



# Removal of polycyclic aromatic hydrocarbons (PAHs) from textile dyeing sludge by ultrasound combined zero-valent iron/EDTA/Air system



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## HIGHLIGHTS

- PAHs were effectively removed by the US/ZEA system under natural conditions.
- US disrupted sludge particles, promoted ZVI corrosion, and enhanced O<sub>2</sub> activation.
- ROS made the predominant contribution to the removal of PAHs in the US/ZEA system.

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## ABSTRACT

This paper proposes a combined ultrasound (US) and zero-valent iron/EDTA/Air (ZEA) system to remove polycyclic aromatic hydrocarbons (PAHs) from textile dyeing sludge. The removal efficiencies of 16 PAHs using ZEA, US/Air (air injected into the US process), and US/ZEA treatments were investigated, together with the effects of various operating parameters. The enhanced mechanisms of US and the role of reactive oxygen species (ROS) in removing PAHs in the US/ZEA system were explored. Results showed that only 42.5% and 32.9% of  $\Sigma$ 16 PAHs were removed by ZEA and US/Air treatments respectively, whereas 70.1% were removed by US/ZEA treatment, (with favorable operating conditions of 2.0 mM EDTA, 15 g/L ZVI, and 1.08 w/cm<sup>3</sup> ultrasonic density). The US/ZEA system could be used with a wide pH range. US led to synergistic improvement of PAHs removal in the ZEA system by enhancing sludge disintegration to release PAHs and promoting ZVI corrosion and oxygen activation. In the US/ZEA system, PAHs could be degraded by ROS (namely  $\cdot$ OH, O<sub>2</sub><sup>-</sup>/HO<sub>2</sub><sup>•</sup>, and Fe(IV)) and adsorbed by ZVI, during which the ROS made the predominant contribution. This study provides important insights into the application of a US/ZEA system to remove PAHs from sludge.

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## 1. Introduction

Textile dyeing sludge generated by the textile industry causes serious environmental problems. According to the China Environment Statistical Yearbook, in 2016 around 4.65 million tons of textile dyeing sludge were discharged (80% moisture content). In the textile industry, considerable dyes and additives are added in the production process. These additives lead to the formation of refractory intermediates during multiple wastewater treatment processes. The refractory intermediates include polycyclic aromatic

hydrocarbons (PAHs) and aromatic amines (Ning et al., 2014, 2015). Due to their hydrophobic nature, PAHs remain on precipitated sludge by binding to the active sludge mass (Stevens et al., 2003). Our recent study elucidated that the contamination level of PAHs in sludge was as high as 16.7 mg/kg dry sludge in some textile dyeing wastewater treatment plants (Ning et al., 2014). Textile dyeing sludge is not treated appropriately before disposal (landfill or incineration), and recalcitrant compounds, including trace level PAHs, pose a potential threat to the environment (Park et al., 2009; Ning et al., 2014). Due to their polluting nature and their toxic, mutative, carcinogenic, and teratogenic characteristics, 16 PAHs have been listed as priority pollutants by the United States Environmental Protection Agency (Liu et al., 2012). Therefore, effective technologies for removal of PAHs from textile dyeing sludge, before

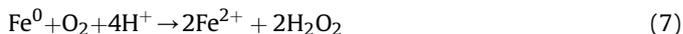
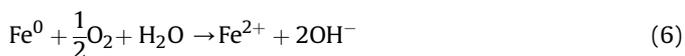
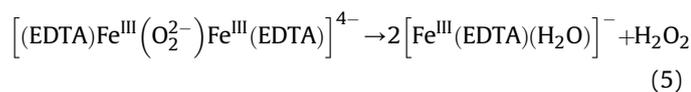
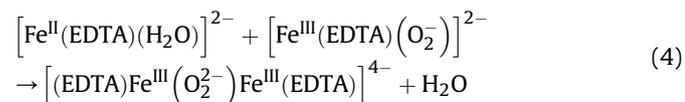
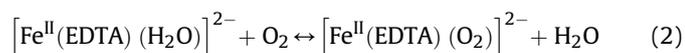
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discharge into the environment, are urgently needed.

Previously, Fenton or Fenton-like processes have been shown to be efficient in removing PAHs from soil, sediment, and sludge (Flotron et al., 2005; Usman et al., 2012; Ranc et al., 2016). The traditional Fenton process is based on a mixture of ferrous salt and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), which can lead to rapid decomposition of organic contaminants (Flotron et al., 2005). For example, for efficacious degradation of PAHs in textile dyeing sludge, our recent study established a combined ultrasound (US) and Fenton process, in which both H<sub>2</sub>O<sub>2</sub> and ferrous iron (Fe<sup>2+</sup>) dosages reached up to 140 mM and initial pH was adjusted to 3 (Lin et al., 2016). However, the high dosage of reaction reagents and acid required resulted in a high cost. Furthermore, at high concentrations, H<sub>2</sub>O<sub>2</sub> is erratic in ambient atmospheres, becoming hazardous during storage, transportation, and handling (Zhou et al., 2009a).

From an economic and environmental perspective, zero-valent iron (ZVI) and molecular oxygen (O<sub>2</sub>) can form a Fenton-like system, which has been extensively applied to the removal of various pollutants, including diclofenac, sulfoxides, and arsenic(III) (Pang et al., 2011; Song et al., 2017). It is known that ZVI can react with O<sub>2</sub> to generate reactive oxygen species (ROS). The ROS include hydroxyl radicals (•OH), superoxide anion/hydroperoxyl radicals (O<sub>2</sub><sup>•-</sup>/HO<sub>2</sub><sup>•</sup>), and high-valent iron species (Fe(IV)) (Keenan and Sedlak, 2008a; Pang et al., 2011). However, due to the low yield of ROS generation in the ZVI/O<sub>2</sub> system, diverse organic and inorganic chelating agents such as oxalate, nitrilotriacetic acid, ethylenediaminetetraacetic acid (EDTA), and tetrapolyphosphate are added to enhance ROS production (Keenan and Sedlak, 2008b; Kim et al., 2015). Among these chelating agents, EDTA can form a complex with Fe<sup>2+</sup> and then break down the O–O bond of O<sub>2</sub>, spontaneously producing H<sub>2</sub>O<sub>2</sub> through a series of complex reactions (Eqs. (1)–(5)) and eventually promoting generation of ROS in the ZVI/EDTA/Air (ZEA) system (Seibig and Eldik, 1997). In the ZEA system, the source of Fe<sup>2+</sup> is attributed to iron corrosion (Eqs. (6) and (7)) (Keenan and Sedlak, 2008b; Zhou et al., 2009a). Furthermore, EDTA is a widely used chelating agent in textile industries (Zhou et al., 2009b). It is inevitable that large amounts of EDTA in textile wastewater effluent could potentially remobilize with metals, thus contaminating groundwater and drinking water (Nowack, 2002). It would be advantageous to utilize the EDTA contained in textile wastewater to remove contaminants from the textile dyeing sludge via a ZEA system.



US has physical and sonochemical effects based on the phenomenon of acoustic cavitation. Cavitation generates intense convection in the matrix, due to the phenomena of ultrasonic oscillation, microturbulence, and shock waves (Patidar et al., 2012). At the same time, large numbers of micro-bubbles are produced, which grow and then collapse. The collapse of micro-bubbles generates local areas of high energy. Temperature and pressure can reach levels of 4000–15,000 K and 100–5000 bar respectively within a microsecond (Flannigan and Suslick, 2005; Sajjadi et al., 2016). These extreme conditions are responsible for the formation of highly reactive hydroxyl radicals, which represent the sonochemical effect of cavitation (Tiehm et al., 2001). US can assist and strengthen Fenton or Fenton-like processes for degrading various recalcitrant organic compounds. Li et al. (2013) reported that a combined US/Fenton system could facilitate removal of TOC/COD/color in ammunition wastewater. Zhang et al. (2013) also revealed that a combined US/Fenton process was more effective at eliminating petroleum hydrocarbons in oily sludge than either US or Fenton treatment in isolation. Furthermore, Zhou et al. (2009a) observed significant synergistic effects for degradation of both 4-chlorophenol and EDTA when US was introduced into a ZEA system. It appears that the combination of US and ZEA enhances contaminant removal from sludge. However, to our knowledge, there have been no studies using a US/ZEA system for removal of recalcitrant organic compounds, such as PAHs, from textile dyeing sludge.

Therefore, the specific objectives of the present study are: (1) to explore the effects of US on the ZEA system and on textile dyeing sludge; (2) to investigate the effects of different parameters, including ZVI and EDTA dosages, ultrasonic density, and pH on removal efficiencies of PAHs; (3) to compare removal efficiencies for 16 PAHs in textile dyeing sludge by ZEA, US/Air (air injected into the US process), and US/ZEA treatments; and (4) to explore the role of ROS in PAHs removal in the US/ZEA system.

## 2. Materials and methods

### 2.1. Materials

A standard solution containing 16 PAHs was purchased from O2si Smart Solutions (Charleston, SC, USA) at a concentration of 2000 mg/L; this included the following low molecular weight PAHs (LMW PAHs): naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorine (Fl), phenanthrene (Phe), and anthracene (Ant); and the following high molecular weight PAHs (HMW PAHs): fluoranthene (Flu), pyrene (Pyr), benz[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), dibenz[a,h]anthracene (DBA), indeno[1,2,3-cd]pyrene (InP), and benzo[ghi]perylene (BP). Naphthalene-D8, acenaphthene-D10, phenanthrene-D10, chrysene-D12, and perylene-D12 were used as internal standards. Fluorine-D10 and pyrene-D10 were employed as surrogate standards. ZVI particles (purity >99%) with a diameter between 0.15 and 0.25 mm and a saturation magnetization of 19.4 emu/g were obtained from Xiya Reagent Company (Shandong, China). Ethylenediaminetetraacetic acid disodium dihydrate salt (purity 99.0–101.0%) was purchased from CNW Technologies GmbH. All organic solvents of high-performance liquid chromatography (HPLC) grade were obtained from Fisher Scientific (USA). Silica gel (100–200 mesh) was obtained from the Qingdao Haiyang Chemical Company (Shandong, China) and activated at 130 °C for 16 h. Alumina (100–200 mesh) was purchased from Aladdin (Shanghai, China) and dried at 450 °C

for 12 h.

## 2.2. Sludge samples

Textile dyeing dewatered sludge was collected from a textile wastewater treatment plant in Guangzhou City, Guangdong Province, China. A large quantity of high moisture content sludge was critical for our experiments, but this was difficult to transport and store compared to dewatered sludge. Dewatered sludge samples processed by plate-frame pressure filtration were therefore collected. These were then transferred to the laboratory and kept at constant temperature (4 °C) prior to analysis. The characteristics and contents of 16 PAHs in the sludge are given in Table S1. The sludge characteristics are presented in Table S2.

## 2.3. Experimental set-up and procedure

US treatments were conducted in a 0–1800 W sonicator (Scientz JY99-IIDN, China, 20 kHz) equipped with a sealed converter and a titanium probe tip (25 mm in diameter and 320 mm in length), operated in a pulse mode of 3 s on and 2 s off. A cylindrical reactor (1 L volume) with a cooling jacket and a circulating temperature controller were used to maintain the temperature at  $25 \pm 1$  °C during all treatments. Air was continuously supplied to the slurry by an air pump at a flow rate of 1.0 L/min. To ensure the air dispersed evenly, a porous aerator at the end of the air tube was fixed to the bottom of the reactor. A power basic stirrer, controlled at 200 rpm, was applied to ensure sufficient mixing of the chemicals and slurry during the ZEA process.

Before the experiments, a sludge sample (500 mL, 98% moisture content) was prepared by mixing the dewatered sludge with the corresponding amount of pure water. EDTA solution (0–3.0 mM) was added in advance to the sludge samples, and reactions were initiated by adding ZVI powder (5–30 g/L) and aerating the air. The ultrasonic generator was immediately exposed to the slurry (ultrasonic density between 0.36 and 1.08 w/cm<sup>3</sup>), and samples were taken at given intervals (10, 20, 40, 60, and 90 min). Initial pH (between 3.0 and 9.0) of the sludge samples was adjusted using diluted sulfuric acid and sodium hydroxide. All experiments were conducted in triplicate.

To investigate the actual oxidant species within the textile dyeing sludge treated by US/ZEA, a series of experiments were carried out by adding different radical scavengers to the sludge sample. The compounds 2-propanol and benzoquinone were chosen as scavengers specifically for •OH and O<sub>2</sub><sup>•-</sup>/HO<sub>2</sub><sup>•</sup>, while dimethyl sulfoxide was used as a scavenger for •OH and Fe(IV) (Zhou et al., 2014; Cheng et al., 2016). These scavengers were initially added separately into the sludge sample.

## 2.4. Analytical methods

The sludge sample was separated by centrifugation at 4000 rpm for 15 min following the different treatments. After centrifugation, the solid residue was freeze-dried in a vacuum freeze dryer (12 h, –60 °C) before extraction. The supernatant was quickly filtered for further analyses using a 0.22-μm membrane. Extraction of PAHs was carried out in an ultrasonic bath (40 kHz, KQ300D, China) at 400 W, following our previous study (Lin et al., 2016). Analysis of PAHs concentrations was carried out using an Agilent 7890A gas chromatograph with 5975C mass spectrometer. Further details of the extraction of PAHs and GC/MS analytical conditions are given in the Supplementary Material (Text S1).

The pH value of the sludge sample was measured by a digital pH meter (pHS-3C, Leici, China). The measurement of sludge organic matter (SOM) was conducted using a loss-on-ignition method, as

reported in our previous study (Lin et al., 2016). Dissolved total organic carbon (DOC) in the filtrate was measured using a TOC analyzer (TOC-V<sub>CPH</sub>, Shimadzu, Japan). A 1, 10-phenanthroline method was used to determine the concentration of Fe<sup>2+</sup> and total dissolved iron (TFe) by UV absorption at 510 nm (Harvey et al., 1955). The surface morphologies of multiple sludge samples were examined using a scanning electron microscope (SEM) (S-3400 N, Hitachi, Japan). Further details of these analyses are given in the Supplementary Material (Text S2).

## 3. Results and discussion

### 3.1. Changes of dissolved iron ions in multiple systems

Dissolved Fe<sup>2+</sup> and TFe were detected in multiple systems and the results are presented in Fig. 1. The iron in dewatered sludge had an effect on the reaction systems, which was introduced by adding a large quantity of iron coagulant before sludge dehydration. As shown in Fig. 1a, about 20.7 mg/L TFe (Fe<sup>3+</sup>) was detected immediately, while Fe<sup>2+</sup> was not detected in the raw sludge sample. Fe<sup>3+</sup> could drastically precipitate as Fe(OH)<sub>3</sub> (Table S3), reaching almost zero at 30 min in the absence of EDTA. TFe concentration increased steadily for the first 30 min (36.4 mg/L) in the US/ZEA system. As previously reported, chelating agents have been developed to solubilize metal ions and keep them in solution, thus the presence of EDTA could increase the concentration of dissolved TFe (Keenan and Sedlak, 2008b). During the first 40 min, concentrations of Fe<sup>2+</sup> in the US/ZEA system were higher than that in the ZEA system. This suggested that US could promote ZVI corrosion into Fe<sup>2+</sup> through continuous cleaning and refreshing of the ZVI surface, which was covered by an iron oxide film, a hydroxide layer, and tiny sludge particles, and thus enhance inter-phase mass transfer in the heterogeneous ZVI redox system (Hung et al., 2000). As shown in Table S3, Fe<sup>2+</sup> began to form hydroxide precipitates as Fe(OH)<sub>2</sub> at pH ≥ 7.90; however, pH in the US/ZEA system was 7.59 at 30 min (Fig. S1a). After 30 min, the concentration of Fe<sup>2+</sup> in the US/ZEA system quickly decreased compared to the ZEA system, implying that most Fe<sup>2+</sup> was involved in activation of O<sub>2</sub> to produce H<sub>2</sub>O<sub>2</sub> (reactions (1)–(5)) rather than precipitating as Fe(OH)<sub>2</sub> in the US/ZEA system. As reported, O<sub>2</sub> activation (Eq. (3)) is the rate-limiting

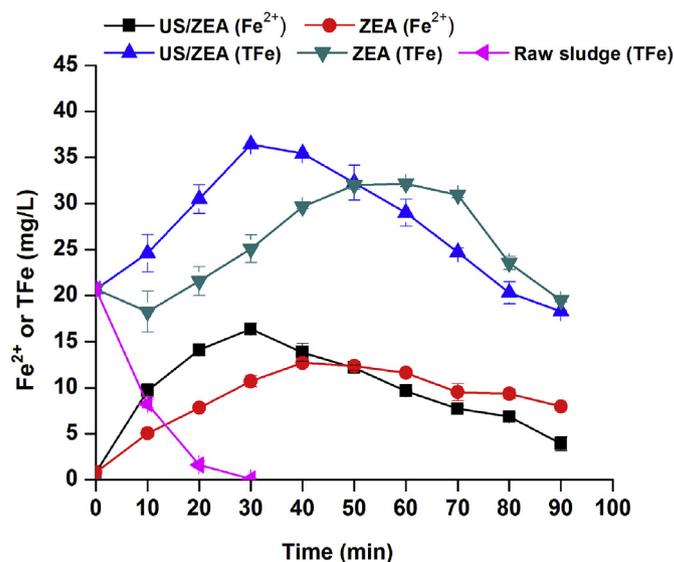


Fig. 1. Dissolved Fe<sup>2+</sup> and TFe in multiple systems. Initial condition: EDTA = 2.0 mM, ZVI = 15 g/L, and ultrasonic density = 1.08 w/cm<sup>3</sup> under natural conditions.

step because  $O_2$  exhibits strong stability in its spin-triplet ground state and the kinetic barrier needs to be overcome (Seibig and Eldik, 1997). After US is induced,  $O_2$  can be trapped in the bubbles produced by the ultrasonic waves, which then leads to the formation of O atoms. Compared to  $O_2$ , the O atom is unstable and can be easily activated (Zhou et al., 2010). In addition, the dissolved oxygen (DO) concentration in the US/ZEA system was consistently lower than in the ZEA system, even over a prolonged period (Fig. S1b), which also indicated that US could promote the  $O_2$  activation process.

### 3.2. Effect of US on sludge

Due to the generation of acoustic cavitation, US treatment has proved effective in sludge disintegration by disrupting sludge floc (Pilli et al., 2011). The main sludge disintegration mechanisms generated by US treatment are powerful hydro-mechanical shear forces, sonochemical and thermal effects, in which hydro-mechanical shear forces is the most significant mechanism (Tiehm et al., 2001; Pilli et al., 2011). In particular, bacteria cell walls are broken down by the hydro-mechanical shear forces generated during the US process; thus sludge solids are disintegrated, then large sludge particles are broken down into smaller particles, and finally organic compounds (intracellular and extracellular) are released into the soluble phase (Tiehm et al., 2001; Mohapatra et al., 2011). In this study, the sludge disintegration after US treatment was confirmed by observing changes in the levels of SOM and DOC, and the morphology of the sludge.

The changes of SOM and DOC in multiple systems are shown in Fig. 2. In this study, initial SOM was 37.8%. Slight variation in SOM was observed after ZEA treatment, with a slight decrease to 36.9% at 90 min. This suggested that ZEA was a mild system and had an insignificant effect on damaging sludge particles, which is in accordance with the findings of Cao et al. (2013). Interestingly, DOC concentration increased smoothly during the ZEA process over the first 60 min. This could be due to the reaction of organic matter on the surface of sludge particles with ROS, releasing carbonaceous organic intermediates into the soluble phase (Ranc et al., 2016). However, during the US/Air process, the SOM value decreased, while initially DOC increased rapidly. This result could be due to the conversion of organic matter from sludge to the soluble phase after US treatment, as described above. Meanwhile, sonochemical

reactions can degrade organic compounds by pyrolytic processes inside the cavitation bubbles and by  $\cdot OH$  generated in the bulk liquid (Tiehm et al., 2001). Thus, the content of DOC declined over time. In the case of US/ZEA treatment, the source of DOC was the generation of intermediates and SOM release, and thus DOC increased sharply initially.

The morphologies of multiple sludge samples were investigated using a SEM (magnification: 2000 $\times$ ) (Fig. S2). The SEM micrographs of raw sludge showed an inhomogeneous structure with granular shapes. Sludge particles were marginally crushed after ZEA treatment, demonstrating that this system had limited disruptive effect on sludge samples. Conversely, many fine particles were observed once US was introduced, i.e., in US/Air and US/ZEA treatments. These morphological changes clearly demonstrate that US could completely break down sludge particles.

### 3.3. Effect of operational parameters on PAHs removal

#### 3.3.1. Effect of EDTA and ZVI

ZVI and EDTA significantly influenced PAHs removal due to their contribution to  $H_2O_2$  and ROS generation. Comparative experiments with different initial EDTA concentrations (0, 0.5, 1.0, 2.0, and 3.0 mM) and ZVI dosages (5, 10, 15, 20, and 30 g/L) were carried out at 60 min. For conveniently discussing the removal efficiencies of PAHs, the PAHs are displayed as 2-, 3-, 4-, 5-, 6-ring, LMW, HMW and  $\Sigma 16$  PAHs (Table S1). Given that the optimum parameters for each of the PAHs at maximum removal efficiency were not entirely consistent, optimum conditions were determined based on the removal efficiency of  $\Sigma 16$  PAHs. Fig. 3a shows that in the absence of EDTA in the ZEA system, removal efficiencies of LMW, HMW, and  $\Sigma 16$  PAHs were only 17.4, 14.1, and 15.3% respectively. Considerable enhancement was observed when the initial EDTA concentration was increased to 2.0 mM, with removal efficiencies of LMW, HMW, and  $\Sigma 16$  PAHs being 46.5, 40.0, and 42.5% respectively. EDTA played an important role in the reactions because it could enhance ZVI corrosion and  $O_2$  activation (Eqs. (1)–(5)) (Noradoun et al., 2003; Keenan and Sedlak, 2008b). Thus, a higher EDTA concentration could facilitate the generation of  $H_2O_2$  and ROS, eventually increasing the removal efficiencies of PAHs. However, when the EDTA concentration was further increased to 3.0 mM, removal efficiencies of LMW, HMW, and  $\Sigma 16$  PAHs decreased slightly (45.6,

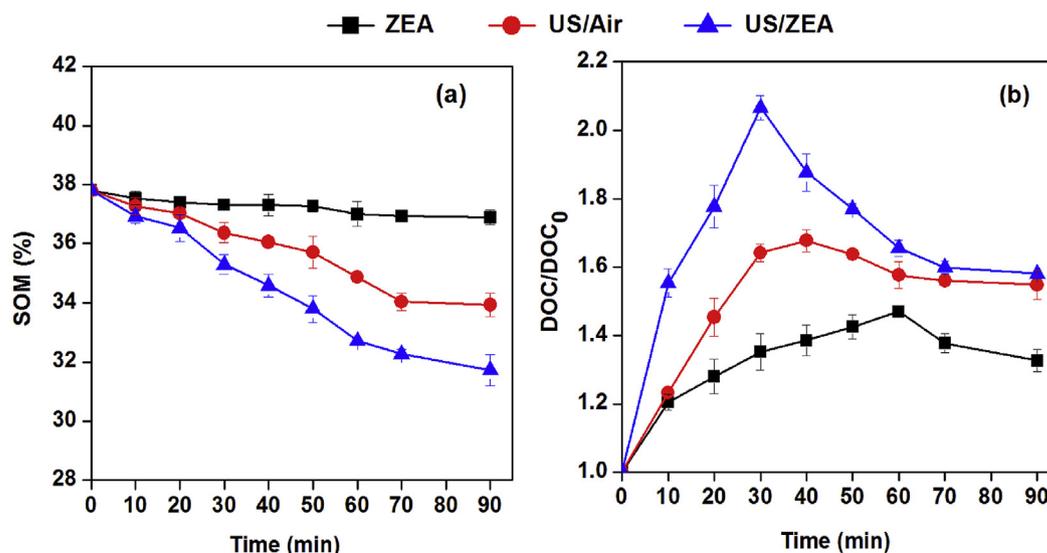


Fig. 2. Changes of (a) SOM and (b) DOC in multiple systems. Initial condition: EDTA = 2.0 mM, ZVI = 15 g/L, and ultrasonic density = 1.08 w/cm<sup>3</sup> under natural conditions.

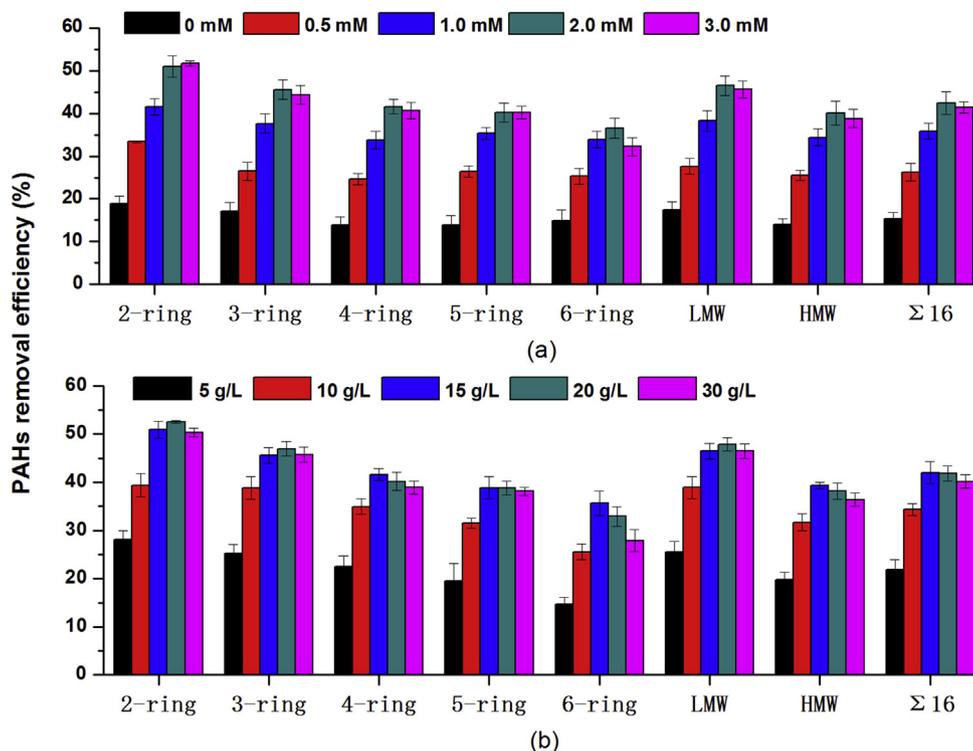


Fig. 3. Effect of (a) EDTA (ZVI = 15 g/L) and (b) ZVI (EDTA = 2.0 mM) on PAHs removal by ZEA treatment at 60 min under natural conditions.

38.8, and 41.3% respectively), implying that excessive EDTA had a negative effect on PAHs removal. This could be due to excessive EDTA inhibiting the formation of  $[\text{Fe}^{\text{II}}(\text{EDTA})(\text{O}_2)]^{2-}$  (Eq. (2)), which is indispensable for the production of  $\text{H}_2\text{O}_2$  (Noradoun and Cheng, 2005). The processes controlling ROS generation and PAHs removal were therefore impeded.

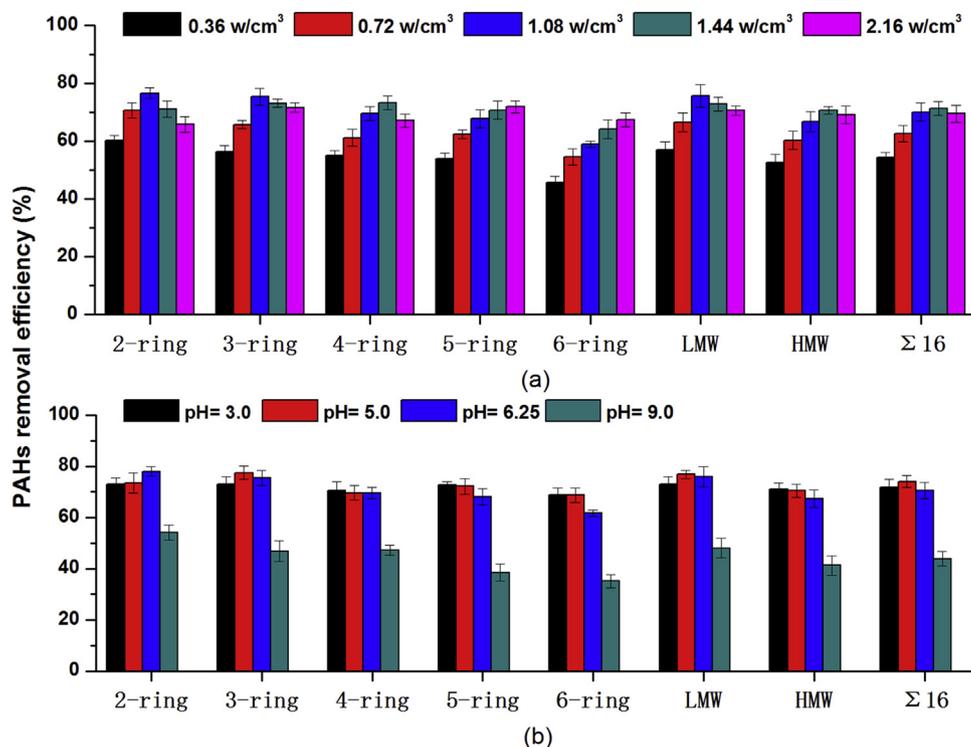
As illustrated in Fig. 3b, the removal efficiencies of LMW, HMW, and  $\Sigma 16$  PAHs were much lower (at only 25.5, 19.7, and 21.9% respectively) with the addition of a ZVI dose of 5.0 g/L. With an increased ZVI dosage, the surface area of contact between DO and ZVI increased, promoting the ZVI oxidation process and the formation of  $\text{Fe}^{2+}$  (Eqs. (6) and (7)). The abundant  $\text{Fe}^{2+}$  could enhance the subsequent production of  $\text{H}_2\text{O}_2$  and also that of ROS (Zhou et al., 2008). As expected, removal efficiencies of all PAHs increased as ZVI dosage rose to 15 g/L. However, slight variations in  $\Sigma 16$  PAHs removal efficiency were observed when ZVI dosage increased from 15 to 20 g/L. In addition, most PAHs removal efficiencies declined with further addition of ZVI to 30 g/L. It could be that the excessive dosage of ZVI not only limited the mass transfer efficiency of  $\text{O}_2$  (Lu and Wei, 2011) but also resulted in more consumption of  $\text{O}_2$  and  $\text{H}_2\text{O}_2$  (Zhou et al., 2009a). This possibly offset enhancement during the process of  $\text{H}_2\text{O}_2$  formation and reduced ROS generation. In general, initial EDTA concentration of 2.0 mM and ZVI dosage of 15 g/L were optimal for removal of PAHs from textile dyeing sludge.

### 3.3.2. Effect of ultrasonic density and pH

The combined US/ZEA treatment was used to remove PAHs from textile dyeing sludge, using ultrasonic densities of 0.36, 0.72, 1.08, 1.44, and 2.16  $\text{w}/\text{cm}^3$  at 60 min. The test conditions were kept at 2.0 mM of EDTA and 15 g/L of ZVI under natural conditions (initial pH: 6.25). As shown in Fig. 4a, a gradual increase in removal efficiencies of all PAHs was observed with ultrasonic density increasing from 0.36 to 1.08  $\text{w}/\text{cm}^3$ . This indicated that higher ultrasonic intensity had a positive effect on contaminant removal due to an

increase in the number of active cavitation bubbles (Pétrieur et al., 2007). The highest removal efficiencies of 2- and 3-ring PAHs, 4-ring PAHs, and 5- and 6-ring PAHs were obtained at ultrasonic densities of 1.08, 1.44, and 2.16  $\text{w}/\text{cm}^3$  respectively, while average removal efficiencies were 75.6, 73.3, and 70.4% respectively. It has been reported that more energy is required for degradation of HMW PAHs during the US process (Manariotis et al., 2011); therefore, high ultrasonic intensity was favorable for degradation of 5- and 6-ring PAHs. Meanwhile, hydrophobic HMW PAHs might be more easily pyrolyzed into LMW PAHs (Lin et al., 2016). In addition, since the sum of content percentages of the 2-, 3-, and 4-ring PAHs reached up to 90.62% (Table S1), excessively high ultrasonic intensity might result in strong sludge particle disintegration and the release of more of these adsorbed PAHs. The removal efficiencies of 2-, 3-, and 4-ring PAHs thus decreased slightly as ultrasonic intensity further increased. In the case of  $\Sigma 16$  PAHs, variations in removal efficiency became less apparent when ultrasonic intensity increased from 1.08 to 2.16  $\text{w}/\text{cm}^3$ . Consequently, ultrasonic intensity of 1.08  $\text{w}/\text{cm}^3$  was applied in the experiments so as to avoid high energy consumption.

The removal of selected PAHs, treated for 60 min with different initial pH values (i.e., 3.0, 5.0, 6.25, and 9.0), was characterized at 2.0 mM of EDTA, 15 g/L of ZVI, and with an ultrasonic density of 1.08  $\text{w}/\text{cm}^3$ . The results are presented in Fig. 4b. In the US/ZEA system, the removal efficiencies of  $\Sigma 16$  PAHs showed only slight discrepancies at pH 3.0, 5.0, and 6.25 (removal efficiencies of 71.8, 74.1, and 70.6% respectively). These results indicated that this system could be used with a wide pH range. The removal efficiencies of LMW and HMW PAHs reached maximum values at pH 5.0 (76.9%) and pH 3.0 (71.1%) respectively. All removal efficiencies declined significantly when initial pH was increased to 9.0 because it limited formation of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  (Englehardt et al., 2007). In this study, pH 6.25 (natural conditions) was selected for PAHs removal to avoid sludge acidification.



**Fig. 4.** Effect of (a) ultrasonic density (under natural conditions) and (b) pH (ultrasonic density = 1.08 w/cm<sup>3</sup>) on PAHs removal by US/ZEA treatment. Initial condition: EDTA = 2.0 mM, ZVI = 15 g/L, and reaction time = 60 min.

### 3.4. Comparison of PAHs removal with different treatments

Fig. 5 compares the time courses of PAHs removal by ZEA, US/Air, and US/ZEA treatments with 2.0 mM of EDTA, 15 g/L of ZVI, and ultrasonic density of 1.08 w/cm<sup>3</sup> under natural conditions. As shown in Fig. 5a, removal efficiency of Σ16 PAHs increased with reaction time and slightly increased when the reaction time was increased from 60 min (42.5%) to 180 min (46.6%) during the ZEA process. With US/Air treatment, removal efficiencies of LMW, HMW, and Σ16 PAHs at 60 min were only 36.7, 30.8, and 32.9% respectively (Fig. 5b). It has been reported that PAHs degradation mechanisms during the US process are oxidized by •OH and pyrolytic decomposition (Laughrey et al., 2001). Fig. 5c demonstrates that with US/ZEA treatment, removal efficiencies of LMW, HMW, and Σ16 PAHs at 60 min increased to 75.6, 66.8, and 70.1% respectively. Oh et al. (2016) reported that lighter and more water-soluble PAHs in sludge are preferentially released into the soluble phase by US treatment. LMW PAHs therefore had better removal performance than HMW PAHs in the ZEA, US/Air, and US/ZEA systems owing to their higher solubility (Table S1).

PAHs are efficiently adsorbed onto the surface of sludge and slowly penetrate cavities (Jonsson et al., 2009). As discussed above, the ZEA process had an insignificant effect on sludge disintegration; thus ROS produced during the ZEA process only removed the PAHs that had adsorbed onto the surface of the sludge. The results differed when US was introduced as US could completely break down the sludge particles. Considerable organic compounds, including PAHs, could be released from the sludge cavities. Therefore, US/Air and US/ZEA processes could degrade PAHs not only on the sludge surface but also in the interior of sludge (Lin et al., 2016). Meanwhile, the greater contributors (by percentage) to total PAHs content included 2-ring PAHs (19.82%), 3-ring PAHs (18.83%), and 4-ring PAHs (51.97%) (Table S1). Removal ratios of these PAHs decreased between 60 min and 90 min during both the US/Air and

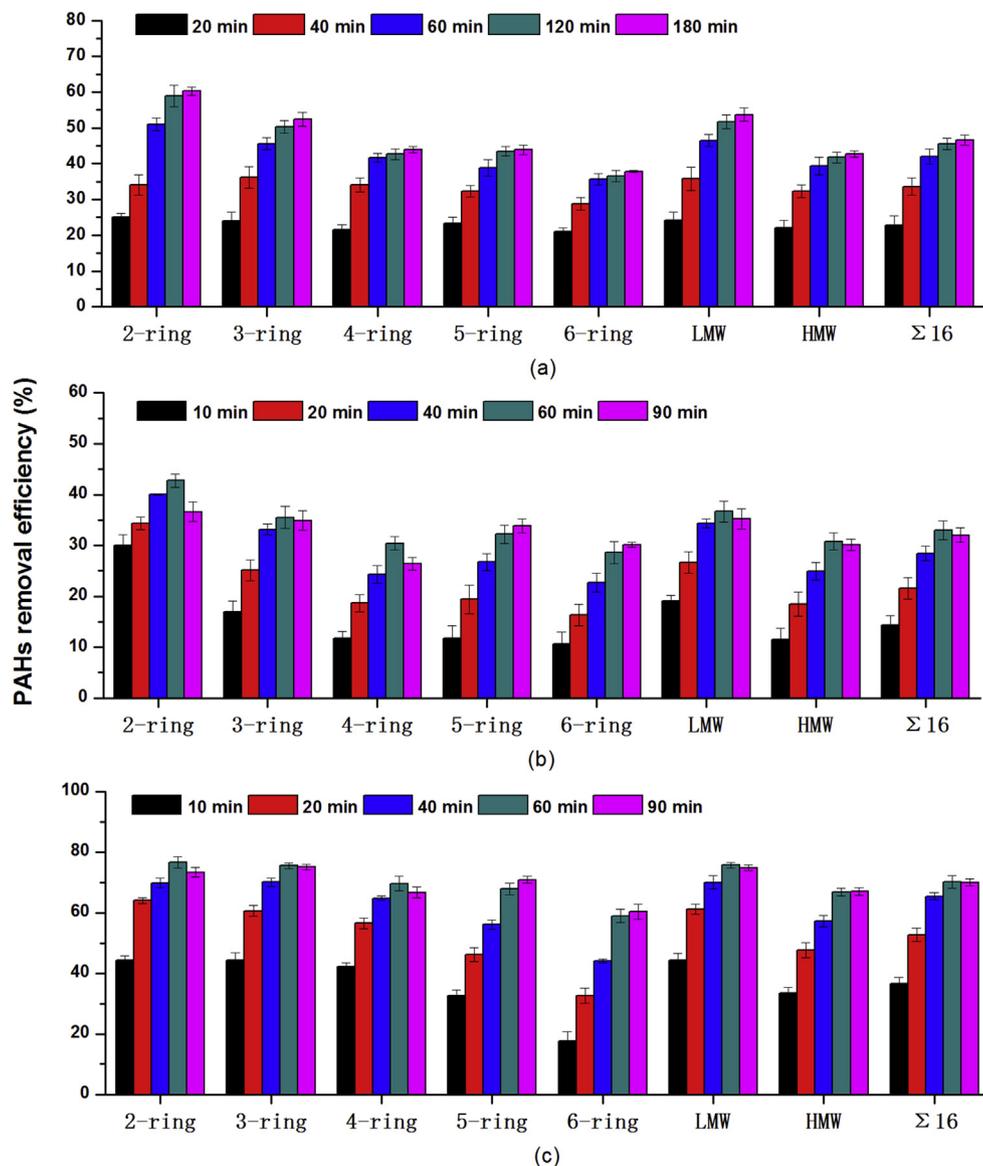
US/ZEA processes. A possible explanation for this is that a large proportion of these PAHs were strongly adsorbed onto the sludge surface or inside the sludge cavities; therefore, more PAHs were released to the soluble phase with the introduction of US. In addition, the concentration of Fe<sup>2+</sup> decreased during the US/ZEA process (Fig. 1), while EDTA was simultaneously degraded over time (Zhou et al., 2009a). Thus, the decreases in Fe<sup>2+</sup> and EDTA concentrations might result in a decrease in ROS production.

As noted above, 70.1% of Σ16 PAHs was removed within 60 min in the US/ZEA system, but only 46.6% removal was achieved in the ZEA system over 180 min. Table S4 compares the removal rate constants of PAHs in the multiple treatments. The rate constants of all PAHs in the US/ZEA system were significantly greater than in the ZEA and US/Air systems. In addition, the synergy indices of all PAHs being treated by the US/ZEA system were >1.0, indicating that US had a synergistic effect on the removal of PAHs. Similar synergistic effects in US/Fenton and US/KMnO<sub>4</sub> systems are noted in previous reports (Liang et al., 2016; Lin et al., 2016).

To examine the effects of ZVI reuse on PAHs removal, ZVI residue was recycled using a magnet. Experiments were performed using the recycled ZVI residue in US/ZEA treatment under the same conditions (i.e., 2.0 mM of EDTA, 15 g/L of fresh ZVI, ultrasonic density of 1.08 w/cm<sup>3</sup>, and natural pH at 60 min). The results for the removal efficiencies of PAHs in the reused US/ZEA system are illustrated in Fig. S3. Removal efficiencies of LMW, HMW, and Σ16 PAHs with second re-use were 54.8, 49.6, and 51.5% respectively, and with third re-use were 41.3, 36.2, and 38.1% respectively. This demonstrated that the ZVI residue retained a significant ability to remove PAHs from textile dyeing sludge.

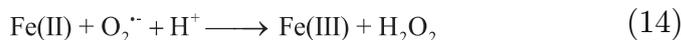
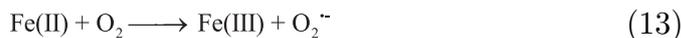
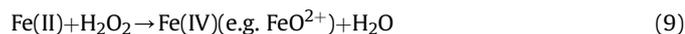
### 3.5. Enhancement mechanism of ROS production by US/ZEA treatment system

As reported previously, •OH, O<sub>2</sub><sup>•-</sup>/HO<sub>2</sub><sup>•</sup>, and Fe(IV) are the main



**Fig. 5.** Comparison of (a) ZEA, (b) US/Air, and (c) US/ZEA treatments on the removal of PAHs. Initial condition: EDTA = 2.0 mM, ZVI = 15 g/L, and ultrasonic density = 1.08 w/cm<sup>3</sup> under natural conditions.

types of ROS generated through Fenton-like reactions in ZEA systems, as described by Eqs. (8)–(14) (Rose and Waite, 2002; Pham et al., 2009; Zhou et al., 2014). At the same time, Fe(III) can also be reduced to Fe(II) through reaction (15) (Tokumura et al., 2011), while the ZVI redox cycle in the ZEA system is then established by reactions (3), (8), (11), and (13)–(15). Fe(II) and Fe(III) represent the sum of all free and complex ferrous and ferric species. The mechanism for ROS production is illustrated in Fig. S4. This is expected to follow similar pathways as previously described, with some modifications (Zhou et al., 2010).



Noradoun et al. (2003) proposed three possible O<sub>2</sub> activation schemes in the ZVI/EDTA system: (1) a heterogeneous activation at the ZVI surface; (2) a homogeneous activation by EDTA; and (3) a heterogeneous activation producing Fe(IV) on the surface of the ZVI

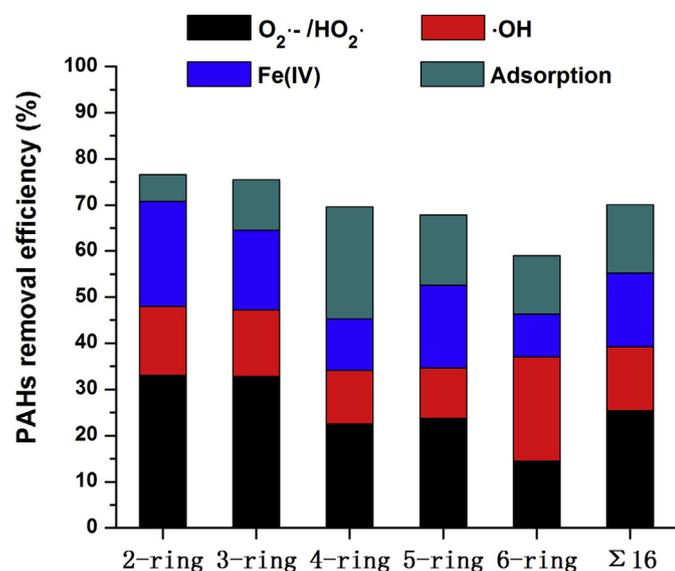


Fig. 6. The contributions of three radicals and adsorption for PAHs removal by US/ZEA treatment. Initial condition: EDTA = 2.0 mM, ZVI = 15 g/L, ultrasonic density = 1.08 w/cm<sup>3</sup>, and reaction time = 60 min under natural conditions.

particles. The reactions of ZVI oxidized by O<sub>2</sub> could occur on the ZVI surface or could involve transfer of electrons through an iron layer (Zečević et al., 1989). Significant amounts of H<sub>2</sub>O<sub>2</sub> could be produced during the 2-electron transfer process, especially after an oxide coating had been formed on the surface (Joo et al., 2005). In the US/ZEA system, these reactions for ZVI corrosion, O<sub>2</sub> activation, and further ROS species generation might occur on or adjacent to the ZVI surface. As noted above, organic compounds, including PAHs, could be released from sludge cavities in the presence of US. Based on their highly hydrophobic nature, PAHs molecules in the soluble phase had a higher tendency to be adsorbed onto or around the ZVI surface, and therefore, might be removed more quickly than other organic compounds with lower hydrophobicity or hydrophilicity. Meanwhile, PAHs removal was achieved via adsorption onto the ZVI surface, defined as “adsorption” (Shimizu et al., 2012). Moreover, no PAHs were detected in the supernatant in any instance, suggesting that PAHs rarely remained in the aqueous phase due to their highly hydrophobic nature.

As described previously, PAHs could be degraded by three radicals and be adsorbed by ZVI. The contribution of adsorption was estimated by subtracting the total contribution of the three radicals from the overall PAHs removal efficiency. As shown in Fig. 6, for the Σ16 PAHs, the contributions of  $\cdot OH$ , O<sub>2</sub><sup>•−</sup>/HO<sub>2</sub><sup>•</sup>, Fe(IV), and adsorption were 13.9, 25.4, 16.0, and 14.8% respectively. In general, O<sub>2</sub><sup>•−</sup>/HO<sub>2</sub><sup>•</sup> and Fe(IV) were mainly responsible for degrading 2- and 3-ring PAHs; adsorption was typically responsible for removing 4-ring PAHs; and  $\cdot OH$  was responsible for degrading 6-ring PAHs. Moreover, adsorption had an inconspicuous effect on 2-ring PAH (i.e., NaP) removal (5.7%) due to its highest water solubility coefficient (Table S1). Obviously, ROS made the predominant contribution to the removal of all PAHs in US/ZEA system.

#### 4. Conclusion

This study demonstrated that 16 PAHs in textile dyeing sludge could be effectively removed by a combined US/ZEA treatment process. US led to synergistic improvement of PAHs removal in the ZEA system, because it enhanced disruption of sludge particles to release PAHs and promoted ZVI corrosion and O<sub>2</sub> activation. EDTA

concentration, ZVI dose, and ultrasonic density had a considerable influence on PAHs removal. However, unlike the traditional Fenton process, the US/ZEA system could be used for PAHs removal under natural conditions. The removal regularities of individual PAHs were related to their water solubility and their content in the textile dyeing sludge. In the US/ZEA system, three types of ROS (O<sub>2</sub><sup>•−</sup>/HO<sub>2</sub><sup>•</sup>,  $\cdot OH$ , and Fe(IV)) and adsorption contributed differently to the removal of the PAHs, with ROS providing the greatest contribution. US/ZEA treatment could therefore potentially be applied to PAHs removal from textile dyeing sludge. This work also provides valuable insights into the use of EDTA in sludge wastewater for the removal of organic pollutants in the sludge.

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#### Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.chemosphere.2017.10.043>.

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