



Enhanced degradation of 2,4-dichlorophenoxyacetic acid by pre-magnetization Fe-C activated persulfate: Influential factors, mechanism and degradation pathway

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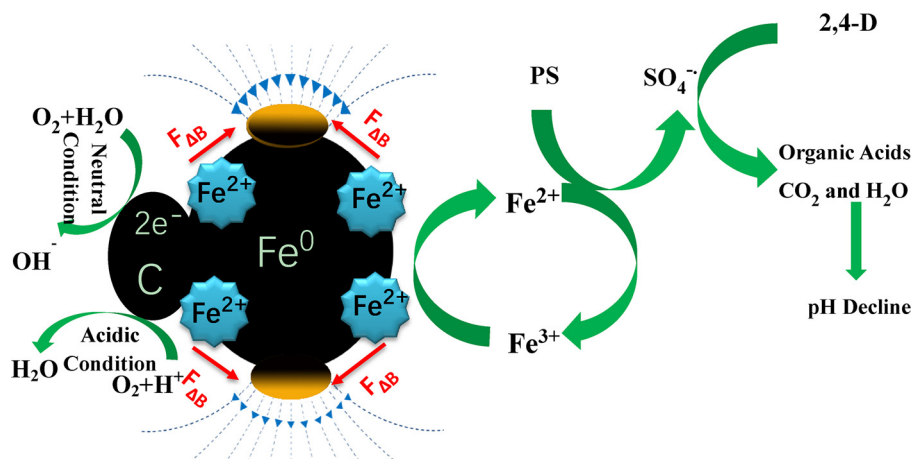
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GRAPHICAL ABSTRACT



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ABSTRACT

2,4-dichlorophenoxyacetic acid (2,4-D) is one of the most applicable herbicides in the world, its residue in aquatic environment threatens the human health and ecosystems. In this study, for the first time, inexpensive Fe-C after pre-magnetization (Pre-Fe-C) was used as the heterogeneous catalyst to activate persulfate (PS) for 2,4-D degradation, proving that Pre-Fe-C could significantly improve the degradation and dechlorination. The results indicated the stability and reusability of Pre-Fe-C were much better than pre-magnetization Fe⁰ (Pre-Fe⁰), while the leaching iron ion was lower, indicating that using Pre-Fe-C not only reduced the post-treatment cost, but also enhanced the removal and dechlorination efficiency of 2,4-D. Several important parameters including initial pH,

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Fe-C dosage, PS concentration affecting 2,4-D degradation and dechlorination by Pre-Fe-C/PS were investigated and compared with that of Fe-C/PS, observing a 1.2–2.7 fold enhancement in the degradation rate of 2,4-D. The Fe-C and Pre-Fe-C were characterized by scanning electron microscopy (SEM), energy dispersive X-ray (EDX) and SEM-EDX-mapping, suggesting that the content of Fe and O changed more obviously after magnetization. The degradation intermediates, such as chloroquinol, 2-chlorophenol, were identified by a gas chromatography mass spectrometry (GC/MS) and an ion chromatography (IC), and a possible degradation pathway was proposed.

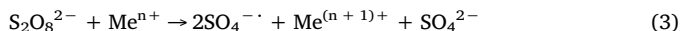
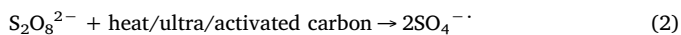
1. Introduction

2,4-dichlorophenoxyacetic acid (2,4-D), a common herbicide and plant growth regulator, has been widely used to control annual and perennial broad-leaved weeds and increase agricultural productivity in recent decades [1]. 2,4-D is a toxic and persistent substance which is classified as an endocrine disruptor for human [2,3]. It has been reported that the presence of 2,4-D in water resource causes various health impacts on animals and humans [4,5]. Furthermore, due to its non-volatility and poor biodegradability, 2,4-D has been frequently detected in both surface water and groundwater around the world [6]. Hence, to efficiently treat the water contaminated with this kind of pollutant, powerful degradation methods are required.

Recently, several methods have been applied to remove 2,4-D from water, such as adsorption [7–9], photodegradation [10], biological degradation [1,11], electrochemical degradation [12–14] and advanced oxidation processes (AOPs) [15–17]. Among the above methods, AOPs can effectively degrade recalcitrant components by free radicals, among which hydroxyl radical ($\cdot\text{OH}$) is the one of the most important oxidative agent ($E^\circ = 2.7\text{ V}$). Though $\cdot\text{OH}$ could oxidize many organic compounds, the process applications has been limited by factors such as the short life span and restricted pH (Fenton reaction) [18]. Presently, sulfate radical ($\text{SO}_4^{\cdot-}$), as a powerful oxidant with $E^\circ = 2.5\text{--}3.1\text{ V}$, has been paid more attention to the removal of organic contaminants [19–21]. It is non-selective and effective for the oxidation of organic pollutants [22] and could be generated by the activation of persulfate (PS) by the following Eq. (1) [23–26].



PS can be activated by different methods to produce the sulfate radicals [27]. These methods include the use of ultraviolet [28], heat [29], transition metal ions [30], such as Co^{2+} and Fe^{2+} , and activated carbon [31] as shown in Eqs. (2)–(3). Since they are relatively inexpensive, nontoxic and effective, iron species have been widely used in water and wastewater treatment. Although Fe^{2+}/PS could achieve rapid degradation of recalcitrant organic pollutants [32], Fe^{2+} would be rapidly oxidized to form Fe^{3+} , resulting in poor utilization of PS and iron in a homogeneous process. Moreover, excess Fe^{2+} will consume the generated sulfate radicals via Eq. (4) [33].

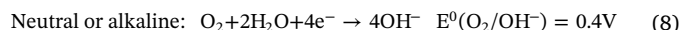
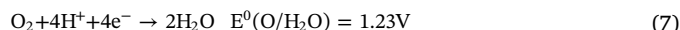
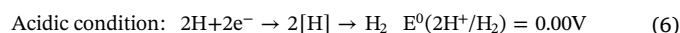


Hence, many heterogeneous PS catalysts have been extensively investigated [34–37], among which iron and its oxides and their composites have been much concerned [38–42]. Because of low cost, no electricity consumption and high efficiency, Fe-C micro-electrolysis has been widely used to treatment of various wastewaters [43–46]. In the Fe-C micro-electrolysis system, a large number of microscopic galvanic cells are formed between Fe and C, and then Fe(II) and [H] are formed during the corrosion reaction, which are highly active and can easily decompose most of organic pollutants. The major reactions associated with Fe activation of C are expressed in Eqs. (5)–(8).

Anodic:



Cathodic:



In addition, coagulation, co-precipitation and adsorption reactions can also remove organic compounds [47]. Nevertheless, it could not completely degrade most of organic contaminants. Hence, Fe-C micro-electrolysis requires improvement (e.g., combination with PS) to become an efficient, versatile, and adaptive alternative for the treatment of organic wastewater. In addition, Fe is a kind of ferromagnetic material which can sustain their magnetization properties (magnetic memory) after being exposed to magnetic field of certain intensity [48], our previous work has shown that taking advantage of the magnetic memory of Fe (pre-magnetization) could

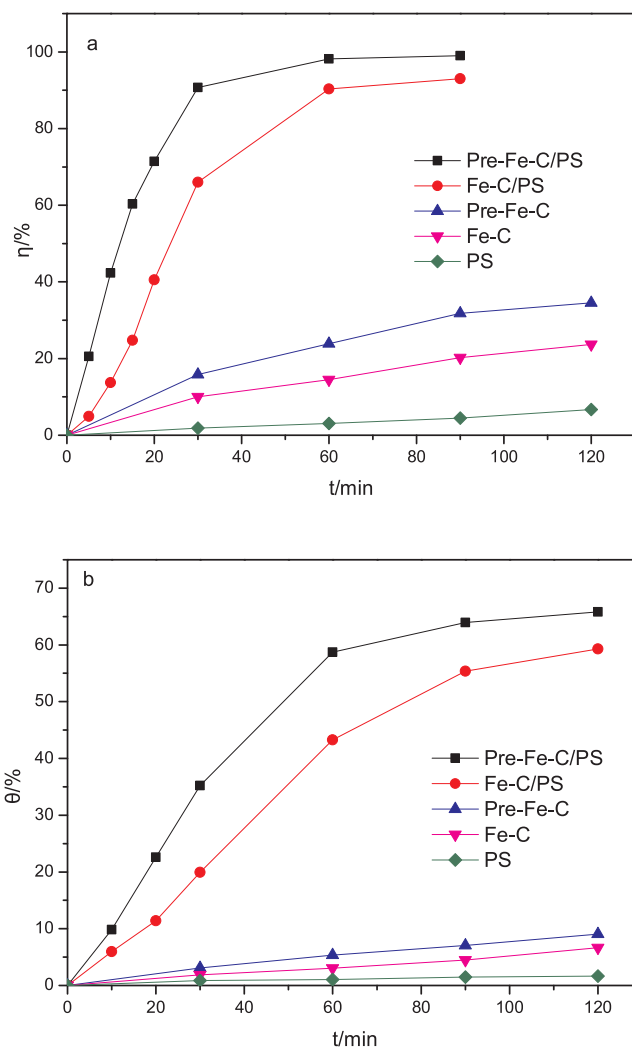


Fig. 1. Removal and dechlorination of 2,4-D by PS, Fe-C alone or pre-Fe-C alone and by Fe-C/PS process and pre-Fe-C/PS process.

Reaction conditions: 2,4-D 20 mg/L, PS 1 mM, Fe-C 0.5 g/L, pH 3.

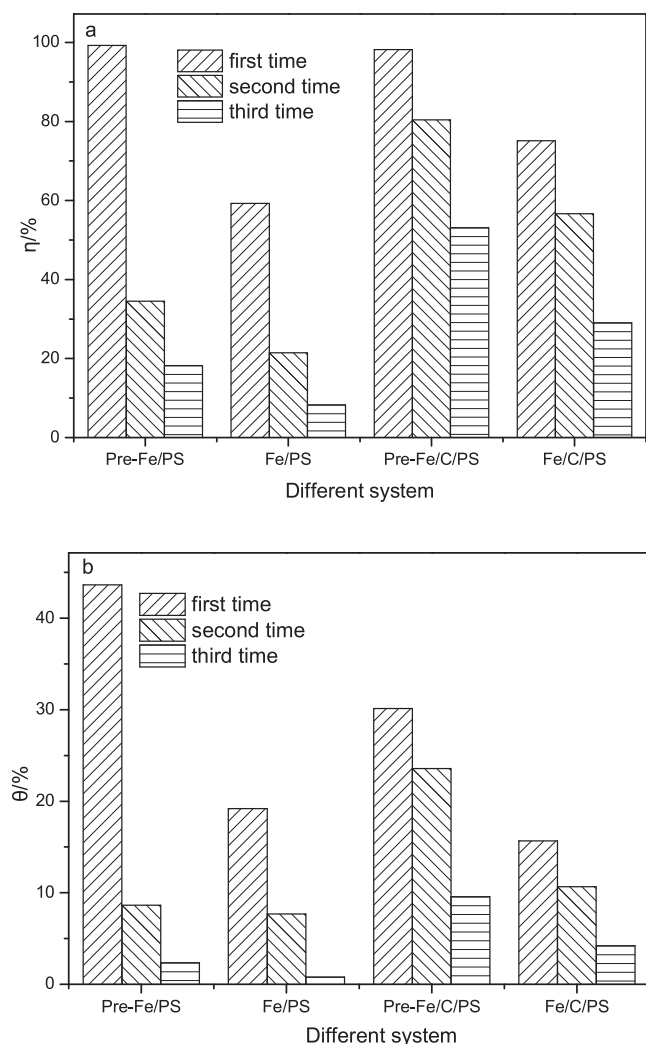


Fig. 2. Removal of 2,4-D by Fe-C/PS and Fe⁰/PS process. (a) the removal efficiency of 2,4-D, (b) the dechlorination efficiency of 2,4-D.

Reaction conditions: 2,4-D 20 mg/L, PS 1 mM, Fe-C 0.102 g/L, Fe⁰ 1 mM, pH 7.

improve the ability of the Fe⁰ to degrade the organic pollutants [49–51]. However, to the best of our knowledge, there are no studies using pre-magnetization to improve the reactivity of Fe-C (Fe-C is composed of iron, tiny carbon particles and other impurities through sinter at high temperature) to catalyze persulfate to degrade pollutants.

In this context, a novel method (Pre-Fe-C/PS) was proposed to investigate the 2,4-D degradation and dechlorination in the present work. The objects of this study were to (1) explore the feasibility and advantages of Pre-Fe-C/PS system; (2) investigate important parameters affecting 2,4-D degradation and dechlorination; (3) disclose possible 2,4-D degradation and dechlorination mechanism based on intermediates identification and Fe-C characterization.

2. Experimental

2.1. Chemicals

2,4-D was purchased from Aladdin chemistry Co., Ltd. (Tianjin, China). Fe-C was obtained from Shandong Huayun Huanbao Co., Ltd (Shandong, China) with Fe content of about 50–55%. Methanol and acetic acid were purchased from Aladdin chemistry Co., Ltd. (Tianjin, China), which were HPLC grade. PS, H₂SO₄ and NaOH were purchased

from the Sinopharm Group Chemical Reagent Co., Ltd. (Shanghai, China). All solutions were prepared with deionized water.

2.2. Experimental procedures

The method of Pre-Fe-C/PS was as same as our previous work [49]. Batch experiments were conducted to explore the influences of initial pH (3–10), PS dosage (0.5–2.0 mM), and Fe-C dosage (0.125–0.75 g/L) on the performance of 2,4-D degradation by Fe-C/PS and Pre-Fe-C/PS. NaOH (0.1 mol/L) and H₂SO₄ (0.1 mol/L) were used to adjusted initial pH value. The solution was mixed by a mechanical stirrer at 350 rpm during the reaction. At the given intervals, about 2.5 mL solutions was sampled by plastic syringes and filtered through a 0.22 μm membrane filter.

2.3. Analytical methods

The concentration of 2,4-D was analyzed by a high performance liquid chromatograph (HPLC Dionex Ultimate 3000, USA) on a C18 column (3 μm, φ 3.0 × 100 mm) at a flow rate of 0.3 mL min⁻¹ and the UV detector was set at 280 nm. The mobile phase was methanol/water/acetic acid (v/v/v) at 60:38:2. The concentrations of Fe²⁺ were determined by spectrophotometric method at 510 nm after complexing with 1,10-phenanthroline. Energy Dispersive X-ray Detector (EDX) was analyzed by EDAX Inc. GENESIS. The morphology of elements on the surface of Fe-C was examined using a scanning electron microscope (SEM) (SHIMADZU SS-550). Cl⁻ was quantified by ion chromatograph (Dionex ICS-900, USA) using an IonPac AS11-HC (Φ4 × 250 mm) column and DS5 conductivity detector. The degradation intermediates were detected by GC-MS (Agilent, 5975 C, USA) equipped with an electrospray ionization (ESI) source and a HP-5MS (0.25 μm, 30 m × 0.25 mm) column. Helium gas was used as the carrier gas at a flow rate of 1.0 mL min⁻¹. Programmed column temperatures were performed as follows: 35 °C held for 1 min; 10 °C/min to 300 °C, held for 1 min. Injection volume was set to 1 μL. Sample injector and detector temperature were 280 °C. Identification and analysis of compounds were carried out with the help of a list database.

The removal efficiency of 2,4-D (η/%), dechlorination efficiency (θ/%) was calculated by Eq. (9) and Eq. (10), respectively.

$$\eta/\% = \frac{c_0 - c_t}{c_0} \times 100 \quad (9)$$

$$\theta/\% = \frac{b_t}{b_0} \times 100 \quad (10)$$

Where c_0 , c_t is the concentration of 2,4-D at initial and given time t , respectively. b_0 is the theoretical concentration of Cl⁻ in solution and b_t is the concentration of Cl⁻ in solution at reaction time t .

The 2,4-D degradation rate constants were calculated using an apparent first order reaction equation, as shown in Eq. (11). Eq. (12) was used to calculate the promotion of reaction rate constant between Pre-Fe-C/PS and Fe-C/PS system.

$$\ln C_t = kt + \ln C_0 \quad (11)$$

$$f = \frac{k_1}{k_2} \quad (12)$$

Where k is the degradation rate constant and t is the reaction time. f is the ratio of k between Pre-Fe-C/PS process and Fe-C/PS process, k_1 is the rate constant of Pre-Fe-C/PS process and k_2 is the rate constant of Fe-C/PS process.

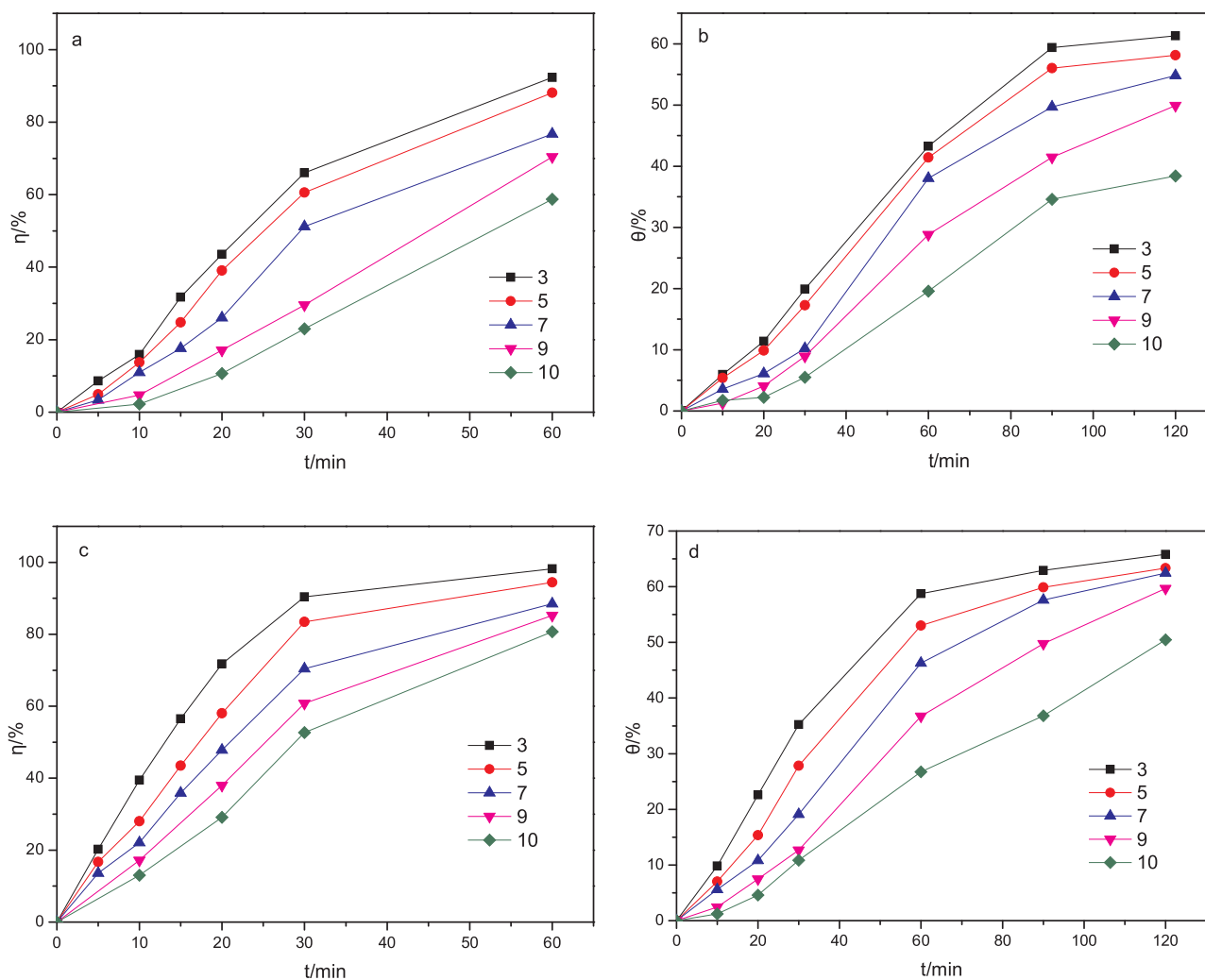


Fig. 3. Influence of 2,4-D removal at different initial pH (a Removal efficiency of 2,4-D by Fe-C/PS system, b The dechlorination efficiency by Fe-C/PS system, c Removal efficiency of 2,4-D by Pre-Fe-C/PS, d The dechlorination efficiency by Pre-Fe-C/PS system). Reaction conditions: 2,4-D 20 mg/L, PS 1.0 mM, Fe-C 0.25 g/L.

3. Results and discussion

3.1. Performance of Pre-Fe-C

Fig. 1 shows the removal and dechlorination efficiency of 2,4-D by Fe-C, Pre-Fe-C, PS, Fe-C/PS and Pre-Fe-C/PS system, respectively. In control experiments, it was found that only a small fraction of 2,4-D (about 6%) was removed by PS alone at 120 min, indicating that no free radical was generated in the absence of catalyst and 2,4-D could be hardly oxidized by PS alone [52]. The removal efficiency of 2,4-D was respectively 23.1% and 35.2% by Fe-C and Pre-Fe-C within 120 min, illustrating that Fe-C micro-electrolysis could remove a part of 2,4-D and pre-magnetization would promote the removal of 2,4-D by micro-electrolysis. However, 90.0% 2,4-D was removed by Fe-C/PS system at 60 min. Surprisingly, the reaction was further greatly accelerated in Pre-Fe-C/PS system, in which 90.0% of 2,4-D removal was achieved within 30 min. These phenomena showed that Fe-C could act as a good provider of iron ion for the activation of PS.

As shown in Fig. 1(b), the dechlorination efficiency of 2,4-D was consistent with the removal efficiency. No chlorine ion was detected in solution, i.e., almost no dechlorination was taken place by PS alone.

After 120 min reaction, the dechlorination efficiency in Fe-C and Pre-Fe-C system was only 7.0% and 11.0%, while, in Fe-C/PS and Pre-Fe-C/PS system, it was much higher, 58.0% and 66.0%, respectively, illustrating that Fe-C could activate PS and Pre-Fe-C could significantly enhance the efficiency to activate PS.

The data presented in Table S1 indicates that the pre-magnetization can improve the reaction rate constants with and without PS. The k_2 was only $2.9 \times 10^{-3} \text{ min}^{-1}$ in Fe-C system, whereas, in Pre-Fe-C system, it was 1.2 folds of that by Fe-C process, which increased to $3.6 \times 10^{-3} \text{ min}^{-1}$. When added PS to system, 2,4-D was removed by micro-electrolysis and advanced oxidation process. Therefore, the k_1 was greatly improved, it was 0.031 min^{-1} and 0.068 min^{-1} by Fe-C/PS and Pre-Fe-C/PS system, respectively.

3.2. Comparison on the reusability of Fe⁰ and Fe-C

In order to compare the properties of 2,4-D removal by Fe⁰ and Fe-C, the degradation of 2,4-D was studied when Fe⁰ and Fe-C (Fe content is roughly the same with Fe⁰) are reused 3 times under neutral conditions. As shown in Fig. 2 (a) and Table S2, in the first cycle, the degradation of 2,4-D by Pre-Fe⁰/PS and Fe⁰/PS Fe⁰ was very rapid, in

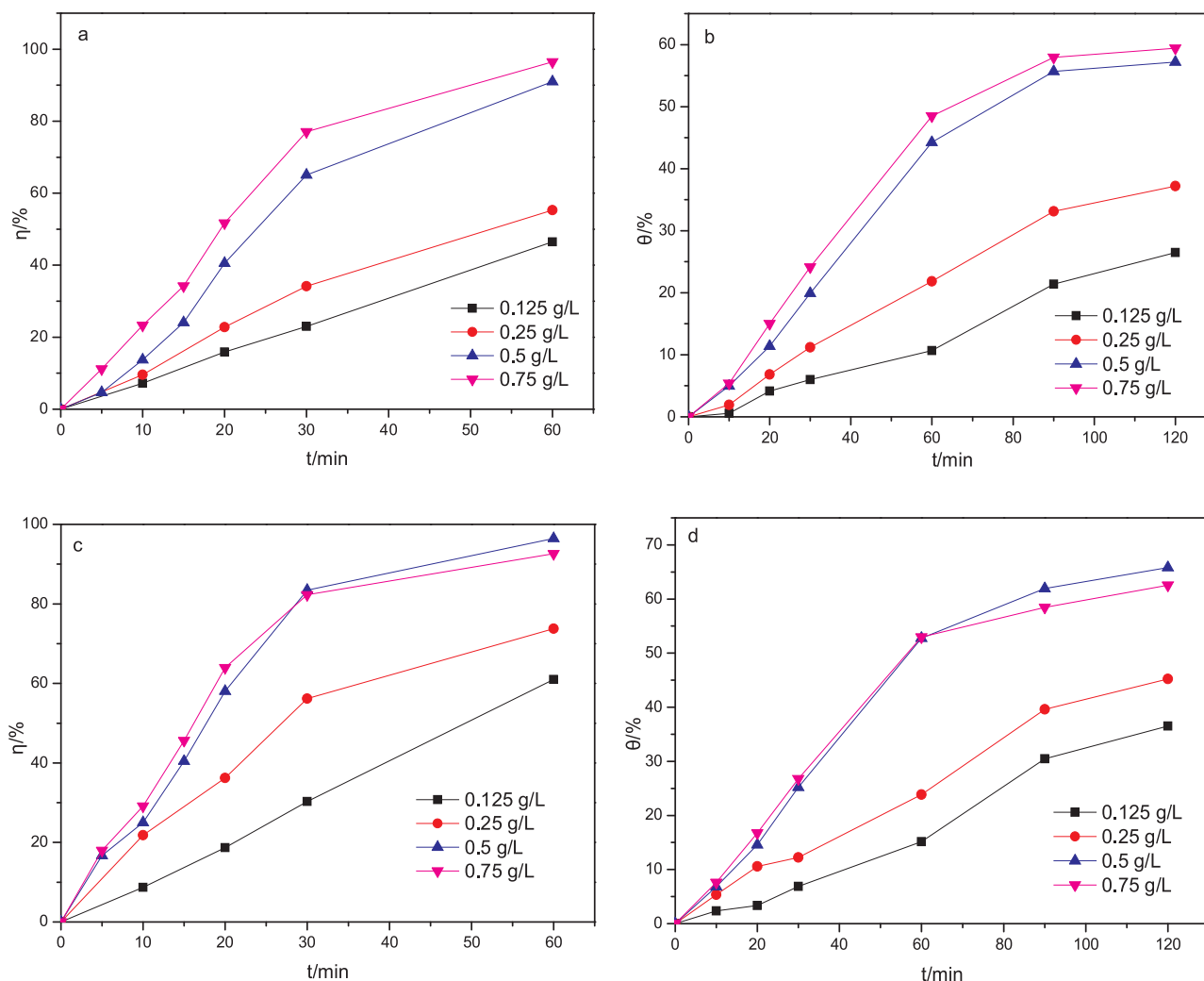


Fig. 4. Influence of 2,4-D removal at different Fe-C dosages (a Removal efficiency of 2,4-D by Fe-C/PS system, b The dechlorination efficiency by Fe-C/PS system, c Removal efficiency of 2,4-D by Pre-Fe-C/PS, d The dechlorination efficiency by Pre-Fe-C/PS system). Reaction conditions: 2,4-D 20 mg/L, PS 1.0 mM, pH 5.

which the degradation efficiency was respectively 99.3% and 60.2% in 60 min, while the k_1 and k_2 was 0.077 and 0.016 min^{-1} (Table S2), respectively. Nevertheless, the degradation efficiency of 2,4-D was 98.1% by Pre-Fe-C/PS system, almost the same as Pre-Fe⁰/PS system, while, it was higher than that of Fe⁰/PS and Fe-C/PS. Then the k_1 and k_2 was 0.059 and 0.023 min^{-1} by Pre-Fe-C/PS and Fe-C/PS (Table S2), respectively. Fig. 2 (b) shows the dechlorination efficiency of different systems, it was respectively 51.0%, 23.0%, 45.5% and 30.5% by Pre-Fe⁰/PS, Fe⁰/PS, Pre-Fe-C/PS and Fe-C/PS system in the first cycle. As known, the generation of sulfate radicals in Fe⁰/PS process was attributed to the Fe²⁺ dissolution [33]. Fig. S1 shows the dissolution of iron ion in both Fe⁰/PS and Fe-C/PS process in the first cycle. Obviously, the dissolution rate of iron ion in the Pre-Fe⁰/PS system was very fast and the total amount of leaching iron ion was much higher than that of several other systems, which could explain the facts that the removal and dechlorination of 2,4-D were faster than others. Although the generation of iron ion in Pre-Fe-C/PS process was similar to Fe⁰/PS system, however, the removal and dechlorination efficiency of 2,4-D were much higher than those of Fe⁰/PS system. One possible reason for the result was that the current of electron transfer by Fe-C

micro-electrolysis could promote PS activation besides iron ion in Fe-C/PS system [53].

In the second cycle, the removal and dechlorination efficiency of 2,4-D decreased rapidly by Fe⁰/PS process, only 34.5% and 21.5% 2,4-D was removed by Pre-Fe⁰/PS and Fe⁰/PS, respectively. Similarly, the dechlorination efficiency was 8.6% and 7.2%, and the k_1 and k_2 was 0.007 and 0.004 min^{-1} (Table S2). However, compared with those in the first cycle, the removal and dechlorination efficiency declined slightly in Fe-C systems, it was respectively 80.5% and 56.5% (Pre-Fe-C/PS); 23.6% and 10.7% (Fe-C/PS), and the k_1 and k_2 was 0.026 and 0.013 min^{-1} (Table S2). Furthermore, when the Fe⁰ and Fe-C were used for the third time, only about 20% 2,4-D was removed by Pre-Fe⁰/PS, the dechlorination efficiency was less than 5%. By Fe⁰/PS process, there was almost no dechlorination and less than 10% 2,4-D was removed. While, 53.1% and 29.1% 2,4-D was removed by Pre-Fe-C/PS and Fe-C/PS, and the dechlorination efficiency was about 10.1% and 4.0%, respectively.

In summary, the stability of Pre-Fe-C was much higher than Pre-Fe⁰ when reused. One possible reason for the result was more iron ion dissolution led to serious corrosion of Pre-Fe⁰ in the first cycle, resulting

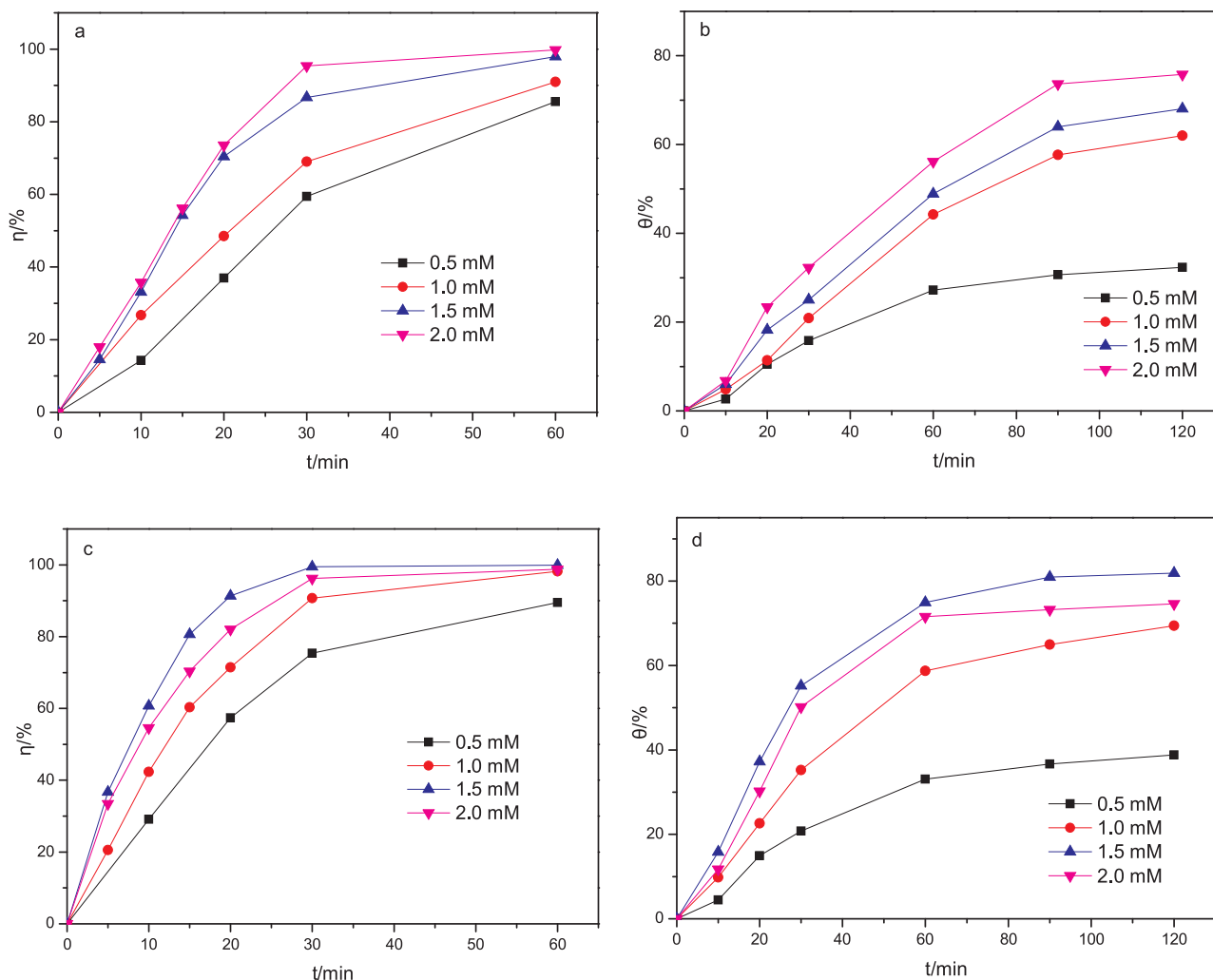


Fig. 5. Influence of 2,4-D removal at different PS dosages (a Removal efficiency of 2,4-D by Fe-C/PS system, b The dechlorination efficiency by Fe-C/PS system, c Removal efficiency of 2,4-D by Pre-Fe-C/PS, d The dechlorination efficiency by Pre-Fe-C/PS system). Reaction conditions: 2,4-D 20 mg/L, Fe-C 0.5 g/L, pH 5.

more oxides covered its surface. While, micro-electrolysis and advanced oxidation reactions occurred simultaneously in Pre-Fe-C system, only a few iron ions were dissolved and consumed in the first cycle. Meanwhile, the active carbon component on the Pre-Fe-C surface would fall off as the reaction proceed, which could update the surface of Pre-Fe-C and maintain the reactivity of the material [54]. In addition, less iron ion dissolution in Pre-Fe-C system would lead to the reduce of the sludge post-treatment cost. Also account for the lower price of industrial Fe-C when comparing with Fe⁰, Pre-Fe-C/PS with low sludge production but stable performance should be more promising and eco-friendly for organic pollutants degradation.

3.3. Influence of important parameters

3.3.1. Effect of initial pH

As shown in Fig. 3, the effect of initial pH (3–10) on removal efficiency by Pre-Fe-C/PS and Fe-C/PS were evaluated. The degradation efficiency of 2,4-DCP and dechlorination efficiency decreased with the increase of pH from 3.0 to 10.0 in both systems, especially in Fe-C/PS system, they sharply dropped. The degradation efficiency of 2,4-D was 92.3% and 88.1% at 60 min by Fe-C/PS system (Fig. 3 (a)) at pH 3 and

5, and the k_2 was 0.03 and 0.029 min⁻¹, meanwhile, the dechlorination efficiency was 61.3% and 58.1% at 120 min, respectively. However, in Pre-Fe-C/PS system, 90.6% and 83.4% 2,4-D was removed at 30 min at pH 3 and 5. The value of f was 2.26 and 1.84 folds of that by Fe-C/PS process (0.068 and 0.053 min⁻¹), the dechlorination efficiency was 62.3% and 59.1% in 90 min, respectively. A possible reason might be that more Fe²⁺ could be released from the catalyst at acid condition, which would enhance the activation of PS, meanwhile, Fe-C micro-electrolysis reaction was more intense at lower pH value [37]. The Pre-Fe-C could accelerate the corrosion of Fe⁰ and micro-electrolysis reaction, thus, more 2,4-D was removed by Pre-Fe-C/PS.

The 2,4-D removal efficiency at the initial pH values of 7.0, 9.0 and 10.0 was 76.7%, 70.4%, and 58.7% by Fe-C/PS process, respectively, and the dechlorination efficiency was 54.8%, 49.9% and 38.4% in 120 min. While, in Pre-Fe-C/PS system, the 2,4-D degradation efficiency after 60 min treatment was 88.5%, 85.2%, 80.7%, respectively at pH 7–10, and the dechlorination efficiency was 62.4%, 59.7%, 50.5% in 120 min, respectively. Table S3 showed that the k_1 of Pre-Fe-C/PS system was respectively 0.037, 0.034 and 0.025 min⁻¹, which was 2.2, 2.4 and 2.7 folds of that by Fe-C/PS process (0.017, 0.015 and 0.009 min⁻¹). When the pH value increased, Fe-C micro-electrolysis

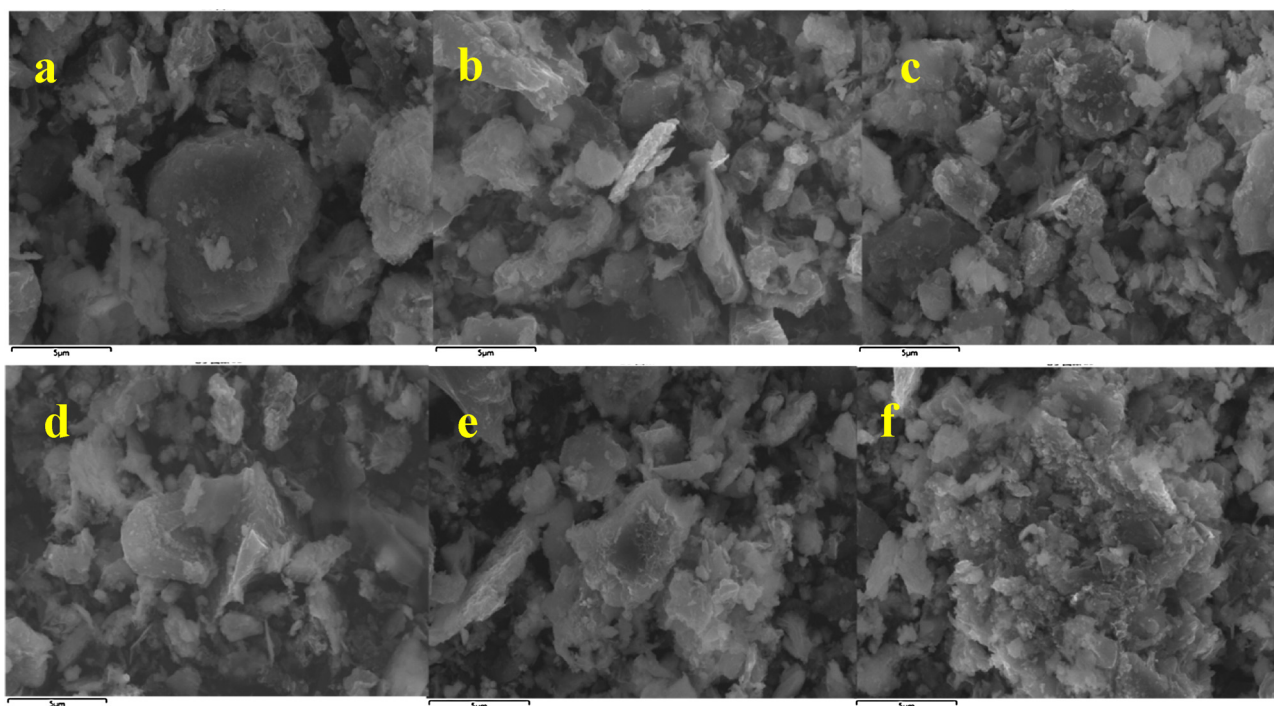


Fig. 6. The SEM of Fe-C and Pre-Fe-C before and after reaction. Reaction conditions: 2,4-D 20 mg/L, PS 1.0 mM, Fe-C 0.5 g/L, pH 7.

reaction intensity gradually reduced, and the generation of SO_4^{2-} also became less at the same time [37]. Therefore, there was a decline in the 2,4-D degradation and dechlorination efficiency. However, pre-magnetization could improve the generation of Fe^{2+} , and then Fe-C micro-electrolysis reaction was accelerated. Hence, the degradation and dechlorination efficiency by Pre-Fe-C/PS process was higher than those by Pre-Fe-C/PS process at any pH value.

3.3.2. Effect of Fe-C dosage

As shown in Fig. 4, the effect of Fe-C dosage (0.125–0.75 g/L) on the removal and dechlorination of 2,4-D was evaluated. Pre-Fe-C/PS led to greater 2,4-D removal and dechlorination than Fe-C/PS at all Fe⁰ dosages. When the Fe-C dosage was 0.125 and 0.25 g/L, there was insufficient Fe^{2+} in Fe-C/PS system, which could not effectively catalyze PS to generate SO_4^{2-} , and thus only 46.5% and 55.2% 2,4-D was removed in 60 min, and the dechlorination efficiency was 26.5% and 37.2% in 120 min (Fig. 4 (a) and (b)), respectively. While, the removal and dechlorination efficiency were respectively 61.1% and 36.5% (0.125 g/L Fe-C); 73.8% and 45.2% (0.25 g/L Fe-C) by Pre-Fe-C/PS (Fig. 4 (c) and (d)). When the Fe-C dosage was 0.5 g/L, the removal and dechlorination efficiency of 2,4-D was respectively 91.2% and 57.2%. With the increase of Fe-C (0.75 g/L), the removal and dechlorination efficiency of 2,4-D became slightly higher, while, the k_2 increased rapidly from 0.011 to 0.048 min^{-1} (The detailed rate constants are listed in Table S3). However, the removal and dechlorination efficiency of 2,4-D reached the maximum at 96.8% and 65.8% respectively by Pre-Fe-C/PS when the Fe-C dosage was 0.5 g/L, while the maximum value of k_1 was 0.057 min^{-1} at 0.75 g/L Fe-C (the values of k (10^{-3}) increased progressively from 0.016 to 0.057 min^{-1} (Table S4)). The proposed reason for this was that in the Pre-Fe-C/PS system the Fe^{2+} dissolution was faster than that in Fe-C/PS system, the 2,4-D could be almost completely removed when 0.5 g/L Fe-C was dosed in Pre-Fe-C/PS system. With the increase of Fe-C, more iron ion leached out at the

beginning of reaction, and the removal rate of 2, 4-D was accelerated. With the reaction going on, the excess iron ion would consume SO_4^{2-} [55], which competed with 2,4-D, leading to the decrease of 2,4-D removal and dechlorination efficiency.

3.3.3. Effect of initial PS dosage

PS concentration is a critical parameter in activation of $\text{S}_2\text{O}_8^{2-}$ processes since PS is the source of SO_4^{2-} . Fig. 5 shows that Pre-Fe-C/PS possessed higher 2,4-D removal than Fe-C/PS at all PS dosages (0.5–2.0 mM). The values of k increased progressively from 0.024 to 0.11 min^{-1} and from 0.012 to 0.075 min^{-1} , respectively, in the Fe-C/PS and Pre-Fe-C/PS as shown in Table S5. The 2,4-D removal and dechlorination efficiency reached maximum at the PS dosed 2.0 mM in Fe-C/PS system, however, in Pre-Fe-C/PS system, they reached maximum when the PS dosage was 1.5 mM. With the increase of PS, the value of f increased at first and then decreased, it was respectively 2.0, 2.2, 1.7, 1.4. It might be explained by the following: when PS was insufficient, the Pre-Fe-C could promote the formation of SO_4^{2-} , so 2,4-D was rapidly degraded into other intermediates, observing the increase of k in both systems. However, the competition reactions would be stronger between overdose PS and 2,4-D, which induced the decayed performance when further increased the PS concentration.

3.4. Mechanism exploration

3.4.1. Characteristics of Fe-C

Fig. 6 shows that the SEM surface morphology of Fe-C and Pre-Fe-C before and after reaction in the presence of PS. The surface of original Fe-C was relatively uniform, and some tiny particles on the surface of Fe-C was observed after 15 min reaction, illustrating that Fe-C was corroded due to the dissolution of iron ion. The corrosion of Fe-C increased with the reaction, especially after 60 min reaction. However, the fresh Pre-Fe-C was slightly corroded due to Lorentz force in the

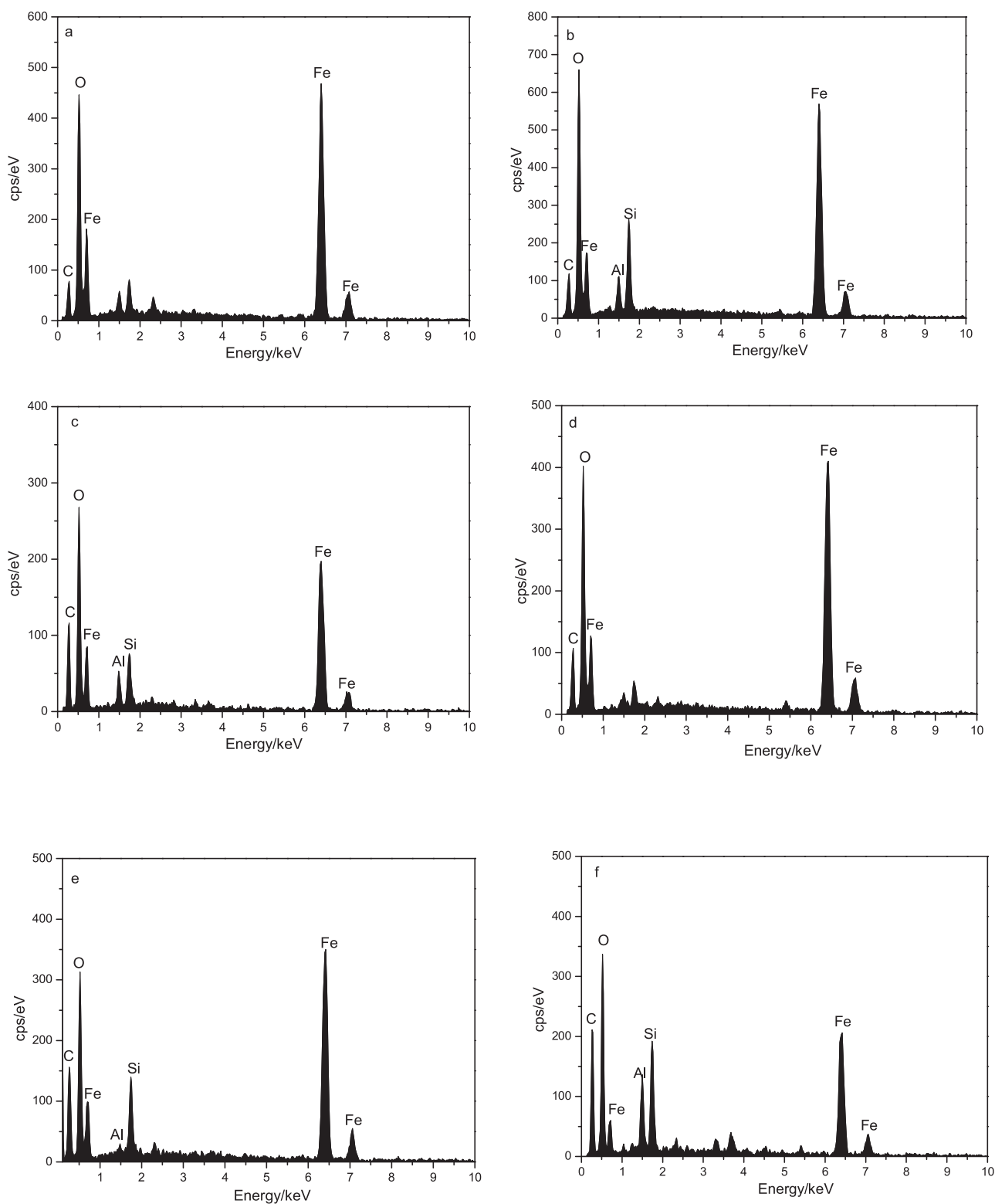


Fig. 7. The EDX spectrum of Fe-C and Pre-Fe-C (a Fe-C 0 min, b Fe-C 10 min, c Fe-C 60 min, d Pre-Fe-C 0 min, e Pre-Fe-C 10 min, f Pre-Fe-C 60 min). Reaction conditions: 2,4-D 20 mg/L, PS 1.0 mM, Fe-C 0.5 g/L, pH 7.

magnetic field. The Fe-C could maintain magnetism after pre-magnetization, and then the Lorentz force [56] played a role in the subsequent reaction [57]. Therefore, the extent of corrosion of Pre-Fe-C was more obvious than that of Fe-C after 15 min and 60 min.

To investigate possible changes of iron species after pre-magnetization and degradation, the change of Fe element was analyzed by EDX,

and the results are shown in Fig. 7 and Table S6. The Fe-C is composed of C, O, Fe, Si and other elements in this study. The content of Fe gradually decreased during reaction in both systems, while, the O content increased, indicating that the surface of Fe-C was oxidized and iron ion leached in the reaction process. However, the change of Fe and O content in Pre-Fe-C/PS system were more obvious than those of Fe-C/

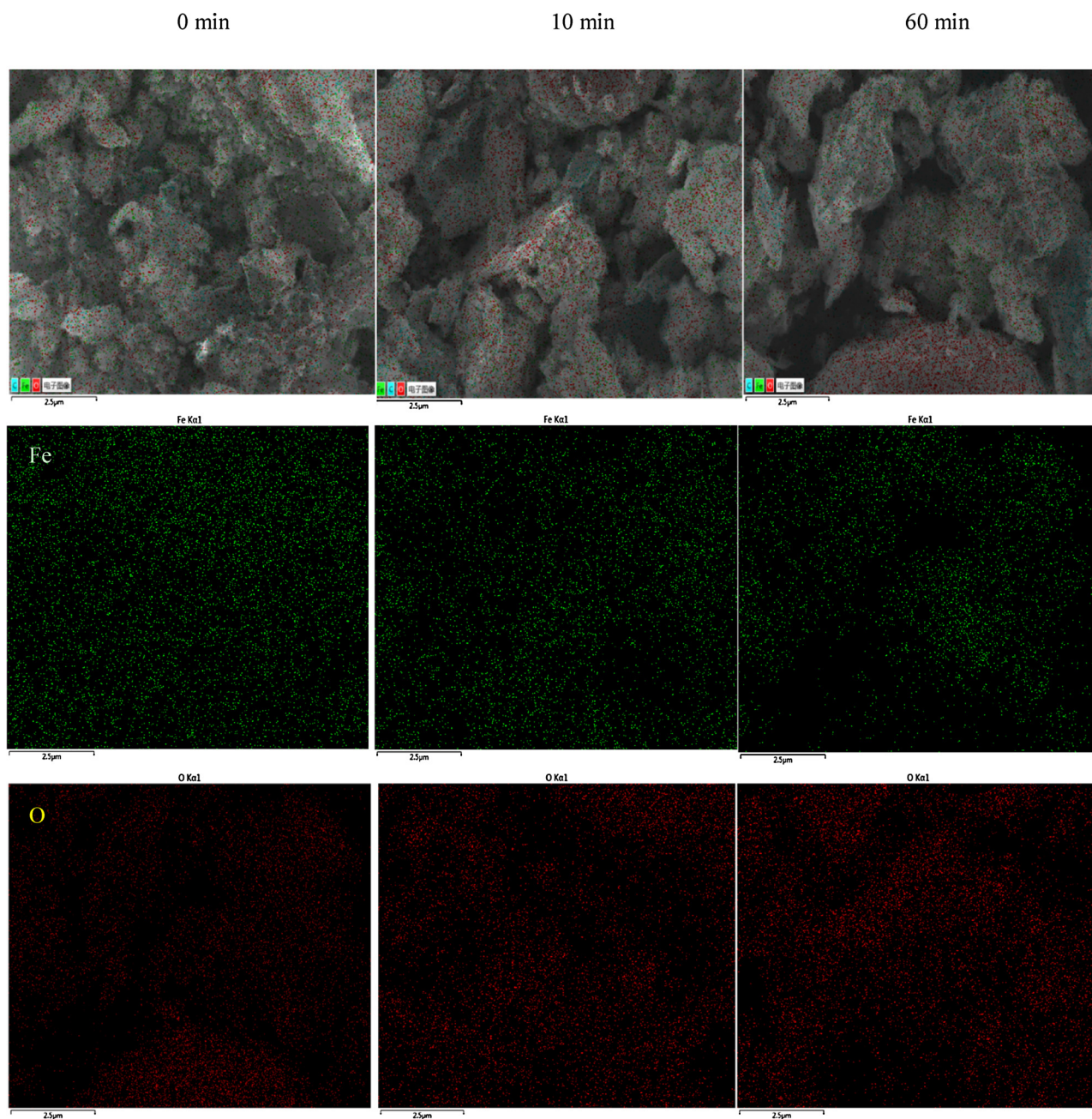


Fig. 8. The SEM-EDX-mapping of Fe-C before and after reaction. Reaction conditions: 2,4-D 20 mg/L, PS 1.0 mM, Fe-C 0.5 g/L, pH 7.

PS system. It can be seen from Table S6, the Fe content of Fe-C before reaction was about 61.0%, O content was about 25.1%, after 60 min reaction, the Fe and O content was respectively about 37.4% and 28.3%. While, the Fe content was about 54.7% on the surface of Pre-Fe-C before reaction and the O content was about 23.2%, the Fe and O content was respectively about 26.7% and 30.3% after 60 min reaction. The phenomena suggested that Pre-Fe-C could promote iron ion leaching, hence, there was more O content on the surface of Pre-Fe-C.

In order to more intuitively explain the change of corrosion of Fe-C in the process of reaction, the change of Fe element was analyzed by EDX-mapping test, and the results are shown in Fig. 8 (Fe-C) and Fig. 9 (Pre-Fe-C), respectively. The Fe content gradually decreased, while, the O content increased with the reaction in both systems, which was

consistent with the results of SEM analysis. However, the change of Fe and O on the surface of Pre-Fe-C were more obvious than those of Fe-C. The Fe content on the surface of Pre-Fe-C was less than that of Fe-C due to slightly corroded with the action of magnetic field, as the reaction went on, the more iron ion leached in Pre-Fe-C/PS system. The results were consistent with SEM and EDX test results.

3.4.2. Degradation intermediates analysis

The formation of intermediates during the degradation of 2,4-D in both Fe-C/PS and Pre-Fe-C/PS system was identified by HPLC, GC/MS and IC. Some products were detected by GC/MS (as shown in Table S7 and Fig. S2), which included 2,4-dichlorophenol (2,4-DCP), 4-chlorocatechol (4-CC), 2-chlorohydroquinone (2-CHQ), 2-chloro-1,4-

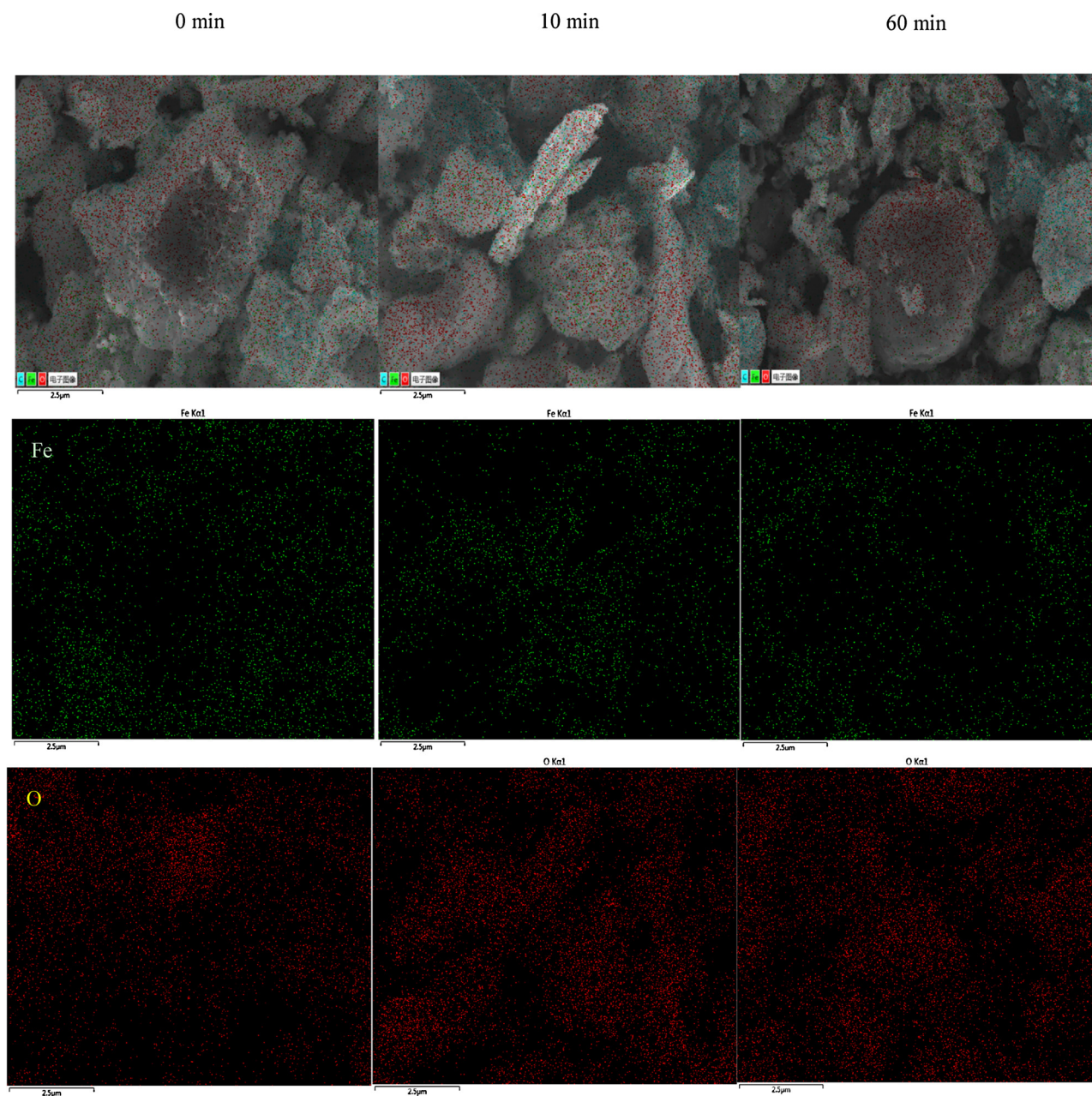
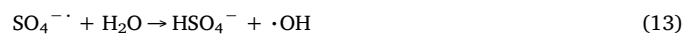


Fig. 9. The SEM-EDX-mapping of Pre-Fe-C before and after reaction. Reaction conditions: 2,4-D 20 mg/L, PS 1.0 mM, Fe-C 0.5 g/L, pH 7.

benzoquinone (2-CBQ), *p*-benzoquinone (PBQ), 2-chlorophenol (2-CP) or 4-chlorophenol (4-CP) and some small-molecule acids, such as acetic acid and formic acid. In addition, some small-molecule acids (oxalic acid, fumaric acid, maleic acid, formic acid and acetic acid) were also identified by HPLC (as shown in Fig. S3). The results were consistent with previous reports [58–60].

Based on the products were detected by GC/MS, HPLC and IC, a possible degradation reaction pathway of 2,4-D by Pre-Fe-C/PS and Fe-C/PS system was deduced, as shown in Fig. 10. First of all, $\text{SO}_4^{\cdot-}$ would attack the C–O bond, and 2,4-D was decayed to 2,4-DCP and glycolic acid. And then the glycolic acid was oxidized into CO_2 and H_2O with the action of activated radicals. Secondly, due to the presence of $\cdot\text{OH}$ in

system (Eq. (13)), 2,4-DCP would be converted into 4-CC, 2-CHQ and 1,2,4-benzotriol (BZ) which have also been reported by previous researches [60] through the chlorine substitution by hydroxyl group, and further transformed to 2-CBQ and PBQ by dechlorination or oxidation. Simultaneously, 2,4-DCP also could be attacked by $\text{SO}_4^{\cdot-}$ or $\cdot\text{OH}$ to form 2-CP or 4-CP, which were further oxidized to PBQ and other substances by activated radicals. Afterwards, the benzene ring would be opened by $\text{SO}_4^{\cdot-}$ or $\cdot\text{OH}$ or further oxidized to generate small molecule organic acids, such as oxalic acid, acetic acid and formic acid, which were completely oxidized to CO_2 and H_2O .



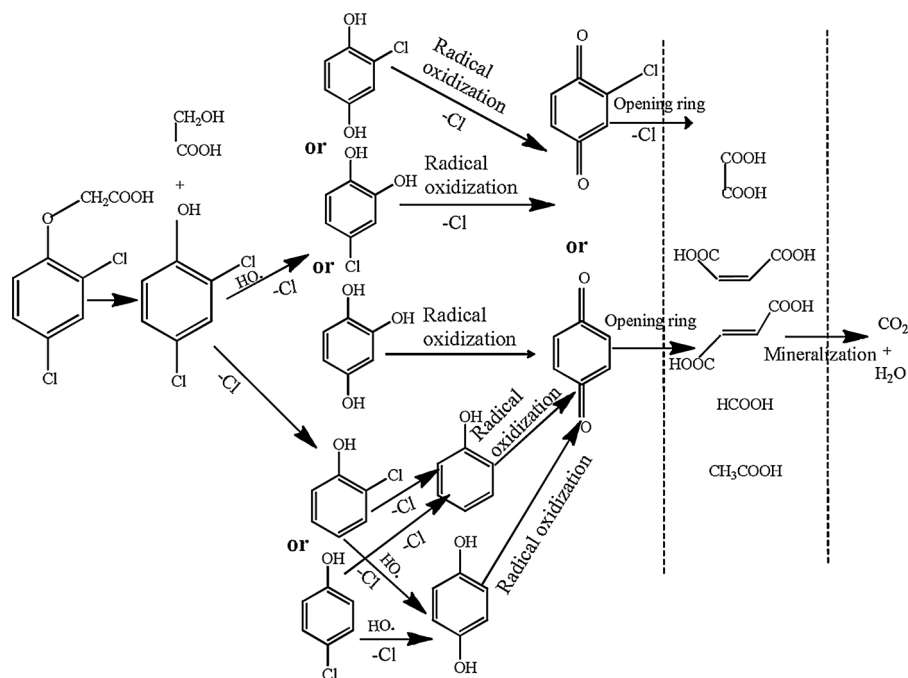


Fig. 10. The proposed degradation pathway of 2,4-D.
Reaction conditions: 2,4-D 20 mg/L, PS 1.0 mM, Fe-C 0.5 g/L, pH 7.

4. Conclusions

The degradation of 2,4-D was investigated by Pre-Fe-C/PS process for the first time. Compared to Fe-C/PS system, the Pre-Fe-C/PS system induced a significant improvement in the removal efficiency of 2,4-D and dechlorination efficiency. The reusability tests indicated that the reusability and stability of Fe-C were better than Fe⁰ and the leaching of iron ion was lower than (Pre)-Fe⁰/PS system. 53.1% and 29.1% 2,4-D was removed when Pre-Fe-C and Fe-C was used for the third time, which was higher than Pre-Fe⁰ (34.5%) and Fe⁰ (21.5%) reused for second time. The SEM, EDX and EDX-mapping analyses suggested the acceleration of Fe²⁺ release after Fe-C pre-magnetization. Based on the identification of degradation intermediates, a possible degradation pathway of 2,4-D was proposed.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.jhazmat.2018.04.035>.

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