$^{2+}$ is produced by the reaction between S$_2$O$_8^{2-}$ and Fe$^{3+}$ in the presence of S$_2$O$_8^{2-}$. Therefore, in a homogeneous system, there is a cycle between Fe$^{2+}$ and Fe$^{3+}$. As an oxidant, SO$_4^{2-}$ can also be consumed by itself or excess Fe$^{2+}$ and S$_2$O$_8^{2-}$ (Equations (3)–(5)) (Kusic et al. 2011; Zhang et al. 2014), which can render a lack of SO$_4^{2-}$ for organics degradation. On top of that, SO$_4^{2-}$ can react slowly with H$_2$O to form HO$^-$ (Equation (6)) (Olmez-Hanci et al. 2013).

$$S_2O_8^{2-} + Fe^{3+} \rightarrow Fe^{2+} + SO_4^{2-} + SO_2^{4-} \quad (k = 15.33M^{-1}s^{-1})$$  

(1)

$$S_2O_8^{2-} + Fe^{3+} \rightarrow Fe^{2+} + S_2O_8^{*}$$  

(2)

$$SO_4^{2-} + SO_4^{2-} \rightarrow 2SO_4^{2-} \quad (k = 4.0 \times 10^8M^{-1}s^{-1})$$  

(3)

$$SO_4^{2-} + Fe^{2+} \rightarrow Fe^{2+} + SO_2^{4-} \quad (k = 4.6 \times 10^9M^{-1}s^{-1})$$  

(4)

$$SO_4^{2-} + S_2O_8^{2-} \rightarrow S_2O_8^{*} + SO_2^{4-} \quad (k = 6.1 \times 10^5M^{-1}s^{-1})$$  

(5)

$$SO_4^{2-} + H_2O \rightarrow SO_4^{2-} + H^+ + HO^+ (k_{H_2O} < 2.0 \times 10^{-3}s^{-1})$$  

(6)

PS concentration and Fe$^{2+}$ concentration

Some articles (Liu et al. 2012; Long et al. 2014; Rao et al. 2014; Bu et al. 2016, 2017; Nie et al. 2018; Song et al. 2019; Wang et al. 2019c) investigated whether PS alone or Fe$^{2+}$ alone can remove organics at room temperature. Some results (Bu et al. 2016, 2017; Nie et al. 2018; Wang et al. 2019c) showed that neither PS alone nor Fe$^{2+}$ alone can remove organics under normal conditions. However, other results (Liu et al. 2012; Long et al. 2014; Rao et al. 2014; Song et al. 2019) presented that PS can remove 8–15% of organics. One of the possible causes is direct electron transfer oxidation from PS anion to organics, and another possible cause is the photocatalysis of light or temperature towards PS (Liu et al. 2012). Long et al. (2014) found that around 10% of organics were degraded due to the presence of Fe$^{2+}$ alone. The principal reason has been proposed, a series of reactions (Equations (7)–(9)) under aerobic conditions eventually lead to the generation of HO$^-$ that has the ability to degrade organics (Bu et al. 2016). This shows the high concentration of dissolved oxygen in the water can promote the degradation of organics by Fe$^{2+}$ alone. Caré et al. (2015) demonstrated that Fe$^{2+}$ is a reductant in some cases can remove organics however if generated in-situ from iron powder, Fe$^{2+}$ is more reactive since it is accompanied with the formation of additional iron corrosion products (ICPs) responsible for the co-precipitation and sequestration of organics along with reduction.

$$Fe^{2+} + O_2 \rightarrow Fe^{3+} + O_2^• \quad (pH < 7, k < 10^{0.48})$$  

(7)

$$Fe^{2+} + O_2^• + 2H^+ \rightarrow Fe^{3+} + H_2O \quad (k = 1.0 \times 10^7)$$  

(8)

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^+ + OH^- \quad (k = 65 - 76)$$  

(9)

PS and Fe$^{2+}$ concentration in solution are critical parameters to generate SO$_4^{2-}$, and the molar ratio of Fe$^{2+}$ to PS also determines the SO$_4^{2-}$ yield. Usually, the reaction to remove refractory organics is in two stages: at initial stage of reaction, the removal rate of organics increases with the increasing Fe$^{2+}$ concentration or PS concentration; After initial stage, even the concentration of Fe$^{2+}$ or PS continues to increase, the removal rate decreases. This shows that an appropriate molar ratio of Fe$^{2+}$ to PS, rather than higher concentration of Fe$^{2+}$ or PS, can obtain a better removal rate of organics. The most used molar ratio of Fe$^{2+}$ to PS in these studies was 1:1, and followed by 1:2 according some literature (Oh et al. 2009; Liu et al. 2012; Bu et al. 2016; Wang & Wang 2017). From the reaction of Equation (1), we can see that, 1 mole of Fe$^{2+}$ reacts with 1 mole of PS can produce 1 mole of SO$_4^{2-}$. So, theoretically, 1:1 is

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### Table 2 | Reaction conditions and treatment effects in the Fe²⁺/PS system

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<th>Pollutant (Abbreviation)</th>
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<tr>
<td>γ-hexachlorocyclohexane (γ-HCH)</td>
<td>[γ-HCH] = 0.0172 mM, [PS] = 42 mM, [Fe²⁺] = 0.0108 mM, pH = 5.7, t = 4 h, 100%</td>
<td>The γ-HCH oxidation rate constant (k) was relatively constant in the pH range of 3.5-9.0; however, it increased at both pHs 1.5 and 11.0.</td>
<td>Cao et al. (2008)</td>
</tr>
<tr>
<td>Polyvinyl alcohol (PVA)</td>
<td>[Fe²⁺] : [PS] = 1:1, t = 120 min, T = 20 °C, 70%</td>
<td></td>
<td>Oh et al. (2009)</td>
</tr>
<tr>
<td>Orange G (OG)</td>
<td>[OG] = 0.1 mM, [Fe²⁺] = 1.0 mM, [Fe²⁺] : [PS] = 1 : 4, pH = 3.5, t = 30 min, 81.0%</td>
<td>The following ions act as inhibitors are in sequence of NO₃⁻ &lt;Cl⁻ &lt; H₂PO₄⁻ &lt; HCO₃⁻.</td>
<td>Xu &amp; Li (2010)</td>
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<tr>
<td>Propachlor</td>
<td>[Propachlor] = 10 mg/ L, [Fe²⁺] = 2.5 mM, [Fe²⁺] : [PS] = 1:2, pH = 4.0, T = 30 °C, t = 30 h, 60.0%</td>
<td>Neutral or even alkaline levels led to strong hydrolysis of Fe²⁺, which had a negative effect on persulfate activation.</td>
<td>Liu et al. (2012)</td>
</tr>
<tr>
<td>Acetaminophen (APAP)</td>
<td>180 min, 18%</td>
<td>Sodium citrate at an appropriate concentration could improve the APAP degradation.</td>
<td>Deng et al. (2014)</td>
</tr>
<tr>
<td>Orange G (OG)</td>
<td>[OG] = 1.25 mM, [Fe²⁺] : [PS] : [OG] = 10 : 20 : 5, pH = 3.0, T = 25 °C, t = 150 min, 35.0%</td>
<td></td>
<td>Han et al. (2014)</td>
</tr>
<tr>
<td>Toluene</td>
<td>[Toluene] = 1 mM, [Fe²⁺] = 5 mM, [Fe²⁺] : [PS] = 1:4, pH = 7.0, t = 60 min, 70.0%</td>
<td>Excessive dosages of PS and Fe²⁺ inhibited toluene degradation efficiency; the optimal pH was 4.0.</td>
<td>Long et al. (2014)</td>
</tr>
<tr>
<td>Carbamazepine (CBZ)</td>
<td>[CBZ] = 0.025 mM, [Fe²⁺] : [PS] : [CBZ] = 10:40:1, pH = 3.0, t = 40 min, 78.0%</td>
<td>The optimal pH was 4.22; NO₃⁻, SO₄²⁻ and H₂PO₄⁻ inhibited CBZ degradation rate, and Cl⁻ facilitated the decomposition of CBZ.</td>
<td>Rao et al. (2014)</td>
</tr>
<tr>
<td>1,4-dioxane (1,4-D)</td>
<td>[1,4-D] = 100 mg/L, [Fe²⁺] = 1,000 mg/L, [Fe²⁺] : [PS] = 1 : 5, pH = 2.81, T = 40 °C, t = 51 min, 100%</td>
<td>The elevated temperature (50 °C and 60 °C) caused a slight decrease in the degradation rate of 1,4-D with the addition of Fe²⁺.</td>
<td>Zhao et al. (2014)</td>
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<tr>
<td>Levofoxacin (LFX)</td>
<td>[LFX] = 0.075 mM, [Fe²⁺] : [PS] : [LFX] = 1 : 10 : 1, pH = 3.0, t = 1 min, 69.0%</td>
<td></td>
<td>Epold et al. (2015)</td>
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<tr>
<td>Chloramphenicol (CAP)</td>
<td>The effluent of a beef cattle operation [CAP] = 0.05 mM,[PS] = 1 mM, pH = 5.4,[Fe²⁺] = 0.1 mM,20 injections, t = 45 min, 90.1%</td>
<td>HCO₃⁻, NO₃⁻, NO₂⁻, H₂PO₄⁻ and HA demonstrates an adverse effect on CAP oxidation. Adding a low Cl⁻ concentration into solution can facilitate CAP degradation, but adding a high Cl⁻ concentration can inhibit CAP degradation.</td>
<td>Nie et al. (2015)</td>
</tr>
<tr>
<td>Reactive Black (RB5)</td>
<td>[RB5] = 0.01 mM, [Fe²⁺] = 8 mM, [Fe²⁺] : [PS] = 1.50, pH = 7.78, t = 4 h, 98.0%</td>
<td>The higher initial concentration of RB5, the lower decolorization efficiency; the degradation rate of RB5 decreased with increasing pH; Cl⁻ could inhibit the degradation rate of RB5.</td>
<td>Satapanajaru et al. (2015)</td>
</tr>
<tr>
<td>Atrazine (ATZ)</td>
<td>[ATZ] = 20 μM, [Fe²⁺] = 0.4 mM, [Fe²⁺] : [PS] = 1:1, t = 10 min, 57.0%</td>
<td>Low initial ATZ concentration was favorable for ATZ degradation rate.</td>
<td>Bu et al. (2016)</td>
</tr>
<tr>
<td>Ranitidine (RAN)</td>
<td>[PS] = 100 μM,[Fe²⁺] = 100 μM, [RAN] = 28.5 μM, pH = 6.45, T = 25 °C, t = 60 min, 96%</td>
<td>Under sequential spiking of Fe²⁺, higher degradation efficiency 96% of RAN is obtained.</td>
<td>Naim &amp; Ghauch (2016)</td>
</tr>
<tr>
<td>Atrazine (ATZ)</td>
<td>[ATZ] = 10 μM, [Fe²⁺] = 0.03 mM, [PS] = 1.0 mM, pH = 4.0, t = 15 min, 29.4%</td>
<td></td>
<td>Bu et al. (2017)</td>
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Table 2 | continued

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<tr>
<td>Amicarbazone (AMZ)</td>
<td>[AMZ] = 0.0414 mM, [Fe^{2+}]: 0.134 mM, [PS] = 2.5 mM, pH = 3.0, t = 60 min, 35.0%</td>
<td>The actual composition of wastewater inhibited the degradation rate of SMX.</td>
<td>Graça et al. (2017)</td>
</tr>
<tr>
<td>Sulfamethoxazole (SMX)</td>
<td>[SMX] = 0.05 mM, [PS] = 4 M, [Fe^{2+}]:[PS] = 1:1, T = 25 °C, t = 120 min, pH = 3.0, 100%</td>
<td></td>
<td>Wang &amp; Wang (2017)</td>
</tr>
<tr>
<td>Ketoprofen (KTP)</td>
<td>[PS] = 0.5 mM, [Fe^{2+}]: [PS] = 7.87 μM, pH = 6.15, T = 25 °C, t = 60 min, 98%</td>
<td>The optimal [Fe^{2+}]:[PS] ratio is 5:1.</td>
<td>Amasha et al. (2018)</td>
</tr>
<tr>
<td>Crystal violet (CV)</td>
<td>[CV] = 40 mg/L, [Fe^{2+}]: [PS] = 3:4, pH = 7.0, t = 90 min, 41.0%</td>
<td>The optimal initial pH for degradation CV was 7.0.</td>
<td>Chen et al. (2018)</td>
</tr>
<tr>
<td>Bisphenol A (BPA)</td>
<td>[BPA] = 0.0877 mM, [PS] = 4.385 mM, [Fe^{2+}]: [PS] = 0.0877 mM - 0.877 mM, pH = 7.0, T = 25 °C, t = 60 min, 85.5% - 99.70%</td>
<td>A small amount of sodium citrate in the Fe^{2+}/PS system can lead to significant promotion of BPA removal in the rapid phase, and restore Fe^{3+} to Fe^{2+} to provide sustained activator for the slow phase. However, excessive sodium citrate can also inhibit the degradation.</td>
<td>Gao et al. (2018)</td>
</tr>
<tr>
<td>Chloramphenicol (CAP)</td>
<td>[CAP] = 0.05 mM, [Fe^{2+}]: [PS] = 0.2 mM, [Fe^{2+}]: [PS] = 2:3, pH = 3.0, t = 100 min, 27.2%</td>
<td>Lower concentration of Cl^- (0.6-6 mM) slightly increased the CAP degradation rate, while higher Cl^- (12-36 mM) concentration inhibited CAP removal.</td>
<td>Nie et al. (2018)</td>
</tr>
<tr>
<td>Chlorotetracycline (CTC)</td>
<td>[PS] = 500 mM, [Fe^{2+}]: [CTC] = 1 mM, t = 2 h, 76%</td>
<td>All Fe^{2+} ions in the case of homogeneous reaction activated above 90% PS to produce SO_4^{2-} which seems to be not efficient in degrading CTC due to scavenging of sulfate radicals by itself and also by excess Fe^{2+} ions.</td>
<td>Pulicharla et al. (2018)</td>
</tr>
<tr>
<td>Trimethoprim (TMP)</td>
<td>[TMP] = 0.05 mM, [PS] = 4 mM, [Fe^{2+}]:[PS] = 1:1, pH = 3.0, T = 25 °C, t = 250 min, 73.4%</td>
<td>The increasing persulfate concentration accelerated the TMP degradation rate; Under the same reaction conditions, the degradation rate of TMP in actual wastewater is 43.6%.</td>
<td>Wang &amp; Wang (2018)</td>
</tr>
<tr>
<td>Acetaminophen (APAP)</td>
<td>[APAP] = 100 mg/L, pH = 6.5, [PS] = 0.8 g/L, [Fe^{2+}]: [APAP] = 0.7 mM, 90 min, 79%</td>
<td></td>
<td>Zhang et al. (2018c)</td>
</tr>
<tr>
<td>2,4,6-trichloroanisole (TCA)</td>
<td>[PS] = 0.24 mM, [Fe^{2+}]: [TCA] = 0.47 μM, pH = 5, T = 20 °C, 60 min, 88%</td>
<td>The degradation of TCA by Fe^{3+}/PS was effective at both acidic and neutral pH comparing with alkaline pH.</td>
<td>Zhang et al. (2018b)</td>
</tr>
<tr>
<td>Diatrizoate (DTZ)</td>
<td>[DTZ] = 5 mg/L, [Fe^{2+}]: [PS] = 1:10, pH = 3.0, T = 25 °C, t = 120 min, 69.0%</td>
<td>The degradation rate of DTZ increased only 3% when pH increased from 3.0 to 9.0, but DTZ degradation rate decreased significantly at pH 11.0; more than 99% of DTZ removal is acquired at 40 °C.</td>
<td>Shang et al. (2019)</td>
</tr>
<tr>
<td>Triphenyl phosphate (TPHP)</td>
<td>[TPHP] = 10 μM, [Fe^{2+}]: [TPHP] = 1,000 μM, [Fe^{2+}]:[PS] = 2:1, pH = 4.0, T = 25 °C, t = 60 min, 80.0%</td>
<td>When pH increased from 4.0 to 9.0, removal rate TPHP was almost no changed.</td>
<td>Song et al. (2019)</td>
</tr>
<tr>
<td>Acetaminophen (ACT)</td>
<td>[ACT] = 0.05 mM, [Fe^{2+}]: [ACT] = 1 mM, [Fe^{2+}]:[PS] = 5:4, pH = 3.0, T = 20 °C, t = 40 min, 70.0%</td>
<td>Initial pH (3.0–9.0) had no insignificant impact on ACT degradation; ACT degradation rate decreased with initial ACT concentration increasing from 0.025 mM to 1 mM.</td>
<td>Wang et al. (2019c)</td>
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the optimal ratio of Fe$^{2+}$ to PS. However, in fact, the optimal ratio can be greater than or less than 1:1, due to the presence of some oxidized or reduced substances in the complex sewage that can consume Fe$^{2+}$ or PS. For example, SO$_4^{2-}$ can react with excess Fe$^{2+}$ or PS (Equations (4) and (5)) without considering the influence of other ions. In addition, the ratio of oxidant (PS) or catalyst (Fe$^{2+}$) concentration to organics concentration is also an important factor for maintaining a better organics removal rate. Some studies (Satapanajaru et al. 2015; Wu et al. 2015; Bu et al. 2016; Nie et al. 2018) stated that the concentration of oxidant or catalyst required is proportional to the concentration of contaminants due to more pollutants require more SO$_4^{2-}$ generated from PS activated by Fe$^{2+}$.

Solution pH

The initial pH of aqueous solution is an important factor influencing the removal efficiency of refractory organics in Fe$^{2+}$/PS system. Some articles (Cao et al. 2008; Xu & Li 2010; Liu et al. 2012; Niu et al. 2012; Long et al. 2014; Rao et al. 2014; Epold et al. 2015; Han et al. 2015a; Satapanajaru et al. 2015; Wu et al. 2016; Nie et al. 2018; Yu et al. 2018; Shang et al. 2019; Song et al. 2019; Wang et al. 2019c) studied the effect of pH ranging from 2.0 to 11.0 on the removal of refractory organics in Fe$^{2+}$/PS system. Based on the results of these articles (Xu & Li 2010; Liu et al. 2012; Niu et al. 2012; Long et al. 2014; Rao et al. 2014; Han et al. 2015a; Satapanajaru et al. 2015; Wu et al. 2016; Nie et al. 2018), the optimum pH range was 3.0–4.0. Within such a pH range, due to acid catalysis on PS, more SO$_4^{2-}$ could be generated from decomposition of PS, which therefore enhanced the removal rate of organics (Nie et al. 2018). When the pH was less than 3.0, refractory organics removal rate decreased because pH < 3.0 promotes the formation of the ferrous complex (Fe(H$_2$O)$_2$)Fe$^{2+}$, which reduces the amount of Fe$^{2+}$ to activate PS, and thus less SO$_4^{2-}$ can be formed. When the initial pH increased from 4.0 to 9.0, the removal efficiency of refractory organics gradually decreased. Four mechanisms are summarized to explain the reason why refractory organics degradation declined with increasing pH:

(1) When the pH is higher than 4.0, free Fe$^{2+}$ turns into Fe$^{2+}$ complexes (Equation (10)), which inhibits the further reaction between Fe$^{2+}$ and PS to form SO$_4^{2-}$ (Xu & Li 2010; Rao et al. 2014; Nie et al. 2018).

$$Fe^{2+} + H_2O \rightarrow FeOH^+ + H^+ \ (k = 1.9s^{-1}) \quad (10)$$

(2) With pH increasing above 4.0, ferric hydroxide complexes, such as FeOH$^{2+}$, Fe$_2$(OH)$_5^{2+}$, Fe(OH)$_3^{2+}$, Fe(OH)$_4^{2-}$, and Fe(OH)$_5^{2-}$ formed in the solution have low activation capacity to generate SO$_4^{2-}$ from PS, thus the efficiency of the refractory organics degradation is reduced (Nie et al. 2018). The equations of generating ferric hydroxide complexes are shown in Equations (11)–(13) (Xu & Li 2010). It can be seen from these equations that hydrogen ion is generated during the reaction and causes the decrease of pH in the solution.

$$Fe^3+ + H_2O \rightarrow FeOH^{2+} + H^+ \ (k = 2.3 \times 10^7 \text{s}^{-1}) \quad (11)$$

$$Fe^3+ + 2H_2O \rightarrow Fe(OH)^{3+} + 2H^+ \ (k = 4.7 \times 10^5 \text{s}^{-1}) \quad (12)$$

$$2Fe^3+ + 2H_2O \rightarrow Fe_2(OH)_4^{4+} + 2H^+ (k = 1.1 \times 10^{7} \text{s}^{-1}) \quad (13)$$

(3) If the pH is higher than 8.5, the present PS in the solution may react with OH$^-$ to form OH$^-$ (Equation (14)) in alkaline solution (Satapanajaru et al. 2015). This results in the rapid decay of SO$_4^{2-}$ (Liu et al. 2012; Satapanajaru et al. 2015). But hydroxyl radical is also strong in its reaction with the organic compounds.

$$SO_4^{2-} + OH^- \rightarrow SO_4^{2-} + ^\cdot OH \quad (14)$$

(4) When the pH is greater than or equal to 8.4, SO$_4^{2-}$ was found to react with HCO$_3^-$ or CO$_3^{2-}$ (Equations (15) and (16)) to form HCO$_3^-$ or CO$_3^{2-}$, any of which has poor oxidizing ability toward organics compared to SO$_4^{2-}$ (Satapanajaru et al. 2015).

$$SO_4^{2-} + HCO_3^- \rightarrow SO_4^{2-} + HCO_3^- \text{ at pH} = 8.4 \quad (15)$$

$$SO_4^{2-} + CO_3^{2-} \rightarrow SO_4^{2-} + CO_3^{2-} \text{ at pH} > 8.4 \quad (16)$$

Several articles (Epold et al. 2015; Shang et al. 2019; Song et al. 2019; Wang et al. 2019c) claimed that an initial solution pH (3.0–7.0) has no significant effect on removing refractory organics. Wang et al. (2019c) investigated the degradation of acetaminophen (ACT) in the Fe$^{2+}$/PS system at different initial pH (3.0, 5.0, 7.0 and 9.0), and found that the degradation of ACT was around 70% after a 30-min reaction at each of initial solution pH. In the article by Wang et al. (2019c), regardless of how the initial pH changed (from 3.0 to 9.0), the pH of the solution after 1-min reaction dropped
rapidly to 3.0, which demonstrates the degradation of ACT was not affected by the initial pH in Fe$^{2+}$/PS system. Song et al. (2019) studied the effect of increasing pH from 4.0 to 9.0 on the degradation efficiency of triphenyl phosphate (TPhP) in Fe$^{2+}$/PS process and found that degradation efficiency of TPhP was not impacted by pH changes. Epold et al. (2015) investigated levofloxacin (LFX) degradation at different pH (3.0, 5.0, 7.0 and 9.0) in Fe$^{2+}$/PS system, and the degradation rates of LFX acquired were almost as same as pH from 3.0 to 7.0, while the degradation rate of LFX was decreased by about 10% at pH of 9.0. Shang et al. (2019) studied the influence of initial pH (3.0, 5.0, 7.0, 9.0 and 11.0) on diatrizoate (DTZ) degradation. It was found that DTZ degradation rate was increased to only 3% when the pH was increased from 3.0 to 9.0. However, DTZ degradation efficiency dropped significantly as the initial pH increased from 9.0 to 11.0. Shang et al. (2019) proposed that the decreased DTZ degradation at initial pH of 11.0 is due to the reduction of Fe$^{2+}$ that tended to be hydrolyzed to ferric hydroxide and ferrous hydroxide under alkali conditions.

The findings of Cao et al. (2008) were different from the above articles. They testified that both low (pH = 1.5) and high pH (pH = 11.0) were more favorable for oxidation of Lindane in Fe$^{2+}$/PS system. The proposed reason is that Lindane is easily catalyzed hydrolysis by acid or base.

**Anions concentration**

Some inorganic anions, such as HCO$_3^-$, NO$_3^-$, NO$_2^-$, SO$_4^{2-}$, H$_2$PO$_4^-$ and Cl$^-$, in the water either have a positive or negative effect on sulfate radicals-based oxidation. This inorganic anion can either promote or inhibit the degradation of refractory organics in the Fe$^{2+}$/PS system. The conclusions from some articles (Xu & Li 2010; Ghauch et al. 2013; Rao et al. 2014; Naim & Ghauch 2016; Bu et al. 2017; Amasha et al. 2018; Nie et al. 2018; Song et al. 2019; Wang et al. 2019c) indicated that NO$_3^-$, SO$_4^{2-}$, H$_2$PO$_4^-$ and HPO$_4^{2-}$ could inhibit degradation of refractory organics, while Cl$^-$, HCO$_3^-$ could play both positive and negative effects on refractory organics removal. The inhibition effect of NO$_3^-$, SO$_4^{2-}$, H$_2$PO$_4^-$, HCO$_3^-$ and Cl$^-$ is attributed to the reactions occurring between inorganic anions and SO$_4^{2-}$ (Equations (17)–(20)). H$_2$PO$_4^-$, NO$_3^-$, Cl$^-$ and HCO$_3^-$ could react with SO$_4^{2-}$, then generate HPO$_4^{2-}$, NO$_3^-$, Cl$^-$ and CO$_3^{2-}$, respectively. Because the redox potential of HPO$_4^{2-}$, NO$_3^-$, Cl$^-$ and CO$_3^{2-}$ are lower than that of SO$_4^{2-}$, the replacement of these free radicals with SO$_4^{2-}$ leads to a decrease in the rate of degradation of refractory organics in Fe$^{2+}$/PS system. Phosphate is a special case in PS systems activated by iron species. In fact phosphate is a good complexant for Fe$^{2+}$ species to form FeH$_2$PO$_4^{2-}$ and FePO$_4$ (Ghauch 2008) and this is why inhibition occurs. Unless done in Fe$^{2+}$ free solution, phosphate can generate in heat activated PS medium some phosphate radicals as mentioned here (Ghauch & Tuqan 2022).

As for the effect of SO$_4^{2-}$ on refractory organics removal, the possible reason is due to the high ion strength that hinders the decomposition of PS (Rao et al. 2014). In addition, SO$_4^{2-}$ can reduce the reduction potential of half reaction of SO$_4^{2-}$ ($E^{0}_{SO_4^{2-}/SO_4^{2-}}$), which also results in the reducing ability of SO$_4^{2-}$ oxidation on refractory organics (Rao et al. 2014). One proposal for the positive effect of Cl$^-$ on the organics degradation is that the formation of chlorine-containing radicals (Cl$^-$ and Cl$_2^-$) and free available chlorine (Cl$_2$) through a series of chain reactions (Equations (21)–(24)) enhances the refractory organics removal (Rao et al. 2014; Wang et al. 2019c). Among these free radicals, Cl$_2^-$ as a stronger oxidizing property is major free radical when the Cl$^-$ concentration reached 10.0 mM (Wang et al. 2019c). From the research of Song et al., 100 mM HCO$_3^-$ enhanced TPhP degradation to 66.6% in Fe$^{2+}$/PS process (Song et al. 2019). There are two possible reasons to explain the promotion of TPhP degradation by carbonate (Song et al. 2019). Firstly, HCO$_3^-$ can easily react with electron-rich organic pollutants like TPhP. Alternatively, high concentration of HCO$_3^-$ can stimulate the decomposition of PS into SO$_4^{2-}$, and promote the TPhP removal.

\[
H_2PO_4^- + SO_4^{2-} \rightarrow HPO_4^{2-} + HSO_4^- (k = 6.0 \times 10^4 M^{-1} s^{-1})
\]  
\[
NO_3^- + SO_4^{2-} \rightarrow NO_3^+ + SO_4^2- (k = 3.6 \times 10^5 M^{-1} s^{-1})
\]  
\[
Cl^- + SO_4^{2-} \rightarrow Cl^- + SO_4^2- (k = 4.7 \times 10^4 M^{-1} s^{-1})
\]  
\[
HCO_3^- + SO_4^{2-} \rightarrow CO_3^{2-} + H^+ + SO_4^2- (k = 2.8 \times 10^6 M^{-1} s^{-1})
\]  
\[
SO_4^{2-} + Cl^- \rightarrow Cl^- + SO_4^{2-}
\]  
\[
Cl^+ + Cl^- \rightarrow Cl_2^-
\]  
\[
Cl_2^- + Cl_2^- \rightarrow Cl_2 + 2Cl^- (23)
\]  
\[
Cl^+ + Cl^- \rightarrow Cl_2
\]
Chelating agents

Because too much or too little Fe$^{2+}$ in solution has an adverse effect on activating PS to generate SO$_4$$^{2-}$, the chelating agents were used in Fe$^{2+}$/PS system to avoid the drawback of alone utilization of Fe$^{2+}$. Various chelating agents were added to aqueous solution in the form of acids or salts to chelate with Fe$^{2+}$, such as hydroxylamine (HA), citric acid (CA), oxalic acid (OA), tartaric acid (TA), ethylenediaminetetraacetate (EDTA), (S,S)-ethylenediamine-N,N,N’-disuccinate (EDDS), sodium thiosulfate (Na$_2$S$_2$O$_3$), diethylene triamine pentaacetic acid (DTPA) and epigallocatechin-3-gallate (EGCG) (Zhou et al. (EGCG) (Zhou et al. 2015; Han et al. 2014, 2015a; Ji et al. 2014; Wu et al. 2015, 2016; Bu et al. 2017; Yu et al. 2018). Han et al. (2014), Wu et al. (2015) and Wu et al. (2016) concluded that HA is an effective chelating agent that could alleviate Fe$^{3+}$ accumulation and accelerate Fe$^{2+}$ regeneration (Equations (25)–(27)); the results shows an addition of HA can promote refractory organics removal rate.

\[
\begin{align*}
\text{Fe}^{3+} + \text{NH}_2\text{OH} & \rightarrow \text{NH}_2\text{O}^* + \text{Fe}^{2+} + \text{H}^+ \quad (25) \\
\text{Fe}^{3+} + \text{NH}_2\text{O}^* & \rightarrow \text{NHO} + \text{Fe}^{2+} + \text{H}^+ \quad (26) \\
5\text{Fe}^{3+} + 2\text{H}_2\text{O} + \text{NH}_2\text{O}^* & \rightarrow \text{NO}_3^- + 5\text{Fe}^{2+} + 6\text{H}^+ \quad (27)
\end{align*}
\]

In the article by Ji et al. (2014), three kinds of chelating agents, CA, EDTA, and EDDS, were used to assist Fe$^{2+}$ in activating PS. The study of their effects on antibiotics degradation indicates that CA and EDTA both have some promoting effect on sulfamethoxazole (SMX) degradation, while CA, EDTA, and EDDS did not show a significant impact on ciprofloxacin (CIP) degradation, which means that the effects of the chelating agents varies from different targeted contaminants. The article by Zhou et al. (2015) testified the addition of Na$_2$S$_2$O$_3$ could facilitate the removal of diuron by about 25% compared with no Na$_2$S$_2$O$_3$ added under the same conditions. This was due to Na$_2$S$_2$O$_3$, acting as a buffer, balancing the amount of Fe$^{3+}$ and Fe$^{2+}$, as Equations (28)–(30).

\[
\begin{align*}
\text{XS}_2\text{O}_5^- + \text{YFe}^{2+} & \rightarrow \text{Complexanion} \quad (28) \\
\text{Complexanion} + S_2\text{O}_5^- & \rightarrow \text{Fe}^{3+} + \text{SO}_4^{2-} + \text{SO}_4^{2-} + \text{residue} \quad (29) \\
S_2\text{O}_5^- + \text{Fe}^{3+} & \rightarrow \text{Fe}^{2+} + 1/2\text{S}_4\text{O}_6^- \quad (30)
\end{align*}
\]

EGCG as green tea extract, was tested by Bu et al. (2017), and the result showed that EGCG could enhance the degradation rate of atrazine from 70% to 100% between pH 2.0 and 7.0. Owing to the strong chelating and reducing ability of EGCG, it accelerated the transformation rate from Fe$^{3+}$ to Fe$^{2+}$, as showed in Equations (31)–(33) (Bu et al. 2017).

\[
\begin{align*}
\text{Fe}^{3+} + \text{EGCG} & \rightarrow [\text{Fe(EGCG)}]^+ + 2\text{H}^+ \quad (31) \\
[\text{Fe}_2(\text{EGCG})]^2+ & \rightarrow \text{Semiquinone type product} \quad (32) \\
\text{Semiquinone type product} + 2\text{Fe}^{3+} & \rightarrow \text{Benzoquinone type product} + 2\text{Fe}^{2+} \quad (33)
\end{align*}
\]

From the above research results on chelating agents, we know that some chelating agents can promote the efficiency of Fe$^{2+}$ activation reaction under certain conditions in the Fe$^{2+}$/PS process, and these reaction conditions need to be further explored. In another point, the chelating agents used in the Fe$^{2+}$/PS system should be considered not to cause secondary pollution to the solution and to be easily biodegraded.

**ZERO-VALENT IRON-RELATED ACTIVATORS**

Zero-valent iron (Fe$^0$)

Although Fe$^{2+}$ appears to be a good activator for PS, Fe$^{2+}$/PS systems still have some limitations such as scavenging effect of excess Fe$^{2+}$ on SO$_4$$^{2-}$, conversion of Fe$^{2+}$ to iron hydroxide precipitation, and acidic pH of the solution. Fe$^0$ has been widely studied as an alternative source of Fe$^{2+}$ because it can gradually release ferrous iron into the water.

In a Fe$^0$/PS system, Fe$^0$ is corroded under aerobic (Equation (34)) or anaerobic (Equation (35)) conditions to form Fe$^{2+}$; the formed Fe$^{2+}$ further reacts with PS to generate SO$_4$$^{2-}$, which is consistent with Equation (1). Moreover, based on Equation (36), SO$_4$$^{2-}$ could be generated straight through electron transformation from Fe$^0$ to S$_2$O$_5$$^{2-}$. According to Equation (37), the recycling of Fe$^{2+}$ on the surface of Fe$^0$ can effectively avoid the accumulation of excess Fe$^{2+}$ so that the amount of iron hydroxide reproduction can be reduced in the Fe$^0$/PS system.

\[
\begin{align*}
2\text{Fe}^0 + \text{O}_2 + 2\text{H}_2\text{O} & \rightarrow 2\text{Fe}^{2+} + 4\text{OH}^- \quad (34) \\
\text{Fe}^0 + 2\text{H}_2\text{O} & \rightarrow \text{Fe}^{2+} + 2\text{OH}^- + \text{H}_2 \quad (35) \\
\text{Fe}^0 + S_2\text{O}_5^- & \rightarrow \text{Fe}^{2+} + 2\text{SO}_4^{2-} + 2\text{SO}_4^{2-} \quad (36) \\
\text{Fe}^0 + 2\text{Fe}^{3+} & \rightarrow 3\text{Fe}^{2+} \quad (37)
\end{align*}
\]

Table 3 summarizes the reaction conditions and degradation efficiency of some refractory organics using Fe$^0$ as
Table 3 | Reaction conditions and EC treatment effects in the Fe⁰/PS system

<table>
<thead>
<tr>
<th>Pollutant (Abbreviation)</th>
<th>Parameters and degradation rate</th>
<th>Remarks</th>
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<tbody>
<tr>
<td>Polyvinyl alcohol (PVA)</td>
<td>[Fe⁰]/[PS] = 1:1, 120 min, T = 20 °C, [PS] = 250 mg/L, PVA = 47.1-50.2 mg/L, 100%</td>
<td>The optimal persulfate to Fe⁰⁺ or Fe⁰ molar ratio was found to be 1:1.</td>
<td>Oh et al. (2009)</td>
</tr>
<tr>
<td>Naphthalene (NAP)</td>
<td>[NAP] = 10 mg/L, [PS] = 42 mM, [Fe⁰] = 1 g/L, T = 20 °C, pH = 5.0, 5 min, 99%</td>
<td>The initial pH of 5.0 changed to around 2.3 in the NAP/PS/Fe⁰ systems after reaction.</td>
<td>Liang &amp; Guo (2010)</td>
</tr>
<tr>
<td>2,4-dinitrotoluene (DNT)</td>
<td>[PS] = 250 mg/L, [Fe⁰] = 1 g/L, [DNT] = 50 mg/L, t = 300 min, 91%</td>
<td>As a persulfate-activating agent, Fe⁰ is more effective and longer-lasting than Fe²⁺ and potentially more suitable for environmental applications.</td>
<td>Oh et al. (2010)</td>
</tr>
<tr>
<td>4-chlorophenol</td>
<td>[Fe⁰] = 0.20 g/L, [4-chlorophenol] = 0.156 mM; [PS] = 0.78 mM, no pH adjustment, t = 1 h, 88%</td>
<td>The removal of 4-chlorophenol with Fe⁰/PS was 86% and 80% at pH 3.0 and 6.0, respectively.</td>
<td>Zhao et al. (2010)</td>
</tr>
<tr>
<td>p-chloroaniline (PCA)</td>
<td>[PCA] = 0.05 mM, [PS] = 2.5 mM, [Fe⁰] = 0.70 g/L, pH = 6.8, t = 300 min, 64.5%</td>
<td>The PCA degradation was higher under acidic conditions (pH 2.0 and 4.0) compared to alkaline conditions. Complete degradation of PCA was obtained by ZVI-activated persulfate at pH 4.0 at 12 min.</td>
<td>Hussain et al. (2012)</td>
</tr>
<tr>
<td>Sulfamethoxazole (SMX)</td>
<td>[Fe⁰] = 17.85 mM, [PS] = 1.0 mM, [SMX] = 39.51 mM, pH = 5.54, t = 2 h, 91%</td>
<td>Reactions with acid-washed MIPs (wFe/SMX) were more successful than those carried out with un-washed MIPs (nwFe/SMX).</td>
<td>Ghauch et al. (2015)</td>
</tr>
<tr>
<td>Acetaminophen (APAP)</td>
<td>[Fe⁰]/[PS] = 1:1, 180 min, 93.19%</td>
<td>The Fe⁰/PS system was effective in a broader pH range from 3.0 to 8.5; heat could enhance the APAP degradation.</td>
<td>Deng et al. (2014)</td>
</tr>
<tr>
<td>Aniline</td>
<td>[Fe⁰] = 0.4 g/L, [Aniline] = 0.05 mM, T = 25 °C, [PS] = 2.5 mM, pH = 7.0, t = 300 min, 89%</td>
<td>The optimum pH for degradation of aniline was 4.0 in which 100% degradation efficiency was achieved after 10 min reaction.</td>
<td>Hussain et al. (2014)</td>
</tr>
<tr>
<td>Dibutyl phthalate (DBP)</td>
<td>[DBP] = 5 mg/L, [PS] = 45 mg/L, [Fe⁰] = 0.3 g/L, pH = 6.8, t = 120 min, 84%</td>
<td>The half-lives for the oxidation of DBP in Fe⁰/PS were 30–176 min at pH 3.0–11.0.</td>
<td>Li et al. (2014)</td>
</tr>
<tr>
<td>Acid Orange 7 (AO7)</td>
<td>[AO7] = 30 mg/L, [PS] = 0.3 g/L, [Fe⁰] = 0.5 g/L, pH = 5.8, t = 6 min, 38%</td>
<td>The overall oxidation rate of AO7 was inhibited upon addition of NO₃⁻, NO₂⁻, SO₄²⁻, Cl⁻, CO₃²⁻, HCO₃⁻, H₂PO₄⁻, H₃PO₄ and EDTA, whereas ClO₄⁻, CH₂COO⁻ and HA were found to accelerate AO7 decolorization rates.</td>
<td>Wang et al. (2014)</td>
</tr>
<tr>
<td>Sulfadiazine (SD)</td>
<td>[SD] = 20 mg/L, [PS] = 1.84 mM, [Fe⁰] = 0.92 mM, pH = 7.0, t = 1 h, 45.5%</td>
<td>There was no significant difference on degradation efficiency of TCA under pH 6-8.</td>
<td>Zou et al. (2014)</td>
</tr>
<tr>
<td>Chloramphenicol (CAP)</td>
<td>[CAP] = 0.05 mM, [Fe⁰] = 1 mM, [PS] = 1 mM, pH = 5.4, t = 15 min, 95%</td>
<td>The optimal molar ratio of CAP/ZVI/PS is 1:20:20.</td>
<td>Nie et al. (2015)</td>
</tr>
<tr>
<td>Sirius Red F3B (SRF3B)</td>
<td>[SRF3B] = 25 mg/L, pH = 6.0, [PS] = 5 mg/L, [Fe⁰] = 0.5 g/L, 10 min, 95% decolorization 120 W/L US</td>
<td>The PS/(Fe⁰) system shows a practically feasible process for SRF³B decolorization under conditions of initial pH &lt; 9.0, high PS and Fe⁰ dosages, and high temperatures.</td>
<td>Weng et al. (2015)</td>
</tr>
<tr>
<td>Para-Chlorophenol (PCP)</td>
<td>[PS] = 15 mM, [Fe⁰] = 1 g/L, [PCP] = 50 mg/L, pH = 5.0, T = 25 °C, t = 120 min, 70%</td>
<td>The degradation efficiency of PCP gradually decreases to 51.7% when the ZVI reuse time is increased.</td>
<td>Ahmadpour &amp; Yengejeh (2016)</td>
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<tbody>
<tr>
<td>Triton X – 45 (TX – 45)</td>
<td>[TX – 45] = 20 mg/L, [Fe⁰] = 1 g/L, [PS] = 2.5 mM, pH = 5.0, t = 60 min, 90%</td>
<td>TX – 45 and TOC removals were most efficient under acidic and neutral pH values with addition of 2.5 mM PS.</td>
<td>Temiz et al. (2016)</td>
</tr>
<tr>
<td>Alachlor</td>
<td>[Alachlor] = 5 mg/L, [Fe⁰] = 0.3 mL, [PS] = 1.0 mL, T = 30 °C, 60 min, 100%</td>
<td>The reaction rate is significantly influenced by factors such as Fe⁰ dosage, PS dosage, initial pH, temperature, NOM, citrate and anions.</td>
<td>Wang et al. (2016b)</td>
</tr>
<tr>
<td>Direct Red 23 (DR23)</td>
<td>[DR23] = 0.1 mL, [PS] = 5 mL, [Fe⁰] = 0.5 mL, pH = 6, T = 25 °C, t = 15 min, 95%</td>
<td>A promising decolorization was observed in the PS oxidation process activated with Fe⁰ aggregates. The decolorization efficiency in the PS/Fe⁰ system was further enhanced by US (PS/Fe⁰/US) or heat (PS/Fe⁰/55 °C).</td>
<td>Weng &amp; Tsai (2016)</td>
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<tr>
<td>Orange G (OG)</td>
<td>[OG] = 0.2 mL, [PS] = 2 mL, [Fe⁰] = 0.2 mL, CuO = 0.1 g/L, T = 25 °C, pH = 5.0, t = 1 h, 50%</td>
<td>Al³⁺, Cl⁻, NO₃⁻ improved the treatment; NH₄⁺, Ca²⁺, and Mg²⁺ did not significantly influence the BTZ removal; and Mn²⁺, Cu²⁺, CO₃⁻, HCO₃⁻, PO₄³⁻, HPO₄²⁻, H₂PO₄⁻, H₂PO₃⁻ inhibited the BTZ degradation.</td>
<td>Wei et al. (2016)</td>
</tr>
<tr>
<td>Bentazon (BTZ)</td>
<td>[Fe⁰] = 4.477 mM, [PS] = 0.262 mM, [BTZ] = 0.021 mL, pH ≤ 7, 100%</td>
<td>RG19 decolorization decreased from 99% to 7%, 21%, and 15% in presence of sodium citrate, sodium EDTA, and sodium oxalate, compared with control test (without chelating agent, 99%) within 10 min.</td>
<td>Ding et al. (2017)</td>
</tr>
<tr>
<td>Reactive Green 19 (RG19)</td>
<td>[RG19] = 0.01 mL, [PS] = 5 mL, [Fe⁰] = 1.0 g/L, pH = 6.0, T = 25 °C, 10 min, 99% sodium citrate, sodium EDTA, and [sodium oxalate] = 1 mM</td>
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<tr>
<td>1,4-dioxane (1,4-D)</td>
<td>[Fe⁰] = 0.2 g/L, CuO = 0.1 g/L, T = 25 °C, 5 min, 90%, pH ≤ 9, 100%</td>
<td>The ERY removal was more favorable under acidic and neutral condition than alkaline condition.</td>
<td>Li et al. (2017b)</td>
</tr>
<tr>
<td>p-nitrophenol (PNP)</td>
<td>[PNP] = 500 mg/L, [Fe⁰] = 30 g/L, [PS] = 12.5 mM, pH = 3.6, T = 25 °C, 3 min, 95%, 60% of dioxane removal</td>
<td>Distributing the Fe⁰ as eight, one-eighth dosages, 95% dioxane removal was achieved; adding sodium hexametaphosphate (SHMP) to the persulfate candles can facilitate persulfate release.</td>
<td>Ji et al. (2017)</td>
</tr>
<tr>
<td>2,4-Dichlorophenol (2,4-DCP)</td>
<td>[Fe⁰] = 1.5 mL, [2,4-DCP] = 4 mL, [PS] = 1 mL, pH = 7.15, 90%</td>
<td>The Pre-Fe⁰/PS system induced a significant improvement in removal efficiency of 2,4-DCP, TOC and de-chlorination, especially at a higher initial pH condition.</td>
<td>Li et al. (2017c)</td>
</tr>
<tr>
<td>Orange G (OG)</td>
<td>[Fe⁰] = 4 mL, [PS] = 4 mL, [OG] = 200 mg/L, pH = 7, 180 min, 28.6%</td>
<td></td>
<td>Pan et al. (2017)</td>
</tr>
<tr>
<td>Sulfadiazine (SDZ)</td>
<td>[Fe⁰] = 1 mL, [PS] = 1 mL, [SDZ] = 20 mL, T = 25 °C, pH = 7.10, 80%</td>
<td>Common aquatic materials including sulfate, nitrate, chloride, perchlorate, and HA all showed a negative effect on SDZ degradation by Fe⁰/PS following a trend of Cl⁻ &lt; ClO₄⁻ &lt; SO₄²⁻ &lt; NO₃⁻ &lt; HCO₃⁻ &lt; HA.</td>
<td>Yang &amp; Che (2017)</td>
</tr>
<tr>
<td>Bisphenol A (BPA)</td>
<td>[BPA] = 0.0877 mM, [PS] = 4.385 mM, [Fe⁰] = 0.0877 mM-0.877 mM pH = 7.0, T = 25 °C, t = 60 min, 85.17% - 100%</td>
<td>The best BPA decomposition effects were obtained when [Fe²⁺]:[PS] = 1:2 and [Fe⁰]:[PS] = 1:2 are applied.</td>
<td>Gao et al. (2018)</td>
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</table>

(continued)
an activator for PS to generate $\text{SO}_4^{2-}$. It can be seen from Table 3 that most of the activation reactions in Fe$^0$/PS system can achieve high refractory organics removal rates of 70–100% in the range of pH 3.0–7.0. Some papers (Oh et al. 2009; Deng et al. 2014; Pulicharla et al. 2018; Zhang et al. 2018b) compared the effects of Fe$^0$ and Fe$^{2+}$ acting as activators for PS on refractory organics removal and all results showed that Fe$^0$ has a better treatment effect on refractory organics degradation than Fe$^{2+}$ under the same conditions of the reaction. Except, the results of Gao et al. (2018) showed that Fe$^0$ and Fe$^{2+}$ both had the same removal effect on bisphenol A removal at neutral pH. Under most conditions, the activation effect of Fe$^0$ on PS is still better than that of Fe$^{2+}$ on PS. Similar to previously discussed Fe$^{2+}$/PS system, the molar ratio of catalyst to oxidant is an important parameter in Fe$^0$/PS system. Low Fe$^0$/PS molar ratio will lead to poor degradation effect on refractory organics due to lack of sufficient active sites for PS activation and $\text{SO}_4^{2-}$ generation, while high Fe$^0$/PS molar ratio will result in less $\text{SO}_4^{2-}$ production and unnecessary Fe$^0$ consumption. According to previous analysis, we know the theoretically optimal ratio of Fe$^{2+}$/PS was 1:1. However, Fe$^0$/PS molar ratio needs to be higher than 1:1 in the bulk solution in order to ensure enough Fe$^0$ that can consistently liberate Fe$^{2+}$ into the water. Moreover, the ratio of catalyst to oxidant ultimately should be determined under specific reaction conditions.

Fe$^0$ shows a good activated effect on PS. However, high concentrations of Fe$^0$ and PS are required, which increases treatment cost. In order to improve efficiency of Fe$^0$ on PS decomposition, researchers used two thin cylindrical neodymium-iron-boron permanent magnets to make Fe$^0$ magnetic, and magnetized Fe$^0$ (or pre-magnetization Fe$^0$) was employed to activate PS for degrading refractory organics, such as orange (OG), 2,4-dichlorophenol (2,4-DCP) (Li et al. 2017c; Pan et al. 2017). It was found that in SEM micrographs, after pre-magnetization, the Fe$^0$ surface was slightly corroded and deposition of tiny particles it was noted on the surface and the BET after pre-magnetization significantly increased from 0.15 m$^2$/g (original Fe$^0$) to 1.94 m$^2$/g, which benefited the mass transfer of Fe$^{2+}$ released from Fe$^0$ (Li et al. 2017c). For these reasons, the degradation rate of refractory organics in the pre-magnetized Fe$^0$/PS is also higher than Fe$^0$/PS system (Li et al. 2017c; Pan et al. 2017).

### Nano-sized zero-valent iron

To further improve the efficiency of Fe$^0$/PS system, nFe$^0$ has been used to activate PS for refractory organics removal because of high activity of nFe$^0$ compared with Fe$^0$. Better refractory organics removal efficiency has been found in nFe$^0$/PS system than Fe$^{2+}$/PS or Fe$^0$/PS (Al-Shamsi & Thomson 2013; Zhu et al. 2016; Wang et al. 2017; Kim et al. 2018; Lin & Chen 2018). Lin & Chen (2018) used nFe$^0$ for PS decomposition to degrade sulfamethazine (SMT), and the SMT removal rate of 93% was obtained in 5 min with addition of nFe$^0$ of 56 mg/L and PS of 2 mM. Al-Shamsi & Thomson (2013) compared the degradation rate of TCE using three different iron activators of nFe$^0$, Fe$^0$ and Fe$^{2+}$. The TCE degradation rate in 3 min by nFe$^0$/PS was $1.11 \times 10^{-4}$ M/min$^{-1}$, which is higher than that of Fe$^0$/PS ($5.18 \times 10^{-6}$ M/min$^{-1}$) and Fe$^{2+}$/PS.

### Table 3 (continued)

<table>
<thead>
<tr>
<th>Pollutant (Abbreviation)</th>
<th>Parameters and degradation rate</th>
<th>Remarks</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlortetracycline (CTC)</td>
<td>$[\text{Fe}^0] = 1,000 \text{ mM}$, 94%</td>
<td>Whereas in heterogeneous reactions, slow generation and regeneration of Fe$^{2+}$ ions obtained a removal of CTC above 90%.</td>
<td>Pulicharla et al. (2018)</td>
</tr>
<tr>
<td>Rhodamine B (RhB)</td>
<td>$[\text{RhB}] = 50 \text{ mg/L}$, $[\text{PS}] = 1.4 \text{ g/L}$, H$_2$A/Fe$^0 = 1.0 \text{ g/L}$, $T = 25 ^\circ \text{C}$, 60 min, 58%</td>
<td>The optimal PS dosage is 0.3 g/L.</td>
<td>Wang et al. (2018)</td>
</tr>
<tr>
<td>Remazol Golden Yellow (RGY)</td>
<td>$[\text{PS}] = 5 \times 10^{-3} \text{ M}$, $[\text{Fe}^0] = 0.5 \text{ g/L}$, [RGY] = 100 mg/L, pH = 6.0, t = 20 min, 98%</td>
<td>The inhibitory effect of various inorganic salts on decolorization follows the sequence of Na$_2$HPO$_4$ &gt; NaHCO$_3$ &gt; NaClO$_4$ &gt; NaCl &gt; NaNO$_3$ &gt; NaClO$_4$ &gt; no salt.</td>
<td>Weng &amp; Tao (2018)</td>
</tr>
<tr>
<td>2,4,6-trichloroanisole (TCA)</td>
<td>$[\text{PS}] = 0.24 \text{ mM}$, $[\text{Fe}^0] = 0.48 \text{ mM}$, pH = 7, [TCA] = 0.47 mM, temperature: $T = 25 ^\circ \text{C}$; t = 60 min, 18%</td>
<td>CA/Fe$^0$ molar ratio of 2:5, CA promoted the oxidation of TCA by Fe$^0$/PS, but OA and EDTA retarded the reaction. Citric acid(CA),oxalic acid(OA)Fe$^0$/PS had the best performance at pH 2.5.</td>
<td>Zhang et al. (2018b)</td>
</tr>
</tbody>
</table>
Activated persulfate by iron-based materials

Although nFe⁰ has a better effectiveness in activating PS for refractory organics degradation owing to its small particle size, large surface area and high reactivity, its application still faced some practical problems (Fu et al. 2014). Mueller et al. (2012), Fu et al. (2014) and Stefaniuk et al. (2016) all found that high surface energies and inherent magnetism of nFe⁰ lead to agglomerating of nFe⁰ particles, which limits the mobility of nFe⁰ and reduces electron transfer of nFe⁰. In addition, nFe⁰ is easily oxidized by the oxygen as it is exposed to the air, lack of stability and difficulty separating from the water is problematic in terms of practical application. In order to solve the weaknesses of nFe⁰ particles, some materials (such as biochar (BC), reduced graphene oxide (rGO), mesoporous carbon (MC) and montmorillonite) have been used to support nFe⁰.

Biochar (BC) is a low-cost carbonaceous adsorbent generated in an oxygen-limited or oxygen-free environment at high temperatures by pyrolysis of biomass (Yan et al. 2015; Xu et al. 2018b; Luo et al. 2019; Park et al. 2019; Wang et al. 2019a, 2019d). BC has a strong adsorption capacity due to its high surface area (SA)-to-volume ratio and porous properties (Wei et al. 2018; Wang et al. 2019b).
Ahmed et al. (2016) and Ravikumar et al. (2018) found the surface of BC contains abundant oxygen-rich functional groups (such as hydroxyl (–OH) and carboxyl (–COOH)) which can quickly adsorb organic contaminants. Han et al. (2015b) testified because of these unique properties of these functional groups, BC has been used as mechanical supporting material for nFe0 to disperse and stabilize nFe0. In detail, BC has a large specific surface area and a large number of micropores, which can provide a support carbon skeleton for nFe0 to immobilize (Liu et al. 2018; Wang et al. 2019d). nFe0 is stabilized on surface of BC via adsorption, coordination, chelation and bridging (Jiang et al. 2019; Wang et al. 2019d).

Some researchers inferred the PS activation mechanisms in nFe0/BC/PS system, and the basic mechanisms are illustrated as follows (Yan et al. 2015; Xu et al. 2018b; Luo et al. 2019; Park et al. 2019). (1) As nFe0 disperses well on BC surface, Fe3+, gradually formed by oxidation of nFe0, activates PS to form SO42– (Equation (50) and (51)), then generates FeOOH (Equation (52)) which can react with SO42– intermediate (Equations (50) and (51)), then generates FeSO4 (Equation (53)). (2) Nano-Fe0 directly activates PS in nFe0/rGO (Equation (54) and (55)) (Yan et al. 2015; Soubh et al. 2018; Xu et al. 2018a). Owing to the layered structure, rGO has a large specific surface area that provides abundant adsorption sites for the immobilization of nFe0. The mechanism of activating PS in nFe0/rGO is similar to that of nFe0/BC. Except for providing support for nFe0, the functional groups such as –OH and –OH on rGO surface can also catalyze PS to release organic radicals and sulfate radicals, seen as Equations (56) and (57) (Duan et al. 2015; Wu et al. 2018).

Reduced graphene oxide (rGO), is a two-dimensional monolayer with abundant sp2-bonded carbon. It is a versatile matrix used as a support for nFe0 nanoparticles (Yang et al. 2015; Hao et al. 2018; Park et al. 2019; Wu et al. 2018). BC has a large specific surface area that provides abundant adsorption sites for the immobilization of nFe0. The mechanism of activating PS in nFe0/rGO is similar to that of nFe0/BC. Except for providing support for nFe0, the functional groups such as –OH and –OH on rGO surface can also catalyze PS to release organic radicals and sulfate radicals, seen as Equations (56) and (57) (Duan et al. 2015; Wu et al. 2018).

\[
\begin{align*}
\text{Fe}^3+ + 3\text{H}_2\text{O} & \rightarrow \text{Fe(OH)}_3 + 3\text{H}^+ \\
\text{Fe}^3+ + 2\text{S}_2\text{O}_8^{2–} & \rightarrow 2\text{SO}_4^{2–} + 2\text{SO}_2^{2–} \\
\text{Fe}^0 + \text{S}_2\text{O}_8^{2–} + 2\text{H}_2\text{O} & \rightarrow \text{Fe}^{2+} + 2\text{SO}_4^{2–} + 2\text{H}^+ + \text{O}_2 \\
\text{Fe}^0 + \text{SO}_4^{2–} + 2\text{H}_2\text{O} & \rightarrow \text{FeSO}_4^{(5)} + 2\text{OH}^- + \text{H}_2 \\
\text{Fe}^{2+} + \text{H}_2\text{O} & \rightarrow \text{Fe}^{3+} + \text{OH}^- + 1/2\text{H}_2 \\
\text{Fe}^{3+} + 3\text{OH}^- & \rightarrow \text{Fe(OH)}_3
\end{align*}
\]
Some iron-containing compounds such as hematite (Fe₂O₃), magnetite (Fe₃O₄), and ferrous sulfide (FeS), are also explored to activate PS for refractory organics degradation. Teel et al. (2011) evaluated the effects of several soil minerals including hematite on PS activation and found that hematite is capable of activating PS for removal organic pollutants in water. This effect is attributed to the octahedral sites of hematite containing Fe²⁺ that can react with PS to produce SO₄²⁻, according to Equation (1). Figure 2 illustrates the activated mechanism in which PS is activated to generate sulfate radicals for degradation of organic pollutants. The mechanism of the activation of PS by hematite is similar to that by Fe²⁺, but due to the heterogeneous catalysis of hematite, catalytic reactions will occur both on the surface of the Fe₂O₃ and in the solution. Firstly, Fe²⁺ at some sites on the surface of the hematite will adsorb PS in aqueous solution, then react with PS to form SO₄²⁻, SO₂⁻ and Fe³⁺. Fe³⁺ also reacts with PS to form Fe²⁺, which forms a cycle between Fe²⁺ and Fe³⁺ on the surface of hematite. The Fe²⁺ and Fe³⁺ leaking into the solution also undergo the same cyclic reaction as the surface. There is also the formation of SO₄²⁻ during this cycle. SO₄²⁻ formed on the surface of hematite or in the solution can capture and react contaminants to form by-products in water, which ultimately produce carbon dioxide and water. Free radical scavenging experiment in reference (Kermani et al. 2018) have shown that there is also HO’ that could be generated during oxidation of PS by hematite; HO’ also plays a role on degradation of refractory organics. The type of free radicals generated in PS/Fe₂O₃ system are determined by solution pH and the type of targeting contaminants. SO₄²⁻ are usually dominant under an acidic condition, while HO’ prefers a neutral and alkaline environment.

Magnetite nanoparticles (MNP)s have also been studied as a catalyst similar to hematite because they can work under mild reaction conditions and be easily separated and recovered. Magnetite is a magnetic particle, and nanometer magnetite can be synthesized by reverse co-precipitation among FeCl₃·6H₂O + FeSO₄·7H₂O + NH₃·H₂O. Literature (Leng et al. 2013, 2014; Sun et al. 2016; Zhu et al. 2018) demonstrated that treatment effects, reaction conditions and mechanisms of different types of synthetic Fe₃O₄ and its complexes with other materials (biochar, NrGO) to activate PS for effectively degradation of refractory organics. Magnetite contains Fe²⁺/³⁺, which can stimulate decomposition of PS to generate free radicals. However, the Fe²⁺ may have not enough magnetite due to the slow transformation between Fe²⁺ and Fe³⁺ cycles. As a result, modifying surfaces of Fe₃O₄ MNPs and improving the redox cycle of Fe²⁺/³⁺ is a very important research issue (Sun et al. 2016). Some studies investigated polyhydroquinone-coated Fe₃O₄, ascorbic acid modified Fe₃O₄, β-CD immobilized Fe₃O₄ as catalysts for the activation of PS (Leng et al. 2013, 2014; Sun et al. 2016; Zhu et al. 2018). According to Sun et al. (2016), ascorbic acid (H₂A, also called vitamin C), a redox mediator, used to modify Fe₃O₄ MNPs could enhance the ability of activating PS. Under same conditions, the effect of H₂A/Fe₃O₄ on PS activation was greater than that of Fe₃O₄ alone on PS activation. Under H₂A/Fe₃O₄ activation, a removal rate (98.5%) of 2,4-DCP can be obtained, while only 35.1% degradation of 2,4-DCP was achieved in Fe₃O₄/PS system, which was testified that the introduction of H₂A in Fe₃O₄/PS can effectively activate PS for targeting pollutants removal. Nowack (2002) and Dong et al. (2017) all testified that H₂A is an effective chelating and reducing agent that can enhance iron ions released from minerals. The primary mechanism of improved refractory organics degradation in the H₂A/Fe₃O₄/PS process is illustrated in Figure 5. First, H₂A, as a chelating agent, attached on surface of Fe₃O₄.
particles combines with Fe\(^{2+}\) to form chelated iron of Fe\(^{2+}\)-H\(_2\)A through the ligand exchange reaction. Then, Fe\(^{2+}\) enters into aqueous phase initiating a reaction that catalyzes PS to generate SO\(_4^-\)/C\(_0\). In addition, H\(_2\)A can enhance the performance of reduction of Fe\(^{3+}\) to Fe\(^{2+}\) on the Fe\(_3\)O\(_4\) nanoparticle surface and promote more release of Fe\(^{2+}\) from Fe\(_3\)O\(_4\) into solution.

Compared with homogenous Fe\(^{2+}\)/PS system, heterogeneous FeS/PS system also shows a good performance on refractory organics removal (Pu et al. 2014; Yuan et al. 2015; Zhang et al. 2017; Fan et al. 2018). Yuan et al. (2015) found that the application ranges of pH for p-chloroaniline (PCA) fast degradation was from 3.0 to 7.0, while the optimum pH range was from 5.0 to 7.0 for complete degradation of PCA at 150 min according the research of Fan et al. (2018). The PS activation mechanism was affected by the initial solution pH. The mechanism of FeS activating PS is shown in Figure 4. As a solid particle like Fe\(_0\), FeS could continuously release dissolved Fe\(^{2+}\) (Yuan et al. 2015) which would activate PS to produce SO\(_4^-\). In addition, as an electron donor, S\(^{2+}\) was able to reduce Fe\(^{3+}\) to Fe\(^{2+}\) (Fan et al. 2018). Sustainable release of Fe\(^{2+}\) and recycling of Fe\(^{3+}\) by FeS during reaction could avoid surplus Fe\(^{2+}\) consumption and Fe\(^{3+}\) accumulation. Based on this mechanism, when the initial solution pH was 9.0–11.0, the dissolved Fe\(^{2+}\) from FeS was not enough to activate PS and relatively low PCA removal rate was acquired.

**ECONOMIC EVALUATION**

Regarding the methods for iron-based materials to activate PS to degrade organics, we are not only concerned with the efficiency, but also with the cost. Since these methods have not yet been applied in engineering, the cost of chemical agents in small experiments based on different iron materials is calculated and analyzed according to the consumption and price of chemical agents. Table 4 shows the unit price of iron-based materials found on the website of Sigma. Table 5 lists the experimental data such as oxide and catalyst concentration and removal efficiency in several representative small experiments, and also shows the cost of processing 1 L of water after calculation (in US dollars). The cost of each process is the sum of the cost of the catalyst and the oxidizing agent used to achieve an organic removal rate of more than 95%. According to the calculation results, the order of chemical costs from high to low is Fe\(_3\)O\(_4\)/PS, nFe\(_0\)/PS, FeSO\(_4\)·7H\(_2\)O/PS, FeS/PS, Fe\(_2\)O\(_3\)/PS, and Fe\(_0\)/PS. Since the price of the analytical reagent is used as a unit price, the calculation cost is high, and the cost will be reduced in actual engineering. In addition, the difference in the degree of difficult degradation of pollutants also determines that the same system will generate different treatment costs. These data are for reference only for small experimental chemistry costs.

**CONCLUSION AND PROSPECTS**

In summary, a state-of-the-art review is presented on mechanisms, reaction conditions, influencing factors, and treatment effects of iron-based materials for refractory organics degradation via PS activation. The results of recently published articles affirm that activated-PS by
iron-based materials has promising potentials for destruction of refractory organics in water and 100% degradation can be accomplished for some refractory organics under optimized conditions. However, challenges still remain in the improvement of refractory organics degradation rate in actual polluted water treatment using iron-based materials/PS processes, and the practical engineering application of these processes with low costs is also highly anticipated.

The activation performance of iron-based materials can be influenced by the properties and concentrations of activators, pollutants, oxidants, and water quality component along with the reaction conditions (such as pH, temperature, reaction time). Optimization of the experimental conditions is a cornerstone in achieving best removal. Optimization of the experimental conditions (such as pH, temperature, reaction time). Therefore, the key issue is to identify the factors that affect the release of Fe$^{2+}$ and maintain a dynamic balance between Fe$^{2+}$ and Fe$^{3+}$ when using these materials as activators. Novel reactor for the iron-based materials/PS system based on batch or continuous flow need to be designed, and more pilot experiments have yet to be implemented.

In a word, because of the low cost, availability, and environmental friendliness of iron, iron-based materials activation method for PS is expected to have a better prospect with further research in this field.

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### REFERENCES


Naim, S. & Ghauch, A. 2016 Ranitidine abatement in chemically activated persulfate systems: assessment of industrial iron


Wang, X., Du, Y., Liu, H. & Ma, J. 2018 Ascorbic acid/Fe0 composites as an effective persulfate activator for improving the degradation of rhodamine B. *RSC Advances* 8 (23), 12791–12798. https://doi.org/10.1039/C8RA01506F.


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