Synthesis of Novel Core-shell $\text{Fe}^0/\text{Fe}_3\text{O}_4$ as Heterogeneous Activator of Persulfate for Oxidation of Dibutyl Phthalate under Neutral Conditions

Huanxuan Li^{a, b}, Jinquan Wan^{a, b, c*}, Yongwen Ma^{a, b, c}, Yan Wang^{a, b}

^a School of Environment and Energy, South China University of Technology, Guangzhou 510006, PR China

^b The Key Lab of Pollution Control and Ecosystem Restoration in Industry Clusters, Ministry of Education, China, Guangzhou 510006, PR China

^c State Key Lab Pulp and Paper Engineering, South China University of Technology, Guangzhou 510640, PR China

Corresponding author at: School of Environment and Energy, South China University of Technology, Guangzhou 510006, China. E-mail address: ppjqwan@scut.edu.cn (J. Wan).
Tel.: +86 20 87114970, Fax: +86 20 39380560

Abstract: A facile and simple one-step thermal oxidation method was proposed to prepare core-shell $\text{Fe}^0/\text{Fe}_3\text{O}_4$ composites that were acted as an efficient heterogeneous activator of persulfate (PS) for oxidation of dibutyl phthalate (DBP) under neutral conditions. The effects of temperature and reaction time used in the prepared procedure were investigated. The $\text{Fe}^0/\text{Fe}_3\text{O}_4$ composites were characterized using Scanning electron microscopy, X-ray diffraction patterns, Raman spectra and X-ray photoelectron spectroscopy. It was found that the obtained $\text{Fe}^0/\text{Fe}_3\text{O}_4$ composites have been prepared successfully. Catalytic testing showed the $\text{Fe}^0/\text{Fe}_3\text{O}_4$ composites prepared at 400°C for 40 min achieved the highest activity towards PS, which suggested Fe_3O_4 played an important role in the catalytic activity. Increasing PS and $\text{Fe}^0/\text{Fe}_3\text{O}_4$ dosages could accelerate DBP oxidation, 94.7% degradation of DBP was achieved when PS and $\text{Fe}^0/\text{Fe}_3\text{O}_4$

concentrations increased to 1.8 mM and 0.5 g/L, respectively. In addition, $\text{Fe}^0\text{@Fe}_3\text{O}_4$ exhibited excellent reusability according to six consecutive reaction cycles with no obvious loss of catalytic activity. More interestingly, the DBP degradation rate increased in the first three cycles. The mechanism for activating of PS by $\text{Fe}^0\text{@Fe}_3\text{O}_4$ composites involved in their special inter-phase surface which could readily produce $\text{Fe}_{\text{oct}}^{2+}$ species by an efficient electron transfer process that initiated the reaction to generate sulfate radicals ($\text{SO}_4^{\cdot -}$) by a Haber-Weiss mechanism.

Key words: $\text{Fe}^0\text{@Fe}_3\text{O}_4$ composites, Persulfate, Sulfate radicals, Dibutyl phthalate.

1. Introduction

Dibutyl phthalate (DBP), one of phthalic acid esters (PAEs), has received increasing attention in recent years due to its widely used as plasticizer in a variety of industries, including building materials, cosmetics production, transportation, clothing, and medical product packaging [1]. DBP can easily migrate into the environment because it is not chemically bonded to the polymeric materials [2]. Meanwhile, it is prone to accumulate in the soil or sediment and in the aquatic organisms through food chain transmission because of its low solubility in water and high partition coefficients of octanol/water [3]. DBP may be not only estrogenic disrupting compounds (EDCs) but also toxic [4], mutagenic and carcinogenic [5] on the reproductive development even at very low concentration. As a result, both US Environmental Protection Agency and China National Environmental Monitoring Center have classified DBP as a top priority pollutant for risk assessment [6,7]. DBP can be removed by ultrasonic and membrane methods, physical adsorption, microbial degradation and chemical oxidation. However, the results of ultrasonic and membrane methods are inconsistent and still at preliminary stages [8], furthermore, the cost of these methods is expensive. The microbial degradation process is time-consuming, and DBP is poorly degraded

due to its long chains [9]. Adsorptive removal by activated carbon is effective [10], but it simply results in the transport of DBP from one media to another, and therefore does not completely eliminate DBP from the environment; what is more, the cost for the equipment is very high.

Advanced oxidation processes (AOPs) are alternative techniques of destruction of many recalcitrant and toxic compounds in wastewaters, effluents and soils [11-13]. Sulfate radical ($\text{SO}_4^{\cdot -}$, $E^0 = 2.5\text{-}3.1\text{ V}$) [13] induced degradation of refractory contaminants is another developed AOP [14-16] which shows a great potential for the in-situ chemical oxidation (ISCO) for remediation of soil and groundwater. Persulfate (PS) is one of the most widely used oxidants for generating of $\text{SO}_4^{\cdot -}$ by interaction of UV, heat, and transition metal ions [17-19]. Previous studies have indicated that Fe^{2+} is a viable option (Eq. (1)) as a method for accelerating of generating $\text{SO}_4^{\cdot -}$, with high efficiency and no undesired side-products during the oxidation.

However, how to keep suitable Fe^{2+} concentration during the degradation process becomes an enormous obstacle to the Fe^{2+} /PS system [20]. On one hand, the Fe^{2+} /PS system is inappropriate to be operated at neutral pH values due to the hydrolysis and precipitation of Fe^{3+} . On the other hand, Fe^{2+} will react with $\text{SO}_4^{\cdot -}$ at an even higher rate (Eq. (2)) than that of $\text{SO}_4^{\cdot -}$ generation (Eq. (1)) [21,22], which causes the treatment efficiency decline.

Therefore, the potential of alternative catalysts to overcome this drawback and improve the pollutants removal performance is great of interest, making the heterogeneous iron catalyst a good candidate for such a purpose. Heterogeneous iron activators such as zero-valent iron (Fe^0) [23], magnetite (Fe_3O_4) [24], iron hydroxide colloids [25], minerals [26] and other iron oxides have

67 been used to improve the oxidation efficiency with the means of effective utilization of Fe^{2+} . Fe^0
68 has been widely employed because of its high activity towards PS to destroy recalcitrant
69 contaminants including acid orange 7 [23], PCBs [24], and TCE [20]. In addition, Fe^0 can
70 continue to slowly produce Fe^{2+} and overcome the disadvantages of Fe^{2+} as the activator of PS
71 [27].

72 The use of Fe^0 as PS activator has been proved to be highly effective for recalcitrant
73 contaminants removal. However, the direct electron transfer from Fe^0 to produce Fe^{2+} and activate
74 PS is a very slow process in a near neutral pH media, which causes an unsatisfied organic
75 contaminants degradation efficiency. Additionally, our previous research [28] has shown that
76 there is amount of iron oxide layers (Fe_2O_3 , Fe_3O_4 , FeOOH) forming and covering on the surface
77 of Fe^0 accompany with DBP degradation, which strongly influences the further degradation rate of
78 organic contaminants. That is due to that the iron oxides can't activate PS and hinder the electron
79 transfer from Fe^0 core to the solid-liquid interface. However, $\text{Fe-Fe}_2\text{O}_3$ nanostructures have been
80 synthesized and used to activate PS for treatment of organic polluted water more recently [29,30].
81 $\text{Fe}^0/\text{Fe}_3\text{O}_4$ composites also have been showed very high activity for decomposition of H_2O_2 [31].
82 Also, the $\text{Fe}^0@\text{Fe}_3\text{O}_4$ is supposed to show high activity towards PS. Therefore, the understanding
83 of the characteristics of interface between Fe^0 core and iron oxides shell is of great interest to
84 improve the efficiency and widen the application of PS systems in environmental remediation
85 processes. Hence, the feasibility study of PS activated by $\text{Fe}^0@\text{Fe}_3\text{O}_4$ for degradation of DBP and
86 the activation mechanism has been presented in this work.

87 In this paper, $\text{Fe}^0@\text{Fe}_3\text{O}_4$ composites have been prepared by controlled oxidation of Fe^0 with a
88 simple one-step thermal oxidation method that has not been reported to the best of our knowledge.

Fe⁰@Fe₃O₄ composites were completely characterized by Scanning electron microscopy, X-ray diffraction patterns, Raman spectra and X-ray photoelectron spectroscopy measurements. Specifically, the optimal conditions for preparation of Fe⁰@Fe₃O₄ composites, and their reusability and stability were also explored. Based on the systematic results and discussion, the possible mechanism for activation of PS by Fe⁰@Fe₃O₄ to remove DBP in this system was proposed.

2. Materials and methods

2.1 Materials

Details of all chemicals used in this study were included in the Supplementary Material (Text S1) (SI).

2.2 Preparation of Fe⁰@Fe₃O₄ composites

The core-shell Fe⁰@Fe₃O₄ composites were prepared by controlled oxidation of Fe⁰ with H₂O at high temperature. Fe⁰ and H₂O were placed in ceramic boats, respectively, and the ceramic boats were put at the middle of a horizontal quartz tube that was calcined up to the set-up temperature previously. Then the horizontal quartz tube was calcined up on the temperature under high purity nitrogen (99.999%) atmosphere flow (30 mL min⁻¹) for different reaction time. In the preparation process, Fe⁰ was oxidized and converted into Fe₃O₄, and the core-shell Fe⁰@Fe₃O₄ composites were got simultaneously. The oxidation reaction was expressed as follows:

The products were subsequently cooled down under nitrogen (99.999%) atmosphere to room temperature and transferred to a sample vial and kept under nitrogen to avoid slow oxidation by O₂ from the air. Detailed procedures of optimizing preparation conditions for Fe⁰@Fe₃O₄ composites were presented in Text S2 (SI).

2.3 Characterization

The morphologies, crystalline structures, and surface analysis of the prepared core-shell $\text{Fe}^0/\text{Fe}_3\text{O}_4$ composites were measured by Scanning electron microscopy (SEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and Raman spectra. Detailed procedures were described in articles by Li et al [23,28].

2.4 Evaluation of $\text{Fe}^0/\text{Fe}_3\text{O}_4$ reactivity as catalyst

Batch experiments for DBP degradation were performed in 250-mL serum bottles capped with Teflon caps in the dark. In a typical experiment, 100 mL of DBP stock solution (0.018 mM, or 5.0 mg/L) and 0.1 mL of PS stock solution (540 mM) were added simultaneously to the 250-mL Erlenmeyer flask. The initial concentrations of DBP and PS were 0.018 mM and 0.54 mM respectively. After complete mixing, the initial pH value was adjusted to 7.0 with 1.0 M sodium hydroxide (NaOH) or sulfuric acid (H_2SO_4). Then $\text{Fe}^0/\text{Fe}_3\text{O}_4$ (0.05 g) composites were quickly added to the DBP-PS solution. Immediately, the degradation reaction was initiated in a rotary shaker (ZHWY-20102C, Shanghai, China) which was shaken at 180 rpm and $25 \pm 0.2^\circ\text{C}$. At each sampling event, the residual $\text{Fe}^0/\text{Fe}_3\text{O}_4$ composites were separated by magnet block, then 1.0 mL aliquots of reaction solution was taken into a 10-mL serum bottle, and 1.0 mL of ethanol was immediately added to quench the reaction [32]. The sample was filtered through a 0.45- μm nylon membrane filter and analyzed for the concentrations of DBP, Fe^{2+} , and PS. All experiments were carried out in triplicates, the average values and the standard deviations were displayed in the Results and Discussion. To assess the effects of PS and $\text{Fe}^0/\text{Fe}_3\text{O}_4$ dosage on DBP degradation, and the stability and recyclability of $\text{Fe}^0/\text{Fe}_3\text{O}_4$, a series of experiments were carried out, the details of analytic methods were presented in Text S3 (SI).

2.5 Analytical methods

Methods used to quantify DBP concentration, PS concentration and all other analytical measurements and the preparation of DBP contaminant solutions at an initial concentration of approximately 5.0 mg/L (0.018 mM) were described in an article by Li et al [28].

3. Results and discussion

3.1. Characteristics of $\text{Fe}^0 @ \text{Fe}_3\text{O}_4$ prepared under different temperature

3.1.1. Structure of $\text{Fe}^0 @ \text{Fe}_3\text{O}_4$

The chemical compositions and crystallinities of the as-obtained products were studied by X-ray diffraction (XRD) and Raman spectra analysis. As shown in Fig. 1a, metallic iron (JCPDS file No.06-0696) phase with a good degree of crystallinity and Fe_3O_4 (magnetite, JCPDS file No. 19-0629) phase coexisted in the $\text{Fe}^0 @ \text{Fe}_3\text{O}_4$ iron reagent. All the diffraction peaks at 30.5° , 35.7° , 43.1° , 54.2° , 57.7° , and 62.5° can be indexed to the indices (220), (311), (400), (422), (511), and (440) of Fe_3O_4 . Meanwhile, the positions and relative intensities of these reflection peaks agree well with those of Fe_3O_4 particles in the literature [33], which further confirms the existence of Fe_3O_4 in all samples. On the other hand, the relatively strong peaks observed at 44.9° and 65.6° and related to Fe^0 were prominent [34]. And the results are that, as we predicted previously, the intensities of these two peaks reduced along with increasing temperatures. This may be due to the fact that Fe^0 is readily converted to Fe_3O_4 at high temperature in the preparation process. In addition, the peaks intensities of Fe_3O_4 were observed to increase dramatically with increasing the preparation temperature. It can be inferred that the ratio of Fe_3O_4 to Fe^0 in the $\text{Fe}^0 @ \text{Fe}_3\text{O}_4$ composites prepared at high temperature is higher than that at low temperature. Based on the above results, it can be concluded that the $\text{Fe}^0 @ \text{Fe}_3\text{O}_4$ composites are well crystallized and the

materials are prepared successfully. Different from the Fe⁰@Fe₃O₄ prepared under the temperature of 400°C, new peaks assigned to the structure of Fe₂O₃ (hematite, JCPDS file No.25-1402) were detected in the Fe⁰@Fe₃O₄ composites prepared at 500°C and 600°C. This result can only be explained by an oxidation of Fe₃O₄ at high temperatures that are favorable in further oxidation of Fe₃O₄ to the phases Fe₂O₃.

As Fe₃O₄ is rather unstable and is readily reacted with O₂ when expose to air, even at high temperature [35-37]. On the other hand, this result illustrates that a more well crystallized and stable Fe₃O₄ phase is formed to avoid oxidation by oxygen at the temperature of 400°C rather than 500°C and 600°C.

In order to get further insights into the structures of Fe⁰@Fe₃O₄, the prepared composites were measured by Raman spectra, as shown in Fig. 1b. It can be observed that the spectra of sample obtained at 400°C only appeared a low frequency band around 670 cm⁻¹ corresponding to the Fe-O lattice mode of Fe₃O₄ [38], implying the out shell of the composites are pure Fe₃O₄, which is in accordance with XRD analysis. The narrow and sharp peaks at 218 cm⁻¹, 281 cm⁻¹, 398 cm⁻¹, 502 cm⁻¹, and 612 cm⁻¹ are characteristic peaks for Fe₂O₃ as described in another study [39]. Also the broad feature of Raman shift at 1320 cm⁻¹ should be assigned to the second order scattering of α-Fe₂O₃. As can be seen from Fig. 1b, these new bands attributed to α-Fe₂O₃ appeared when the preparation temperature increased to 500°C and 600°C. Also, it is interesting to note that the intensities of all peaks increased rapidly with the increase of temperature, which indicates that the amount of iron oxides as outer shell of the core-shell structured composites increases with higher temperature. This finding is in good agreement with XRD observation. By consideration of the

XRD results and the Raman spectral analysis together, we conclude that the Fe_3O_4 phase gradually forms by thermal treatment of Fe^0 with H_2O and N_2 flow.

To further prove the compositions of the prepared products, as-obtained $\text{Fe}^0/\text{Fe}_3\text{O}_4$ composites were measured by XPS. Fig. 2a shows the survey spectra of $\text{Fe}^0/\text{Fe}_3\text{O}_4$ obtained at different temperatures, and the most significant features were the elements of Fe, O, and adventitious C. The presence of C1s signal may be assigned to the carbon contaminant or carbonate species adsorbed on the surface of $\text{Fe}^0/\text{Fe}_3\text{O}_4$. As shown in the Fe2p XPS spectra (seen in Fig. 2b), all samples showed binding energies of Fe 2p $3/2$ at 709.0 eV and 711.4 eV which are assigned to the lattice Fe^{2+} and Fe^{3+} respectively in Fe_3O_4 , according to the previous study [40]. This clearly shows that Fe^0 is consumed to form the phase Fe_3O_4 in the synthesis process. However, new band at binding energy of 710.8 eV that is attributed to Fe 2p $3/2$ of the lattice Fe^{3+} in $\alpha\text{-Fe}_2\text{O}_3$ ³⁹ appeared while the preparation temperatures were set to 500°C and 600°C. The data are well consistent with XRD and Raman spectral analysis. It has reported that [41] the oxide type oxygen is present at binding energy around 529.5 and 530.6 eV, so the peaks located at 529.8 eV (seen in Fig. 2c) reveal the existence of oxide type oxygen groups in the $\text{Fe}^0/\text{Fe}_3\text{O}_4$ spheres. No obvious signal corresponded to Fe^0 was detected at the low binding energy side of 707 eV in the $\text{Fe}^0/\text{Fe}_3\text{O}_4$ composites. This is ascribed to the high binding energies of Fe2p electrons, which make them hardly emitted with X-ray when they are underneath the composites [31].

3.1.2. Morphology of $\text{Fe}^0/\text{Fe}_3\text{O}_4$

The SEM morphology of prepared $\text{Fe}^0/\text{Fe}_3\text{O}_4$ is showed in Fig. 3 with the same magnification. The $\text{Fe}^0/\text{Fe}_3\text{O}_4$ morphology varied significantly when the preparation temperature was changed. Apparently, the morphology of particles gradually became coarse with the increase of temperature.

This can be further confirmed by detailed SEM morphology where more and more wrinkles were observed on the surface of $\text{Fe}^0/\text{Fe}_3\text{O}_4$ with a temperature increase from 400°C to 600°C. On the other hand, Fig. 3c clearly shows that the as-obtained products were covered by a thin layer which is probably magnetite (Fe_3O_4) according to XRD and Raman spectral analysis. That is why the as-obtained products are typically referred to as “core-shell structured $\text{Fe}^0/\text{Fe}_3\text{O}_4$ ”. The core consists of metallic iron (Fe^0), whereas the outer shell is composed of Fe_3O_4 . As can be seen from the SEM images, the thickness of iron oxides (Fe_3O_4) layer increased with the increase of temperature. Additionally, the EDX analyses (Fig. S1) fully confirms that the composition of as-obtained products comprise Fe and O elements. What is more, the BET surface area of Fe^0 increased after modifying, where the $\text{Fe}^0/\text{Fe}_3\text{O}_4$ composites gave a BET of 3.2174 m^2g^{-1} while the BET surface area of Fe^0 was 2.1518 m^2g^{-1} (Fig. S3).

3.2 Reactivity of $\text{Fe}^0/\text{Fe}_3\text{O}_4$ as PS activator

The reactivity of $\text{Fe}^0/\text{Fe}_3\text{O}_4$ composites as the catalyst of PS was studied by the reaction of degradation of DBP. As a comparison, experiments were carried out in different systems (seen in Fig. 4). It can be clearly seen that less than 10% of DBP was removed from solution over 180 min in the control systems with only PS or $\text{Fe}^0/\text{Fe}_3\text{O}_4$. However, the degradation of DBP became obvious in the system of Fe^0/PS where 67.9% of DBP degradation was observed in 180 min. With addition of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and PS, 14.9% of DBP in aqueous solution was decomposed rapidly within 30 min. Afterward, the decomposition efficiency increased very slightly with longer reaction time. On the contrary, 77.8% of DBP degradation was obtained within 180 min in $\text{Fe}^0/\text{Fe}_3\text{O}_4/\text{PS}$ system. Some researchers have investigated the degradation of organic pollutants in the heterogeneous system. Fang et al. [42] observed that 2,4,4'-trichlorobiphenyl degradation

efficiency was about 70% within 8 h at pH 7.0 in the nano-Fe₃O₄/PS system, but the nano-Fe₃O₄ exhibited no activity after 2h. Also, Wang et al. [43] investigated only about 20% phenol degradation within 180 min on magnetic carbon nanospheres with potassium monopersulfate. Obviously, the Fe⁰@Fe₃O₄ activator greatly enhances PS oxidation efficiency at neutral pH in comparison with other studies. On the other hand, the PS decomposition percentages corresponded to the DBP degradation efficiency in these different systems, as seen in Fig. 4(b). Only 5.1% of PS was remaining in the solutions in Fe⁰@Fe₃O₄/PS system, which further confirms that DBP removal is oxidized by SO₄⁻ rather than adsorbed by Fe⁰@Fe₃O₄.

3.3 Effects of preparation condition on the catalytic activity of Fe⁰@Fe₃O₄

The temperature and reaction time are considered as the most important parameters to influence the structures and properties of Fe⁰@Fe₃O₄, as well as the catalytic activity towards PS. The effects of temperature and reaction time on the degradation of DBP were examined. As seen in Fig. 5a, the preparation temperature of 400°C gave Fe⁰@Fe₃O₄ composites the best activity for PS decomposition, which exhibited a high degradation efficiency (78.9%) of DBP within 180 min. This result may be ascribed to the formation of α-Fe₂O₃ at higher temperatures of 500°C and 600°C according to XRD and Raman Spectral analysis. Because the Fe⁰@Fe₂O₃ composites are remarkably less active towards oxidant compared to Fe⁰@Fe₃O₄ [44]. Another point to be considered to discuss the high reactivity of Fe⁰@Fe₃O₄ is the formation of highly reactive small particles at 400°C during the synthesis procedure. The relatively low temperature, i.e. 400°C is favorable to the formation of small particles on the interface between Fe⁰ and Fe₃O₄, such as wustite (FeO) phase (Eq. (5)) that are well known to present increase reactivity towards electron transfer reactions [37].

Fig. 5b shows the catalyst activity of $\text{Fe}^0/\text{Fe}_3\text{O}_4$ composites prepared at 400°C for different reaction time. As the reaction time shifted from 20 min to 40 min, the removal percentages of DBP increased from 70.0% to 78.9% within 180 min. However, when the reaction time increased to 60 min and 90 min, the DBP degradation dropped to 61.4% and 56.3%, respectively. This phenomenon might be due to formation of optimal ratio of Fe^0 to Fe_3O_4 at 40 min. Alternatively, it is possible that the $\text{Fe}^0/\text{Fe}_3\text{O}_4$ prepared at 400°C with 40 min forms preferred catalyst sites that are particularly susceptible to oxidants attack. Consequently, the subsequent experiments were conducted using the $\text{Fe}^0/\text{Fe}_3\text{O}_4$ composites prepared at 400°C for 40 min.

3.4 Effects of PS and $\text{Fe}^0/\text{Fe}_3\text{O}_4$ dosage on DBP degradation

The influence of PS versus DBP molar ratio ($[\text{PS}]/[\text{DBP}]$) on the DBP degradation was carried out at neutral pH in $\text{Fe}^0/\text{Fe}_3\text{O}_4/\text{PS}$ system. From the results shown in Fig. 6a, it is expected that the concentration of PS appears to be one of the crucial factors affecting the DBP degradation. As the DBP degradation efficiency was noticeable higher at the molar ratio of 10/1 than that of 1/1. PS can be decomposed to generate $\text{SO}_4^{\cdot -}$ with the activation of catalyst, which makes a dominant contribution to the sharply enhanced degradation of organic contaminants. It is reasonable that increasing PS dosage could lead to a higher DBP degradation rate. Consequently, the DBP degradation increased from 60.7%, 78.9%, 89.1% to 94.7% when the molar ratio increased from 20/1, 30/1, 50/1 to 100:1, respectively. However, it is worth noting that the DBP degradation increase was slight when $[\text{PS}]/[\text{DBP}]$ exceed 30/1. The possible explanation is that the excessive $\text{SO}_4^{\cdot -}$ resulted in the well known scavenging of $\text{SO}_4^{\cdot -}$ (Eq. (6)).

$\text{Fe}^0@ \text{Fe}_3\text{O}_4$ serves as activators in the acceleration formation of $\text{SO}_4^{\cdot -}$ in PS oxidation reaction. The amount of $\text{Fe}^0@ \text{Fe}_3\text{O}_4$ was monitored to evaluate the influence on destruction of DBP at pH 7.0. It is evident that (seen in Fig. 6b) the degradation ability of DBP changed with varying $\text{Fe}^0@ \text{Fe}_3\text{O}_4$ dosages. In comparison with the DBP degradation at $\text{Fe}^0@ \text{Fe}_3\text{O}_4$ dosage of 0.1 g/L, there was a considerable accelerating influence when $\text{Fe}^0@ \text{Fe}_3\text{O}_4$ dosage increased to 0.3 g/L. The DBP degradation efficiency achieved 76.9% and 80.1% with $\text{Fe}^0@ \text{Fe}_3\text{O}_4$ dosage of 0.5 g/L and 0.8 g/L, respectively. Interestingly, it is found that there was a drop in DBP degradation rate with further increase of $\text{Fe}^0@ \text{Fe}_3\text{O}_4$ dosage beyond 0.8 g/L. These observations imply that the optimum amount of $\text{Fe}^0@ \text{Fe}_3\text{O}_4$ for achieving the highest DBP degradation efficiency is 0.8 g/L at [PS]/[DBP] molar ratio of 30/1. Most probably, this can be ascribed to the sufficient Fe^{2+} provided by excess $\text{Fe}^0@ \text{Fe}_3\text{O}_4$, which would compete for the $\text{SO}_4^{\cdot -}$ with DBP.

3.5 Reusability of $\text{Fe}^0@ \text{Fe}_3\text{O}_4$

In our previous study [28], it was found that the DBP degradation efficiency decreased with the increase use cycles of Fe^0 . In order to determine the recyclability of modified Fe^0 , $\text{Fe}^0@ \text{Fe}_3\text{O}_4$ were checked by circulating runs in the catalytic degradation of DBP over $\text{Fe}^0@ \text{Fe}_3\text{O}_4/\text{PS}$ systems. The Fig. 7a shows the reusability of $\text{Fe}^0@ \text{Fe}_3\text{O}_4$ for six consecutive reaction cycles after 120 min of reaction. Surprisingly, no obvious loss of the catalytic activity of $\text{Fe}^0@ \text{Fe}_3\text{O}_4$ was observed for DBP decomposition in the first three times. In contrast, it is interesting to note that an enhancement in DBP degradation is presented with the increase of cycles from 1st run to 3rd run, where the removal percentages of DBP increased slightly from 75.2%, 79.2% to 83.8%, respectively. Correspondingly, the consumption of PS in the 2nd run experienced a slight increase, compared to the 1st run (Fig. 7b). The possible explanation is that Fe^{2+} concentration in the

leaching solution of the 2nd run is slightly higher than that of the 1st run (Fig. 7b), which is supposed to facilitate degradation enhancement by homogeneous catalytic oxidation reaction (Eq. (1)). A slight decrease in $\text{Fe}^0\text{@Fe}_3\text{O}_4$ activity was observed after three reaction cycles, the extent of DBP oxidation by PS nearly dropped back to the 1st run for the 5th cycle with a DBP decomposition efficiency of 76.9%.

After catalysis, the $\text{Fe}^0\text{@Fe}_3\text{O}_4$ was analyzed by XRD and Raman spectra. The resulting XRD patterns are depicted in Fig. 7c, it can be seen that the patterns of $\text{Fe}^0\text{@Fe}_3\text{O}_4$ matched very well with that of the fresh prepared $\text{Fe}^0\text{@Fe}_3\text{O}_4$ (Fig. 2a) after two consecutive reaction cycles, confirming that the catalyst is relatively stable structural during the reaction. The small differences were that the peaks intensities of 44.9° and 65.6° corresponding to Fe^0 decreased. Furthermore, both EDX and XPS analysis show that the compositions and structures of the used $\text{Fe}^0\text{@Fe}_3\text{O}_4$ were similar with that of the fresh prepared $\text{Fe}^0\text{@Fe}_3\text{O}_4$ (Figs. S2 and S3) (SI), only the intensities of peaks relative to Fe_3O_4 slightly increased. Moreover, the result of Raman spectra shows that the band at around 670 cm^{-1} assigned to the characteristic band of Fe_3O_4 remained unchanged (Fig. 7d) during the first two cycles. However, new peaks related to Fe_2O_3 noticeably appeared both at XRD pattern (43.2°) and Raman spectra (218 cm^{-1} , 283 cm^{-1} , 398 cm^{-1} and 1320 cm^{-1}) in the samples obtained after the 3rd run. The XRD diffraction peaks of $\text{Fe}^0\text{@Fe}_3\text{O}_4$ composites obtained after the 6th run matched well with the characteristic signals of Fe_3O_4 crystal: 30.5° (311), 53.4° (422), 57.0° (511), and 62.6° (440). However, based on the results of Raman spectra, the $\alpha\text{-Fe}_2\text{O}_3$ phase and the Fe_3O_4 phase coexist in $\text{Fe}^0\text{@Fe}_3\text{O}_4$ composites after 6th run where the signals of $\alpha\text{-Fe}_2\text{O}_3$ with relative spectral intensities showed predominantly. Meanwhile, the intensities of peaks related to Fe^0 and Fe_3O_4 declined significantly while the amount of $\alpha\text{-Fe}_2\text{O}_3$ increased in the sample obtained

after the 6th run, as shown in Fig. 7c. These results clearly illustrate that Fe^0 and Fe_3O_4 are consumed and convert to $\alpha\text{-Fe}_2\text{O}_3$.

3.6 Mechanism for activation of PS by $\text{Fe}^0/\text{Fe}_3\text{O}_4$

It is well-known that Fe^{2+} is the viable specie which can catalyze PS to produce $\text{SO}_4^{\cdot -}$ in the homogeneous systems. However, the concentration of Fe^{2+} releasing from $\text{Fe}^0/\text{Fe}_3\text{O}_4$ composites was less than 2.0 mg/L (Fig. 7b) at the reaction time of 90 min under neutral condition, which is relatively low for activation of PS compared with that of the Fe^{2+}/PS system in this study. Not to mention the DBP degradation rate that was only 21.7% within 90 min in Fe^{2+}/PS system while it was significantly higher in $\text{Fe}^0/\text{Fe}_3\text{O}_4/\text{PS}$ system under the identical condition. These results imply that PS may be activated by $\text{Fe}^0/\text{Fe}_3\text{O}_4$, involving the heterogeneous reaction to form $\text{SO}_4^{\cdot -}$. Furthermore, we previously mentioned that the thickness of Fe^0 in the $\text{Fe}^0/\text{Fe}_3\text{O}_4$ composites was sharply decreased while the amount of Fe_3O_4 increased after six cycles according to the XRD patterns and Raman spectral analysis. That is to say, Fe^0 and Fe_3O_4 involve in the activation reaction in $\text{Fe}^0/\text{Fe}_3\text{O}_4/\text{PS}$ system. In the case of Fe^0 , it is oxidated by PS and Fe^{3+} leaching into the solutions (Eqs. (7)-(8)) and subsequent generation of $\text{SO}_4^{\cdot -}$ with the homogeneous reaction of Fe^{2+} with PS (Eq. (1)) by electron transfer. But the homogeneous reaction makes a small contribution to DBP degradation because of the slow oxidation rate of Fe^0 .

Fe_3O_4 is one of semiconductors with a narrow band gap of 0.1 eV, and shows a very high conductivity with almost metallic character [37,45] that facilitates electron transport. Furthermore, its inverse spinel structure has octahedral sites that could accommodate Fe^{2+} and Fe^{3+} species in a

random order. Therefore, the $\text{Fe}_{\text{oct}}^{3+}$ can be easily reduced to $\text{Fe}_{\text{oct}}^{2+}$ with no structural constrain, and $\text{Fe}_{\text{oct}}^{2+}$ is very reactive in aqueous phase towards PS. Hence, it has been proposed that the core-shell $\text{Fe}^0@ \text{Fe}_3\text{O}_4$ as the activator of PS can promote the electron transfer from the iron compounds to the reaction medium due to the electron transfer from Fe^0 to $\text{Fe}_{\text{magnetite}}^{3+}$ species (Eq. (9)). This is believed to initiate the oxidation reaction on the surface of $\text{Fe}^0@ \text{Fe}_3\text{O}_4$ composites,

accelerating the decomposition of PS to generate $\text{SO}_4^{\cdot -}$. The efficient interface and electron transport between Fe^0 and its oxide has been clearly observed by Regan et al [46]. According to the previous results in this study, this reaction likely takes place on the surface of $\text{Fe}^0@ \text{Fe}_3\text{O}_4$ composites to form probably $\text{Fe}_{\text{oct}}^{2+}$ species and activated PS to produce $\text{SO}_4^{\cdot -}$ via a Haber-Weiss mechanism (Eq. (10)) during the $\text{Fe}^0@ \text{Fe}_3\text{O}_4/\text{PS}$ process.

The concentration of Fe^{2+} at the octahedral sites of magnetite could be improved by the interface reaction (Eq. (11)) between Fe^0 and Fe_3O_4 [37], which had been observed successfully in many

different processes. And it took place along with the formation of oxygen vacancies to make up for the negative charge introduced in the structure [47,48]. On the basis of the above results and discussion, the possible catalytic activation mechanism is proposed to clarify the higher catalytic activity of $\text{Fe}^0@ \text{Fe}_3\text{O}_4$ composites than pure Fe^0 microsphere in the presence of PS (Scheme 1).

4. Conclusion

In this study, a new and simple one-step thermal oxidation method was used to prepare core-shell $\text{Fe}^0@ \text{Fe}_3\text{O}_4$ with Fe^0 , H_2O and high purity nitrogen flow under different conditions

during the prepared procedure. The $\text{Fe}^0/\text{Fe}_3\text{O}_4$ posed a superior catalytic performance towards PS for degradation of DBP at neutral pH values compared with Fe^{2+}/PS and Fe^0/PS systems. Moreover, no obvious loss of the catalytic activity of $\text{Fe}^0/\text{Fe}_3\text{O}_4$ composites was observed for DBP decomposition after five cycles. Interestingly, an enhancement in the DBP degradation efficiency was presented with the increase of cycles from 1st run to 3rd run. We thought that this $\text{Fe}^0/\text{Fe}_3\text{O}_4/\text{PS}$ process involved both homogeneous Fe^{2+} activation reactions in the solution and heterogeneous activation reactions on the $\text{Fe}^0/\text{Fe}_3\text{O}_4$ composites solid surfaces, but the degradation of DBP was predominantly attributable to the heterogeneous activation reactions. The possible mechanism for activation of PS by $\text{Fe}^0/\text{Fe}_3\text{O}_4$ composites was proposed that the high reactivity of $\text{Fe}^0/\text{Fe}_3\text{O}_4$ composites is due to their special inter surface, which can readily produce $\text{Fe}_{\text{oct}}^{2+}$ species by an efficient electron transfer process that initiates the oxidation reaction to generate $\text{SO}_4^{\cdot -}$ by a Haber-Weiss mechanism. The results of these findings not only provide important insights into the development of processes to increase the electron transfer rate from the iron compounds to the reaction medium, but also promote the development of heterogeneous catalysts activating PS technology for oxidation of persistent organic pollutants in water.

Acknowledgments

This work was supported by National Science Foundation of China (Grant No.31570568) State Key Laboratory of Pulp and Paper Engineering (201535) Guangdong High level talent project (201339).

Supplementary material

Supplementary materials associated with this article can be found, in the online version.

References

375 [1] J.H. Niazi, D.T. Prasad, T.B. Karegoudar, Initial degradation of dimethylphthalate by esterases
376 from *Bacillus* species, *FEMS Microbiol Lett.* 196 (2001), 201-205.

377 [2] M. Marega, K. Grob, S. Moret, L. Conte, Phthalate analysis by gas chromatography–mass
378 spectrometry: Blank problems related to the syringe needle, *J. Chromatogr., A* 1273 (2013),
379 105-110.

380 [3] C.S. Chiou, J.L. Shie, C.Y. Chang, C.C. Liu, C.T. Chang, Degradation of di-n-butyl phthalate
381 using photoreactor packed with TiO₂ immobilized on glass beads, *J. Hazar. Mater., B* 137 (2006)
382 1123-1129.

383 [4] J.L. Lyche, A.C. Gutleb, Å. Bergman, G.S. Eriksen, A.J. Murk, E. Ropstad, M. Saunders, J.U.
384 Skaare, Reproductive and Developmental Toxicity of Phthalates, *J. Toxicol. Environ. Health, Part*
385 *B: Critical Reviews.* 12 (2009), 225-249.

386 [5] M. Ghisari, E.C. Bonefeld-Jorgensen, Effects of plasticizers and their mixtures on estrogen
387 receptor and thyroid hormone functions, *Toxicol. Lett.* 189 (2009), 67-77.

388 [6] United States Environmental Protection Agency, Fate of priority pollutants in publicly owned
389 treatment works, Final report, EPA 440/1-82/303 (1982).

390 [7] C.A. Staple, D.R. Peterson, T.F. Parkerton, W.J. Adams, The environmental fate of phthalate
391 esters: A literature review, *Chemosphere* 35 (1997) 667-749.

392 [8] M. Bodzek, M. Dudziak, K. Luks-Betlej, Application of membrane techniques to water
393 purification. Removal of phthalates, *Desalination* 162 (2004) 121-128.

394 [9] J. Ejlertsson, M. Alnervik, S. Jonsson, B.H. Svensson, Influence of Water Solubility,
395 Side-Chain Degradability, and Side-Chain Structure on the Degradation of Phthalic Acid Esters
396 under Methanogenic Conditions, *Environ. Sci. Technol.* 31 (1997) 2761-2764.

- 397 [10] C.Y. Chen, C.C. Chen, Y.C. Chung, Removal of phthalate esters by α -cyclodextrin-linked
398 chitosan bead, *Bioresour. Technol.* 98 (2007) 2578-2583.
- 399 [11] G.P. Anipsitakis, D.D. Dionysiou, Degradation of Organic Contaminants in Water with
400 Sulfate Radicals Generated by the Conjunction of Peroxymonosulfate with Cobalt, *Environ. Sci.*
401 *Technol.* 37 (2003) 4790-4797.
- 402 [12] X.G. Duan, H.Q. Sun, J. Kang, Y.X. Wang, S. Indrawirawan, S.B. Wang, Insights into
403 heterogeneous catalysis of persulfate activation on dimensional-structured nanocarbons, *ACS*
404 *Catal.* 5 (2015) 4629-4636.
- 405 [13] P. Neta, R.E. Huie, A.B. Ross, Rate constants for reactions of inorganic radicals in aqueous
406 solution, *J. Phys. Chem.* 17 (1998) 1027-1082.
- 407 [14] S. Bougie, J.S. Dube, Oxidation of dichlorobenzene isomers with the help of thermally
408 activated sodium persulfate, *J. Environ. Eng. Sci.* 6 (2007) 397-407.
- 409 [15] H.Q. Sun, G.L. Zhou, S.Z. Liu, H.M. Ang, M.O. Tadé, S.B. Wang, Nano-Fe⁰ encapsulated in
410 carbon spheres for oxidation of aqueous phenol with sulphate radicals, *ACS-Appl. Mater.*
411 *Interface.* 4 (2012) 6235-6241.
- 412 [16] H.X. Li, J.Q. Wan, Y.W. Ma, Y. Wang, Z.Y. Guan, Role of inorganic ions and dissolved
413 natural organic matters on persulfate oxidation of acid orange 7 with zero-valent iron, *RSC Adv.* 5
414 (2015) 99935-99943.
- 415 [17] M.G. Antoniou, A.A. Delacruz, D.D. Dionysiou, Degradation of microcystin-LR using
416 sulfate radicals generated through photolysis, thermolysis and e- transfer mechanisms, *Appl.*
417 *Catal., B* 96 (2010) 290-298.
- 418 [18] J.Y. Fang, C. Shang, Bromate Formation from Bromide Oxidation by the UV/Persulfate

419 Process, Environ. Sci. Technol. 46 (2012) 8976-8983.

420 [19] H.V. Lutze, N. Kerlin, T.C. Schmidt, Sulfate radical-based water treatment in presence of
 421 chloride: Formation of chlorate, inter-conversion of sulfate radicals into hydroxyl radicals and
 422 influence of bicarbonate, Water Res. 72 (2015) 349-360.

423 [20] C.J. Liang, C.J. Bruell, M.C. Marley, K.L. Sperry, Persulfate oxidation for in situ remediation
 424 of TCE. II. Activated by chelated ferrous ion. Chemosphere, Chemosphere 55 (2004)1225-1233.

425 [21] G.V. Buxton, T.N. Malone, G.A. Salmon, Reaction of $\text{SO}_4^{\cdot-}$ with Fe^{2+} , Mn^{2+} and Cu^{2+} in
 426 aqueous solution, J. Chem. Soc., Faraday Trans. 93 (1997) 2893-2897.

427 [22] O.A. Travina, Y.N. Kozlov, A.P. Pural, I.Y. Rod'ko, Synergism of the action of the sulfite
 428 oxidation initiators, iron and peroxydisulfate ions, Russ. J. Phys. Chem. 73 (1999) 1215-1219.

429 [23] H.X. Li, J.Q.Wan, Y.W. Ma, Y. Wang, Y.M. Chen, Influence of particle size of zero-valent
 430 iron and dissolved silica on the reactivity of activated persulfate for degradation of acid orange 7,
 431 Chem. Eng. J. 237 (2014) 487-496.

432 [24] G.D. Fang, D.D. Dionysiou, S.R. Al-Abed, D.M. Zhou, Superoxide radical driving the
 433 activation of persulfate by magnetite nanoparticles: implications for the degradation of PCBs,
 434 Appl. Catal., B 129 (2013) 325-332.

435 [25] J.C. Yan, L.H. Zhu, Z.H. Luo, Y.F. Huang, H.Q. Tang, M.F. Chen, Oxidative decomposition
 436 of organic pollutants by using persulfate with ferrous hydroxide colloids as efficient
 437 heterogeneous activator, Sep. Purif. Technol. 106 (2013) 8-14.

438 [26] M. Ahmad, A.L. Teel, R.J. Watts, Persulfate activation by subsurface minerals, J. Contam.
 439 Hydrol. 115 (2010) 34-45.

440 [27] S.Y. Oh, H.W. Kim, J.M. Park, H.S. Park, C. Yoon, Oxidation of polyvinyl alcohol by

441 persulfate activated with heat, Fe^{2+} , and zero-valent iron, J. Hazar. Mater. 168 (2009) 346-351.

442 [28] H.X. Li, J.Q. Wan, Y.W. Ma, M.Z. Huang, Y. Wang, Y.M. Chen, New insights into the role
443 of zero-valent iron surface oxidation layers in persulfate oxidation of dibutyl phthalate solutions,
444 Chem. Eng. J. 250 (2014) 137-147.

445 [29] Z.H. Ai, L.R. Lu, J.P. Li, L.Z. Zhang, J.R. Qiu, M.H. Wu, Fe- Fe_2O_3 core-shell nanostructures
446 as the iron reagent. 2. An efficient and reusable sono-Fenton system working at neutral pH, J. Phys.
447 Chem., C 111 (2007) 7430-7436.

448 [30] L.L. Zhu, Z.H. Ai, W.K. Ho, L.Z. Zhang, Core-shell Fe- Fe_2O_3 nanostructures as effective
449 persulfate activator for degradation of methyl orange, Sep. Purif. Technol. 108 (2013) 159-165.

450 [31] Q. Wang, W.J. Jia, J. Guo, J. Zhang, Controllable synthesis and magnetic property of
451 Fe/ Fe_3O_4 polyhedron synthesized by solvothermal method, J Mater Sci: Mater Electron. 23 (2012)
452 1527-1532.

453 [32] G.P. Anipsitakis, D.D. Dionysiou, Radical generation by the interaction of transition metals
454 with common oxidants, Environ. Sci. Technol. 38 (2004) 3705-3712.

455 [33] T. Wang, L.Y. Zhang, H.Y. Wang, W.H. Yang, Y.C. Fu, W.L. Zhou, W.T. Yu, K.S. Xiang, Z.
456 Su, S. Dai, L.Y. Chai, Controllable Synthesis of Hierarchical Porous Fe_3O_4 Particles Mediated by
457 Poly(diallyldimethylammonium chloride) and Their Application in Arsenic Removal, Appl. Mater.
458 Interfaces. 5 (2013) 12449-12459.

459 [34] W. Wang, M.H. Zhou, Z.H. Jin, T.L. Li, Reactivity characteristics of poly(methyl
460 methacrylate) coated nanoscale iron particles for trichloroethylene remediation, J. Hazard. Mater.
461 173 (2010) 724-730.

462 [35] American Ceramic Society, CERAM Research (Firm), Cambridge Scientific Abstracts, Inc,

463 Ceramic Abstracts, Cambridge Scientific Abstracts, 79 (2000) 2-3.

464 [36] Q. Imtiaz, N.S. Yuzbasi, P.M. Abdala, A.M. Kierzkowska, W. van Beek, M. Broda, C.R.
 465 Muller, Development of MgAl₂O₄-stabilized, Cu-doped, Fe₂O₃-based oxygen carriers for
 466 thermochemical water-splitting, J. Mater. Chem. A 4 (2016) 113-123.

467 [37] Regina C.C. Costa, Flávia C.C.Moura, J.D. Ardisson, J.D. Fabris, R.M. Lago, Highly active
 468 heterogeneous Fenton-like systems based on Fe⁰/Fe₃O₄ composites prepared by controlled
 469 reduction of iron oxides, Appl. Catal., B 83 (2008) 131-139.

470 [38] Y.S. Li, J.S.Church, A.L. Woodhead, Infrared and Raman spectroscopic studies on iron oxide
 471 magnetic nano-particles and their surface modifications, J. Magn. Mater. 324 (2012)
 472 1543-1550.

473 [39] B. Orberger, C. Wagner, R. Wirth, E. Quirico, J.P. Gallien, C. Derré, G. Montagnac, A. Noret,
 474 M. Jayananda, M. Massault, V. Rouchon, Origin of iron oxide spherules in the banded iron
 475 formation of the Bababudan Group, Dharwar Craton, Southern India, J. Asian Earth Sci. 52 (2012)
 476 31-42.

477 [40] A.P. Grosvenor, B.A. Kobe, M.C. Biesinger, N.S. McIntyre, Investigation of multiplet
 478 splitting of Fe 2p XPS spectra and bonding in iron compounds, Surf. Interface Anal. 36 (2004)
 479 1564-1574.

480 [41] P. Ghods, O.B. Isgor, J.R. Brown, F. Bensebaa, D. Kingston, XPS depth profiling study on
 481 the passive oxide film of carbon steel in saturated calcium hydroxide solution and the effect of
 482 chloride on the film properties, Appl. Surf. Sci. 257 (2011) 4669-4677.

483 [42] G.D. Fang, D. D. Dionysiou, D.M. Zhou, Y. Wang, X.D. Zhu, J.X. Fan, L. Cang, Y.J. Wang,
 484 Transformation of polychlorinated biphenyls by persulfate at ambient temperature, Chemosphere

90 (2013) 1573-1580.

[43] Y.X. Wang, H.Q. Sun, H.M. Ang, M.O. Tadé, S.B Wang, Synthesis of magnetic core/shell carbon nanosphere supported manganese catalysts for oxidation of organics in water by peroxymonosulfate, *J. Colloid Interface Sci.* 433 (2014) 68-75.

[44] Flávia C.C. Moura, G.C. Oliveira, H.M. Araujo, José D. Ardisson, Waldemar A.A. Macedo, R.M. Lago, Highly reactive species formed by interface reaction between Fe^0 -iron oxides particles: An efficient electron transfer system for environmental applications, *Appl. Catal., A* 307 (2006) 195-204.

[45] S. Asuhan, H.L Wan, S. Zhao, W. Deligeer, H.Y. Wu, L. Song, O. Tegus, Water-soluble, mesoporous Fe_3O_4 : Synthesis, characterization, and properties, *Ceram. Int.* 38 (2012) 6579-6584.

[46] T.J. Regan, H. Ohldag, C. Stamm, F. Nolting, J. Luning, J. Stohr, R.L. White, Chemical effects at metal/oxide interfaces studied by x-ray-absorption spectroscopy, *Phys. Rev. B* 64 (2001) 214422.

[47] N. Berdunov, S. Murphy, G. Mariotto, I.V. Shvets, Atomically resolved spin-dependent tunneling on the oxygen-terminated Fe_3O_4 (111), *Phys. Rev. Lett.* 93 (2004) 057201.

[48] E. Sikora, D.D. Macdonald, The passivity of iron in the presence of ethylenediaminetetraacetic acid I. General electrochemical behavior, *J. Electrochem. Soc.* 147 (2000) 4087-4092.

Figures

Fig.1 XRD patterns and Raman Spectra of Fe⁰@Fe₃O₄ obtained at different temperature for 40 min (a) XRD patterns,

(b) Raman Spectra.

Fig. 2. The XPS spectra of the as-prepared Fe⁰@Fe₃O₄ composites at different temperature for 40 min: (a) survey; (b)

Fe 2p; (c) O1s.

Fig. 3. SEM images of the prepared $\text{Fe}^0@ \text{Fe}_3\text{O}_4$ under different temperature for 40 min (a): 400°C, (b): 500°C, (c): 600°C; the detailed SEM morphology (d): 400°C, (e): 500°C, (f): 600°C.

Fig. 4. (a) The degradation of DBP versus time in different systems at neutral condition; (b) The PS remaining at 180 min in different systems at neutral condition. Experiment condition: PS = 0.54 mM; DBP = 0.018 mM; Fe⁰@ Fe₃O₄ (400°C, 40 min) = 0.5 g/L; Fe⁰ = 0.5 g/L; FeSO₄·7H₂O = 2.48 g/L; pH = 7.0 ± 0.1; T = 25 °C.

Fig. 5. (a) Effect of temperature on the DBP degradation; (b) Effect of reaction time on the DBP degradation. Experiment condition: PS = 0.54 mM; DBP = 0.018 mM; Fe⁰@Fe₃O₄ = 0.5 g/L; pH = 7.0 ± 0.1; T = 25 °C.

Fig. 6. (a) Effect of PS dosage on the DBP degradation; (b) Effect of $\text{Fe}^0 @ \text{Fe}_3\text{O}_4$ dosage (400°C, 40 min) on the DBP degradation. Experiment condition: PS = 0.54 mM; DBP = 0.018 mM (only for Fig. 5b); $\text{Fe}^0 @ \text{Fe}_3\text{O}_4$ = 0.5 g/L (only for Fig. 5a); pH = 7.0 ± 0.1 ; T = 25 °C.

Fig. 7. (a) Catalyst recycling on degradation of DBP; (b) The variation of Fe^{2+} and PS during reaction cycles; (c) XRD patterns for $\text{Fe}^0 @ \text{Fe}_3\text{O}_4$ after reaction cycles; (d) Raman spectra for $\text{Fe}^0 @ \text{Fe}_3\text{O}_4$ after reaction cycles. Experiment condition: PS = 0.54 mM; DBP = 0.018 mM; $\text{Fe}^0 @ \text{Fe}_3\text{O}_4$ (400°C, 40 min) = 0.5 g/L; pH = 7.0 ± 0.1 ; T = 25 °C.

67

Scheme 1 Possible mechanism for activation of PS by $\text{Fe}^0/\text{Fe}_3\text{O}_4$ was proposed.

68

Graphical Abstract