



Treatment of a simulated sludge by ultrasonic zero-valent iron/EDTA/Air process: Interferences of inorganic salts in polyaromatic hydrocarbon removal

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ABSTRACT

Understanding the occurrence states of persistent organic pollutants such as polycyclic aromatic hydrocarbons (PAHs) in textile dyeing sludge is the key to their further treatment and disposal. Here, the effects of inorganic salts (silicate, sulfate, phosphate, hydroxide, and iron salts) that were typically rich in textile dyeing sludge on PAH adsorption by sludge and PAH degradation by an ultrasound (US) combined zero-valent iron/EDTA/Air (ZEA) system were studied in a simulated sludge system. The results showed that the simulated sludge containing inorganic salts had a larger specific surface area, which was beneficial for the adsorption of PAHs. More low-ring PAHs were adsorbed on the surface of the particles in the simulated sludge because of the inorganic salts, which was conducive to low-ring PAHs degradation by US/ZEA. The PAH removal rates were increased by 15.37% and 11.19%, respectively, in the presence of SiO_3^{2-} and HPO_4^{2-} . The yield of hydroxyl radicals ($\cdot\text{OH}$) was increased by 42.39% and 66.25% by SiO_3^{2-} and HPO_4^{2-} , respectively. The reason was that the oxidation of the ligand ($[\text{Fe}^{\text{II}}(\text{EDTA})]$) formed by ethylenediaminetetraacetic acid (EDTA) and divalent iron was promoted by SiO_3^{2-} and HPO_4^{2-} . The formation of $\cdot\text{OH}$ in the US/ZEA system was inhibited by the corrosion inhibition of SO_4^{2-} on zero-valent iron (ZVI), the reaction of ferric salt with EDTA, and the reaction of $\text{Mg}(\text{OH})_2$ with the ligand ($[\text{Fe}^{\text{II}}(\text{EDTA})]$). This work provides an essential theoretical insight into the role of the inorganic components of sludge in the removal of PAHs by advanced oxidation processes.

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1. Introduction

The textile printing and dyeing industries are some of the most polluting industries. According to the China Environment Statistics Yearbook, 4.65 million tons of textile dyeing sludge (80% moisture content) were produced in 2016. The precipitates of inorganic coagulants (ferric chloride, aluminium sulfate, and polyaluminium chloride (PAC)) are the main components of textile dyeing sludge (Gao et al., 2007). This sludge is a very complex system containing heavy metals, pathogens, and various organic compounds (e.g., phthalate esters, polychlorinated biphenyls, and PAHs) (Liang et al., 2017; Liang et al., 2013; Vanhulle et al., 2008). In addition, various inorganic compounds, such as those of aluminium, iron, silicon, and phosphorus, have been detected in textile dyeing sludge (Zhang et al., 2017a).

Ning et al. (2014) reported that the total concentration of the 16 PAHs ($\Sigma 16$) range 1463 ± 177 – $16,714 \pm 1507$ ng/g in dewatered

textile dyeing sludge from Guangdong. Sixteen PAHs have been identified as priority pollutants by the United States Environmental Protection Agency (USEPA). Low-ring PAHs generally cause acute toxicity, whereas high-ring PAHs have mutagenic and carcinogenic effects on many organisms (Haritash and Kaushik, 2009). Advanced oxidation processes are considered a desirable method to convert PAHs into biodegradable species or to degrade them completely (Ribeiro et al., 2015).

With the development of advanced oxidation processes for the treatment of sludge, the effects of organic and inorganic compounds on sludge degradation requires exploration. In advanced oxidation processes, there is a competitive degradation relationship between sludge organic matter and PAHs. Generally, the aliphatic fractions of the organic matter in sludge are degraded before the PAHs (Ke et al., 2018). Sun et al. (2016) reported positive and negative effects of coexisting solutes (anions, cations, and natural organics) on the removal of pollutants by zero-valent iron (ZVI). Thus, the ZVI degradation system may be inhibited by surface monomeric complexes, Fe-anion complexes and calcium carbonate formed by silicate, sulfate radicals, and calcium ions

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(Dong et al., 2013; Kohn et al., 2005; Liu et al., 2007). However, the oxide film of ZVI is destroyed by sulfate radicals (Yu et al., 2013), which may promote the degradation of organic pollutants by ZVI system. Song et al. (2014) reported that the adsorption of organic compounds by sludge can be adversely affected by calcium, magnesium, sodium, potassium, and cadmium ions. However, previous studies have seldom focused on the effects of inorganic salts on advanced oxidation processes. Thus, it is necessary to explore the effects of inorganic salts on the adsorption of PAHs by sludge and the degradation of PAHs by advanced oxidation processes.

The traditional Fenton process is one of the standard advanced oxidation processes. However, the acidic environment, the ineffectiveness of Fenton reagent, and the large production of iron oxide sludge have limited the widespread application of Fenton oxidation (Pignatello et al., 2006). To solve these problems, a Fenton-like reaction has been proposed. Because ZVI can be used as a heterogeneous catalyst for H_2O_2 production, a Fenton-like system which can generate reactive oxygen species (hydroxyl radicals ($\cdot OH$), superoxide anion/hydroperoxyl radicals, and high-valent iron species) can be formed by ZVI and molecular oxygen (Xu and Wang, 2011). The ZVI/ethylenediaminetetraacetic acid (EDTA)/Air (ZEA) system can also maintain the production of H_2O_2 , and the problem of low yield of reactive oxygen species in ZVI/Air system was solved by ZEA system (Fu et al., 2016). Because of cavitation, ultrasonication (US) has been widely used in the treatment of organic matter. US can also increase the efficiency of advanced oxidation processes. Thus, US is often combined with Fenton-like oxidation for the degradation of textile dyes (Eren, 2012; Zhang et al., 2017b). Furthermore, combined with ZVI and EDTA, US has been applied to wastewater treatment and for the removal of 2,4-dichlorophenol from contaminated soil (Zhou et al., 2014). There was significant synergy in the US/ZEA system, and that this system has a significant effect on the treatment of dyeing wastewater (Zhou et al., 2010, 2009). Therefore, a combined US/ZEA system may enhance the removal of contaminants from sludge.

Zhou et al. (2014) used kaolin clay instead of soil to explore the mechanism of 2,4-dichlorophenol degradation by ZEA. Wei et al. (2018) used amino acids instead of protein-rich sewage sludge as a N-containing model compound to analyse the catalytic mechanism of fast sewage sludge catalytic pyrolysis. Therefore, it is feasible to use this simulated system to explore the mechanisms of interaction of inorganic salts. Coagulated sediment is formed in a mixed solution of PAC and calcium carbonate (Sudoh et al., 2015). Calcium carbonate acts as a coagulant, aiding the formation of larger flocs. Calcium oxide is often used as a pH regulator and phosphorus remover in sewage disposal (Gao et al., 2007). Thus, PAC and CaO may be used to produce simulated sludge, and the inorganic components of textile dyeing sludge may be replaced by simulated sludge. Therefore, the main research objectives of this paper are: (1) to study the composition, particle size, specific surface areas, and microscopic surface properties of simulated sludge; (2) to explore the effects of inorganic salts on the adsorption of PAHs by sludge; and (3) to investigate the effects of inorganic salts on the degradation of PAHs, as well as the degradation mechanism, in the US/ZEA system.

2. Materials and methods

2.1. Materials

The experiment used three chemical standards, including a mixed standard containing 16 PAHs (solvent: benzene/methylene chloride = 1/1), surrogate standards (solvent: methylene chloride) using fluorine-D10 and pyrene-D10, and internal standards (sol-

vent: methylene chloride) which contains naphthalene-D8, acenaphthene-D10, phenanthrene-D10, chrysene-D12, and perylene-D12. These three chemical standards (2000 mg/L) were purchased from O2si Smart Solutions (Charleston, SC, USA) and had a purity of >99.5%. The properties of the 16 PAHs (Jonsson et al., 2007) are presented in Table S1. Polyaluminium ferric chloride (PAFC), PAC, CaO, Na_2SiO_3 , and Na_2HPO_4 were purchased from Tianjin Zhi Yuan Reagent Company. $Mg(OH)_2$ and Na_2SO_4 were purchased from Tianjin Damao Reagent Company. ZVI particles (purity > 99%) with a diameter less than 0.15 mm and the disodium salt of EDTA as a dihydrate were purchased from Aladdin. All inorganic chemicals were analytical grade and used without further purification. All organic chemicals of high-performance liquid chromatography (HPLC) grade were purchased from ANPEL Laboratory Technologies (Shanghai) Inc.

2.2. Sludge samples and simulated sludge

Four kinds of dewatered textile dyeing sludge were collected from four textile dyeing plants (TDP1–4) in different cities in Guangdong Province, China. The samples were stored frozen at 4 °C until analysis. The PAC and PAFC solutions were mixed with CaO (100 mesh) solutions until pH = 7. The mixture was continuously stirred for 10 min with a magnetic stirrer (HMS-901D, China) at 200 rpm (Sudoh et al., 2015). In addition, ultrapure water was added to the two samples until 98% moisture content was achieved. Thus, PAC simulated sludge (S1) and PAFC simulated sludge (S2) were obtained. S1 contained 1% (the mass of dry S1) $Na_2SiO_3 \cdot 9H_2O$, 1% $Mg(OH)_2$, 10% Na_2SO_4 , and 10% $Na_2HPO_4 \cdot 12H_2O$. Finally, six kinds of simulated sludge were obtained, S1, S2, S1 + Na_2SiO_3 , S1 + $Mg(OH)_2$, S1 + Na_2SO_4 and S1 + Na_2HPO_4 .

2.3. Experimental procedure

According to the concentration of $\Sigma 16$ PAHs in TDP1–4, a standard solution containing 16 PAHs ($\Sigma 16$ PAHs = 6400–8000 ng/g, solvent: acetone) was added in the simulated sludge (98% moisture content). The six kinds of simulated sludge (20 mL, $\Sigma 16$ PAHs = 8000 ng/g, each PAH = 500 ng/g) were loaded into 50-mL sealed centrifuge tubes (Teflon NALGENE 3114–0010) and equilibrated on a horizontal shaker for 72 h at 30 °C in the dark. In addition, S1 was extracted at given intervals (0.083, 0.16, 0.5, 1, 2, 6, 9, 12, 48, and 72 h), after which the samples were centrifuged for 10 min at 4000 rpm. Aliquots of the supernatants were extracted thrice with 10 mL *n*-hexane/dichloromethane (4:1, v/v) (see Fig. S1). The solid residues were placed in a fume hood for one week to remove PAHs and then treated as hazardous waste.

Then, 200 mL of the six kinds of simulated sludge ($\Sigma 16$ PAHs = 6400 ng/g, each PAH = 400 ng/g) were loaded into 500 mL sealed conical flask and equilibrated on a horizontal shaker for 9 h at 30 °C in the dark, after which the samples were degraded by the US/ZEA system (operating conditions: 2.0 mM EDTA, 15 g/L ZVI, 1.0 L/min air, 1.08 W/cm³ ultrasonic density for 60 min) (Man et al., 2018). US treatments were operated in pulse mode with 3 s on and 3 s off and maintained at a temperature of 25 ± 1 °C. US treatments were conducted in a 0–1800 W sonicator (Scientz JY99-IIDN, China, 20 kHz) equipped with a titanium probe tip (320 mm in length and 25 mm in diameter) and a sealed converter. The cylindrical reactor with a circulating temperature controller was used to maintain the temperature. A diagram of experimental set-up and actual instruments are shown in Fig. S2, and the experimental set-up has been used in our previous works (Lin et al., 2016). Air was continuously supplied to the simulated sludge by an air pump. After that, the simulated sludge was centrifuged at 4000 rpm for 10 min, and the solid residues were freeze-dried (LGJ-10C, China) at –60 °C for 24 h before extraction.

2.4. Analytical methods

The chemical composition of all sludges was determined by energy dispersive X-ray fluorescence (XRF) spectrometry (EDX-7000, China). The particle size distributions of the sludge samples (98% moisture content) were measured with a laser scattering particle size distribution analyser (LA-960S, Japan). The textile dyeing sludge and simulated sludge were freeze-dried in a vacuum freeze dryer (24 h, -60°C). After that, the specific surface areas of the simulated sludge were measured according to the Brunauer–Emmett–Teller (BET) method with nitrogen adsorption on an ASAP 2020 instrument (Micromeritics, USA); the surface morphologies of sludge were observed by scanning electron microscope (SEM) (LEO1530VP, Germany); the different functional groups in the simulated sludge were identified by Fourier transform infrared (FTIR) spectroscopy (VERTEX 33, Germany) between 4000 and 400 cm^{-1} . The concentration of total dissolved iron (TFe) was detected using the 1,10-phenanthroline method (Jr et al., 1955). The concentration of $\cdot\text{OH}$ was calculated using an ultraviolet–visible spectrophotometer at 664 nm (Cary 100, Agilent) (Iwamori et al., 2016). The PAHs were extracted from freeze-dried simulated sludge thrice for 5 min each using a 240-W ultrasonic bath (JY92-IIN, Ningbo Scientz Biotechnology, China) (Lin et al., 2016). The PAHs were determined by gas chromatography–mass spectrometry (GC–MS, Agilent 7890B GC–5977B MS). The GC–MS analysis conditions and more analytical methods are given in the [Supplementary Material \(Text S1\)](#).

2.5. Quality assurance and quality control

The experiments were conducted without light, and the pH changed little (see [Table S2](#)). Each experiment was repeated three times or more. Routine analysis of the spiked blanks and procedural blanks was performed. The amount of volatilised PAHs in a centrifuge tube and conical flask can be calculated by determining the content of PAHs in the deionised water sample and that in the simulated sludge before degradation. The recoveries of fluorine-D10 and pyrene-D10 in the samples were $77.96 \pm 13.81\%$ and $108.15 \pm 6.82\%$, and that of the 16 PAHs was $85.56 \pm 15.87\%$.

3. Results and discussion

3.1. Characteristics of simulated sludge

The characteristics of the textile dyeing sludge are given in [Table S3](#). The total concentration of the 16 PAHs range 3422.54 ± 106.75 – $13,644.68 \pm 1315.95\text{ ng/g}$ in the dewatered textile dyeing sludge (TDP1-4). The data confirm the similarity between the inorganic characteristics of simulated sludge and that of textile dyeing sludge ([Text S2](#), [Fig. S3](#)). The textile dyeing sludge contained a significant amount of aluminium, iron, silicon, sulfur, phosphorus, magnesium, and other elements. Based on the elemental contents in the textile dyeing sludge, the six kinds of simulated sludge are S1, S2, S1 + Na_2SiO_3 , S1 + Na_2SO_4 , S1 + Na_2HPO_4 , and S1 + $\text{Mg}(\text{OH})_2$. The effect of iron ions in the flocculate on the reaction can be observed by studying PAC and PAFC. SiO_3^{2-} , SO_4^{2-} , and HPO_4^{2-} represent the principal anions in textile dyeing sludge. $\text{Mg}(\text{OH})_2$ represents a class of hydroxides with a dissolution constant lower than that of ferric hydroxide. The characteristics of all simulated sludge are presented in [Table 1](#). The pH values of the six simulated sludge were not significantly different. XRF analysis showed that the significant inorganic oxide components in the simulated sludge were Al_2O_3 , Fe_2O_3 , and SiO_2 , followed by SO_3 and CaO. The contents of Al_2O_3 , Fe_2O_3 , and SO_3 in S1 and S2 were identical. The content of SiO_2 in S2 was 3.6 times that of S1, and the

content of CaO in S1 was 1.6 times that of S2. The optimum flocculation condition for polymeric polysilicate aluminium ferric sulfate is a molar ratio of $\text{Al}/\text{Fe}/\text{Si} = 1:1:1$ (Zhang and Liu, 2015). The high concentration of silica contributed to the flocculation of PAFC. CaO was the alkaline chemical and the core of flocs. PAFC required less CaO as the flocculent. Thus, the different elemental content in the simulated sludge was caused by the different properties of materials themselves. In addition, the inorganic chemical composition of the four kinds of simulated sludge (S1 + Na_2SiO_3 , S1 + Na_2SO_4 , S1 + Na_2HPO_4 , and S1 + $\text{Mg}(\text{OH})_2$) was also similar to the textile dyeing sludge. The morphologies of the simulated sludge particles were studied by SEM (magnification: $10,000\times$ and $20,000\times$) ([Fig. 1](#)). In a vacuum freeze dryer (24 h, -60°C), the water in the S1-2 became solid ice, which sublimated under vacuum. The physical and molecular structures of S1-2 change very little, and its structure and appearance were well preserved. The SEM micrographs showed that the surfaces of the S1 particles had an inhomogeneous schistose structure, whereas the surfaces of the S2 particles were relatively smooth.

The particle size distribution and the textural characteristics of the simulated sludge are presented in [Table 2](#). The particle sizes of the six simulated sludge samples were mainly distributed between 2 and $20\text{ }\mu\text{m}$. The sizes of particles of S2 were larger than those of S1. This is because PAFC has better coagulation performance than PAC at $\text{pH} = 7.0$ – 8.4 (Gao et al., 2003). Nevertheless, the particle size of S1 was reduced by the addition of Na_2SiO_3 , Na_2SO_4 , Na_2HPO_4 , and $\text{Mg}(\text{OH})_2$. The particle size of simulated sludge were as follows: $\text{S1} + \text{Na}_2\text{SO}_4 < \text{S1} + \text{Na}_2\text{HPO}_4 < \text{S1} + \text{Mg}(\text{OH})_2 < \text{S1} + \text{Na}_2\text{SiO}_3 < \text{S1} < \text{S2}$. The BET surface area of S1 was increased by the addition of inorganic salts. The average pore diameter of S1 was increased by Na_2SiO_3 and Na_2HPO_4 . The structure and appearance of simulated sludge would not be damaged by freeze-dried. Thus, sludge flocs were destroyed by inorganic salts. Therefore, the differences between the six kinds of simulated sludge will provide the basis for the conclusions in this paper.

3.2. Effect of inorganic salts on adsorption and degradation of PAHs

3.2.1. Adsorption characteristics of simulated sludge and effect of inorganic salts on adsorption

An experimental study of the adsorption kinetics of S1 was conducted to determine the adsorption equilibrium time. As shown in [Fig. S4](#), PAH adsorption can be divided into two phases: fast adsorption and slow adsorption, as previously reported (Sun et al., 2010; Zhou et al., 2018). Initially, the $\Sigma 16$ PAHs in S1 were rapidly adsorbed, and, subsequently, the adsorption of the $\Sigma 16$ PAHs slowed from 2 h to 9 h. The adsorption amount of $\Sigma 16$ PAHs did not change after 9 h. Thus, the PAHs reached adsorption balance after 9 h. The adsorption process closely followed the pseudo-second-order kinetic model ($R^2 = 0.9999$). Thus, the adsorption of PAHs proceeds through surface exchange reactions until the surface adsorption sites are completely occupied, after which the PAHs diffuse into the particles for further interaction (Crini et al., 2007).

The adsorption effects of five kinds of simulated sludge on PAHs are shown in [Fig. 2](#). The effect of inorganic salts on the adsorption of simulated sludge was studied using different simulated sludge adsorption on PAHs. As shown in [Fig. 2a](#), the adsorption capacity of S1 + Na_2SO_4 to $\Sigma 16$ PAHs is 5.55% lower than that of S1. In contrast, the adsorption capacities of S1 + Na_2SiO_3 , S1 + Na_2HPO_4 , and S1 + $\text{Mg}(\text{OH})_2$ for the $\Sigma 16$ PAHs are 13.77%, 10.71%, and 27.26% higher than that of S1, respectively. Thus, SO_4^{2-} inhibited the adsorption of PAHs in S1, whereas SiO_3^{2-} , HPO_4^{2-} , and $\text{Mg}(\text{OH})_2$ enhanced the adsorption. The particle size of the sludge was reduced after the addition of Na_2SiO_3 , Na_2SO_4 , Na_2HPO_4 , or $\text{Mg}(\text{OH})_2$, and the specific surface area of the sludge increased. One

Table 1
Characteristics of the simulated sludge.

Simulated sludge	Moisture content (%)	pH	Ignition loss (%)	Chemical composition (%)						
				Al ₂ O ₃	Fe ₂ O ₃	SO ₃	SiO ₂	CaO	P ₂ O ₅	MgO
S1	98.10 ± 0.03	7.00 ± 0.01	34.01 ± 0.17	19.58 ± 0.61	12.09 ± 0.70	1.42 ± 0.04	2.45 ± 0.45	17.47 ± 0.72	n	n
S2	98.02 ± 0.01	7.00 ± 0.01	30.61 ± 0.04	19.60 ± 0.48	12.17 ± 1.85	2.67 ± 0.95	8.84 ± 0.90	10.86 ± 1.12	n	n
S1 + Na ₂ SiO ₃	98.12 ± 0.01	7.19 ± 0.04	33.28 ± 0.37	20.56 ± 0.20	12.10 ± 0.08	1.37 ± 0.02	3.52 ± 0.06	17.86 ± 0.07	n	n
S1 + Na ₂ SO ₄	98.09 ± 0.01	7.14 ± 0.01	32.99 ± 0.15	19.19 ± 0.18	12.02 ± 0.08	6.45 ± 0.03	2.00 ± 0.05	17.47 ± 0.07	n	n
S1 + Na ₂ HPO ₄	98.13 ± 0.02	7.08 ± 0.03	31.25 ± 0.87	20.12 ± 0.19	12.70 ± 0.08	1.32 ± 0.02	2.34 ± 0.05	17.35 ± 0.07	1.07 ± 0.03	n
S1 + Mg(OH) ₂	98.10 ± 0.01	7.31 ± 0.04	33.40 ± 0.06	20.68 ± 0.20	12.28 ± 0.07	1.58 ± 0.02	2.18 ± 0.05	17.43 ± 0.08	n	0.13 ± 0.01

n: not detected.

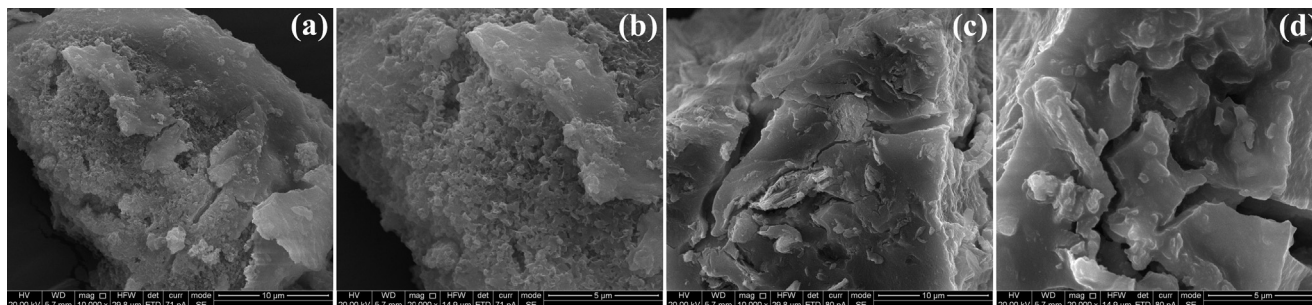


Fig. 1. SEM magnification of the surfaces at (a) S1 10,000×, (b) S1 20,000×, (c) S2 10,000×, and (d) S2 20,000× magnification.

Table 2
The size and the textural characteristics of the simulated sludge particles.

Simulated sludge	Particle size (%)				Surface textural characteristics		
	≤2 μm	2–20 μm	20–200 μm	>200 μm	BET surface area (m ² /g)	Total pore volume (cm ³ /g)	Average pore diameter (nm)
S1	3.46 ± 0.03	70.04 ± 0.11	26.53 ± 0.06	n	23.26 ± 0.12	0.13	14.01
S2	6.24 ± 0.61	65.14 ± 0.05	28.64 ± 0.58	n	1.56 ± 0.25	0.02	41.73
S1 + Na ₂ SiO ₃	3.07 ± 0.09	71.97 ± 0.01	24.96 ± 0.07	n	24.72 ± 0.12	0.15	23.76
S1 + Na ₂ SO ₄	3.20 ± 0.04	75.09 ± 0.05	21.73 ± 0.02	n	50.82 ± 0.48	0.14	11.03
S1 + Na ₂ HPO ₄	1.61 ± 0.02	78.52 ± 0.12	19.87 ± 0.08	n	24.54 ± 0.15	0.13	21.66
S1 + Mg(OH) ₂	5.86 ± 0.02	70.15 ± 1.71	23.99 ± 0.71	n	36.43 ± 0.44	0.18	14.01

n: not detected.

of the possible explanations for the increased adsorption capacity is that a higher specific surface area can adsorb more PAHs, while the PAHs can be adsorbed by Mg(OH)₂ and silicate precipitation. The main absorbance in the FTIR spectra of simulated sludge (Fig. S5) was in the region of 3630–3300 cm⁻¹, which was assigned to O–H stretching of water of crystallisation or that involved in the flocculation of PAC. The peaks at 1634 and 761 cm⁻¹ in the spectra of S1 can be the variable angle vibration and the rocking vibration of H₂O. Therefore, the water in the freeze-dried simulated sludge still has a great influence on the FTIR spectra of simulated sludge. After the contact of the PAHs with the simulated sludge, a peak at 1384 cm⁻¹, which can be assigned to the aromatic ring skeletal stretching appeared. This phenomenon indicates the direct adsorption between PAHs and simulated sludge. Because of the O–H stretching, the peak of aromatic C–H (3030–3070 cm⁻¹) was not obvious. The peaks at 1180 and 1151 cm⁻¹ in the spectra of S1 + PAHs and S1 + Na₂SO₄ + PAHs were linked by O–H to the aromatic nucleus (Weng, 2010). The hydrophilicity of the PAHs was enhanced by –OH, and the adsorption of PAHs by the simulated sludge decreased. In general, Na₂SiO₃, Na₂HPO₄, and Mg(OH)₂ changed the structure and composition of the sludge. In contrast, the inhibition of PAH adsorption by SO₄²⁻ may be attributed to the enhancement of the hydrophilicity of the PAHs.

As shown in Fig. 2b–e, the adsorption of 2–4 ring PAHs was promoted, whereas that of 5–6 ring PAHs was inhibited by SiO₃²⁻ and HPO₄²⁻. The adsorption rate of 2–4 ring PAHs increased by 7.04–

42.32% and 6.48–47.15%, respectively, and that of 5–6 ring PAHs decreased by 5.86–15.72% and 9.56–16.28%, respectively. The adsorption rate of 2 and 4–6 ring PAHs was reduced by 2.51–17.48% by SO₄²⁻. Nevertheless, the adsorption rate of 2–6 ring PAHs was increased by 0.89–48.69% by Mg(OH)₂, and that of 2–4 ring PAHs was increased by 10.11–48.69% by Mg(OH)₂. This indicates that the effect of Mg(OH)₂ on the adsorption of 2–4 ring PAHs was particularly noticeable. In general, the increase in the adsorption rate of low-ring PAHs was more pronounced than that of high-ring PAHs. Because of the large-value octanol–water partition coefficient and high polarisability of the high-ring PAHs, the high-ring PAHs occupied most of the adsorption sites of the simulated sludge (Chen et al., 2004). Some low-ring PAHs were adsorbed on the surface of simulated sludge, and most of them were adsorbed in the small pores of the simulated sludge because the low-ring PAHs were able to diffuse more rapidly into the pores and occupy the adsorption sites (Bogan and Trbovic, 2003). On the addition of inorganic salts, the adsorption sites of simulated sludge increased. Low-ring PAHs occupied more adsorption sites on the simulated sludge surface and small pores because of the high concentration of low-ring PAHs in the aqueous phase after the high-ring PAHs had been adsorbed. Thus, the increase in the low-ring PAH adsorption was more noticeable. Although the adsorption of the Σ16 PAHs was inhibited by SO₄²⁻, the adsorption of three-ring PAHs was promoted by SO₄²⁻. Therefore, the effect of particle size change on the low-ring PAHs in S1 + Na₂SO₄ was greater than that of PAH

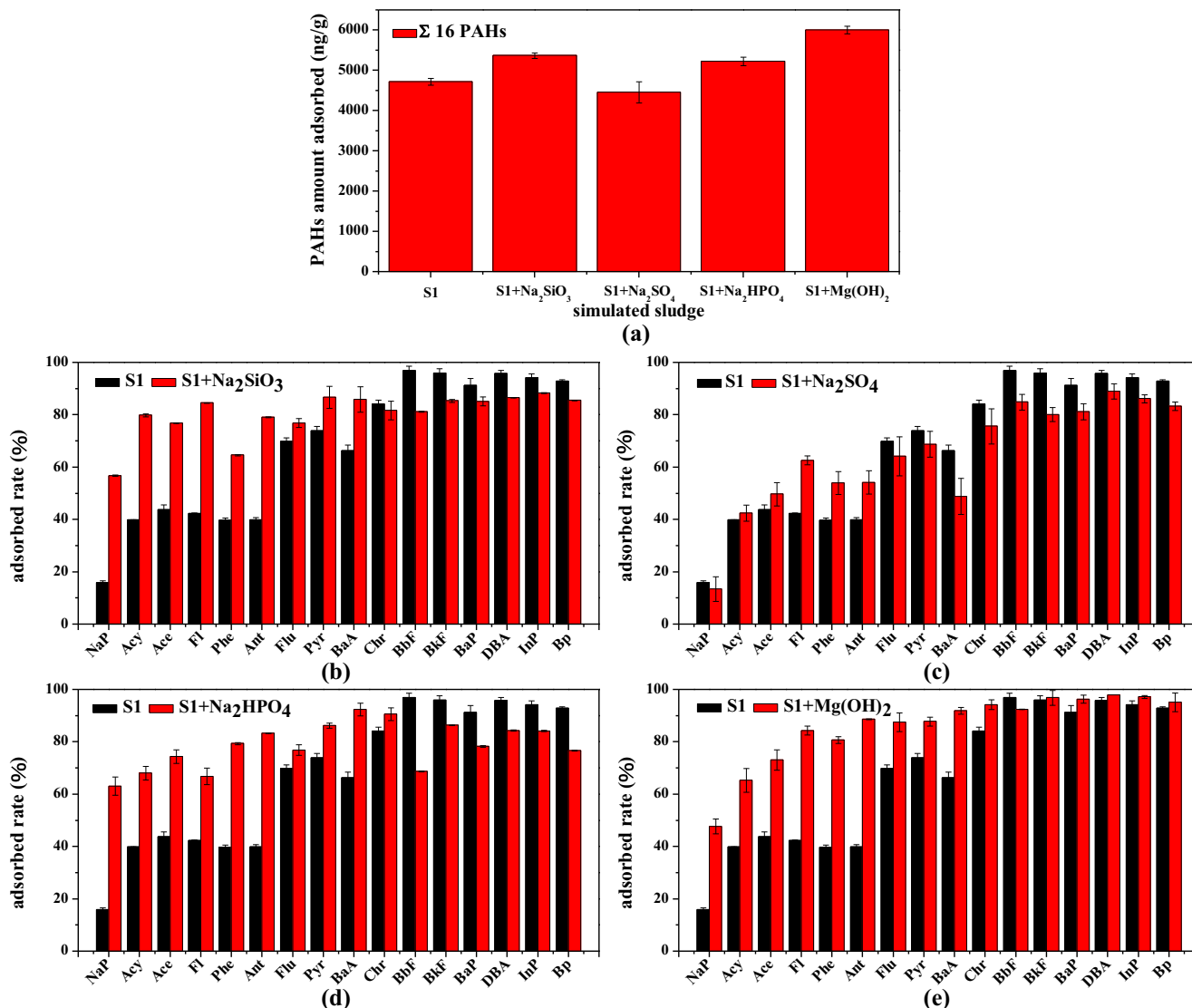


Fig. 2. (a) The adsorption of $\Sigma 16$ PAHs was investigated using five kinds of simulated sludge: the effect of Na₂SiO₃ (b), Na₂SO₄ (c), Na₂HPO₄ (d), and Mg(OH)₂ (e) on the adsorption of 16 PAHs by S1.

hydrophilicity. In sum, the adsorption of PAHs by textile dyeing sludge is promoted by metal hydroxide but inhibited by SO₄²⁻. Therefore, in real textile dyeing sludge, the sequence of effects of inorganic salts on PAHs adsorption could be Mg(OH)₂ > SiO₃²⁻ > HPO₄²⁻ > SO₄²⁻.

3.2.2. Effect of inorganic salts on US/ZEA system

Before the degradation experiments, a 1600 ng PAH standard mixture was injected into 200 mL of S1. After shaking for 9 h, the concentration of $\Sigma 16$ PAHs in the simulated sludge was 4429.21 ± 144.00 ng/g. The results are similar to those for the dewatered Guangdong textile dyeing sludge. The degradation of PAHs in five kinds of simulated sludge by US/ZEA are presented in Fig. 3. As shown in Fig. 3a, the degradation rate of $\Sigma 16$ PAHs in S1 was 68.58%, and the degradation rates of $\Sigma 16$ PAHs in S1 + Na₂SiO₃ and S1 + Na₂HPO₄ were 15.37% and 11.19%, respectively, higher than that of S1. In contrast, the degradation rate of the $\Sigma 16$ PAHs in S1 + Na₂SO₄ was 15.09% lower than that of S1. Thus, the degradation efficiency of PAHs in S1 was enhanced by SiO₃²⁻ and HPO₄²⁻ but inhibited by SO₄²⁻. The influence of Mg(OH)₂ was not evident. As shown in Fig. 3b–e, the degradation rate of twelve PAHs

in S1 + Na₂HPO₄ increased by 5.90% to 47.21% and the degradation rate of fifteen PAHs in S1 + Na₂SiO₃ increased by 2.83% to 48.28%. The degradation rates of the 3 and 4 ring PAHs by SiO₃²⁻, HPO₄²⁻, SO₄²⁻, and Mg(OH)₂ were significantly improved, whereas the degradation efficiencies of the 5 and 6 ring PAHs in S1 + Na₂SO₄ and S1 + Mg(OH)₂ were reduced by 4.50% to 51.60% and 5.83% to 16.79%, respectively. These results provide evidence that the PAH degradation was facilitated by SiO₃²⁻ and HPO₄²⁻, while the degradation of high-ring PAHs was suppressed by SO₄²⁻ and Mg(OH)₂ in S1.

3.3. Mechanism of the effect of inorganic salts on PAH degradation

Man et al. (2018) found that three types of reactive oxygen species ($\cdot$ OH, superoxide anion/hydroperoxyl radicals, and high-valent iron species) and adsorption contributed differently to the removal of the PAHs in the US/ZEA system. ZVI had also been used to adsorb and remove pollutants from water (Huang et al., 2016). In our paper, the dosage of ZVI (15 g/L) in various simulated sludge were the same, so the influence of ZVI adsorption in all kinds of simulated sludge was the same. And the effect of inorganic salts on

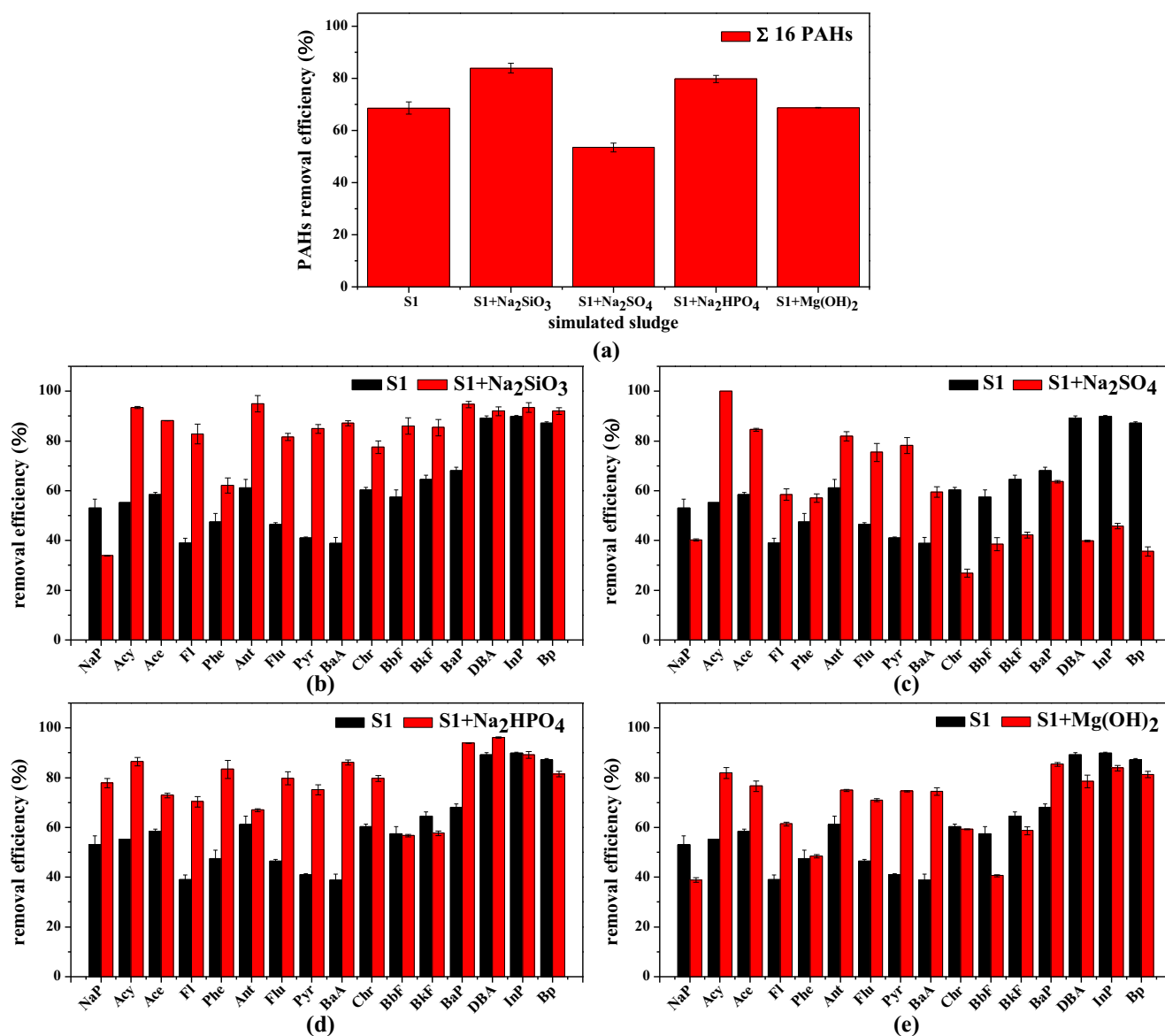
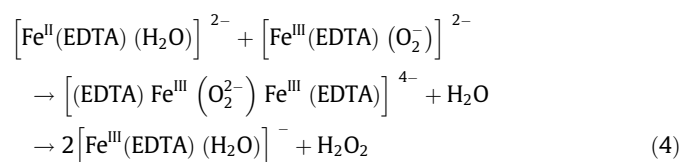
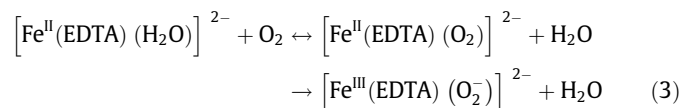
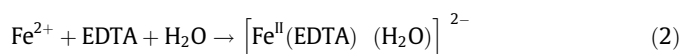
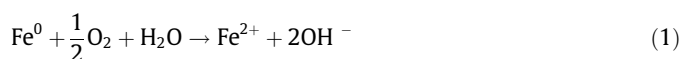


Fig. 3. (a) The degradation of $\Sigma 16$ PAHs in five kinds of simulated sludge by US/ZEA, and the effect of Na₂SiO₃ (b), Na₂SO₄ (c), Na₂HPO₄ (d), and Mg(OH)₂ (e) on the degradation of 16 PAHs in S1.

PAHs degradation was determined by measuring the concentration change of one of reactive oxygen species ($\cdot\text{OH}$). The concentration of TFe and $\cdot\text{OH}$ were measured before and after simulated sludge degradation. The results are shown in Fig. 4, which also lists the ratio of PAH removal efficiency to $\cdot\text{OH}$ content. The results showed that the content of $\cdot\text{OH}$ was proportional to the removal efficiency of PAHs. Therefore, the concentration of $\cdot\text{OH}$ could reflect the oxidative degradation ability of individual systems. The results also showed that the concentration of $\cdot\text{OH}$ in S1 + Na₂SiO₃ and S1 + Na₂HPO₄ was higher than that of S1. Moreover, S1 + Mg(OH)₂ and S1 + Na₂SO₄ showed the opposite effect. Thus, SiO₃²⁻ and HPO₄²⁻ in S1 were favourable for US/ZEA, and SO₄²⁻ and Mg(OH)₂ were not conducive to US/ZEA. In addition, the concentration of TFe in simulated sludge can indicate the degree of corrosion of ZVI. The results showed that four kinds of inorganic salts all had inhibitory effects on ZVI corrosion. The blank test showed that Fe³⁺ in flocs could be released by US.

In the ZEA degradation system, ZVI corrosion produced Fe²⁺ (Keenan and Sedlak, 2008). EDTA formed a ligand with Fe²⁺, acti-

vate oxygen and eventually produced H₂O₂ (Eqs. (1)–(4)). H₂O₂ reacted with the ligand to generate active oxygen, such as $\cdot\text{OH}$ (Seibig and Eldik, 1997).



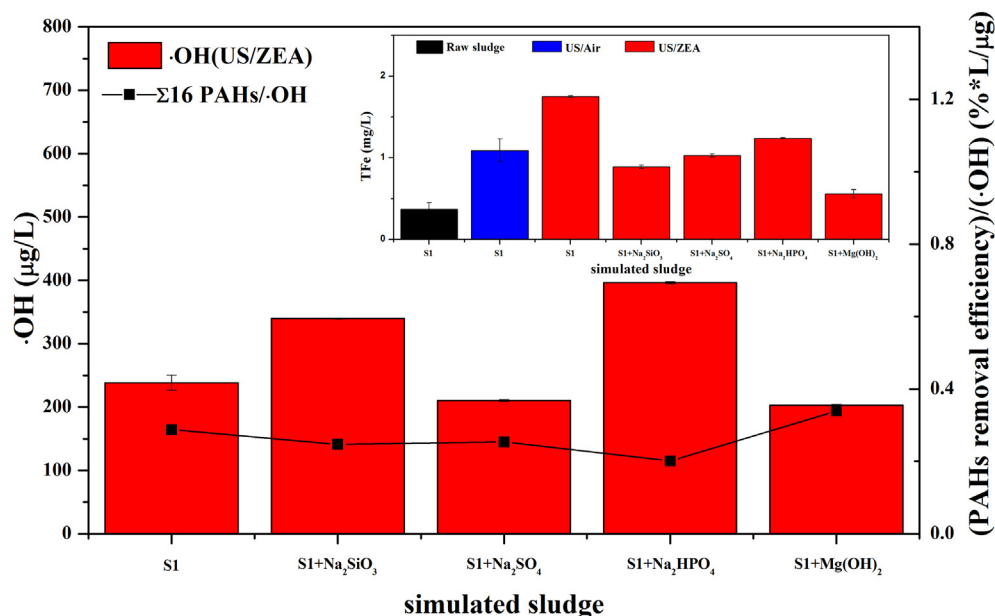


Fig. 4. The $\cdot\text{OH}$ concentration in simulated sludge and the ratio of PAH removal efficiency to $\cdot\text{OH}$ (inserted curve: TFe in simulated sludge). US/ZEA degradation conditions: ZVI = 15 g/L, EDTA = 2.0 mM, ultrasonic density = 1.8 W/cm³, and air = 1.0 L/min. US/air degradation conditions: ultrasonic density = 1.8 W/cm³ and air = 1.0 L/min.

The concentrations of $\cdot\text{OH}$ in US/ZEA(S1 + Na₂SO₄) and US/ZEA(S1 + Mg(OH)₂) were 11.72% and 15.02% lower than US/ZEA(S1), respectively. The effect of SO₄²⁻ may be attributed to the inhibitory effect of SO₄²⁻ on the corrosion of ZVI. The degradation of 1,1,1-trichloroethane was inhibited by the Fe-anion complexes formed by SO₄²⁻ (Yu et al., 2013), and the removal of trichloroethylene by nanoparticulate ZVI was inhibited by SO₄²⁻. Passive oxide film on ZVI surface was formed by ZVI and O₂ during aeration. A complex was formed by iron oxides and SO₄²⁻, which promoted dissolution of iron oxide. However, the Fe-SO₄²⁻ complexes could be accumulated on the ZVI surface when the Fe-SO₄²⁻ complexes did not convert rapidly to the liquid Fe-SO₄²⁻ complexes (Liu et al., 2007). Thus, SO₄²⁻ is an inert substance that can precipitate on the surface of ZVI. The concentration of TFe was the lowest in the US/ZEA(S1 + Mg(OH)₂) system. This may be due to the reaction of the ligand ([Fe^{III}(EDTA)]) with Mg(OH)₂, which produces ferric hydroxide, precipitating and inhibiting ZVI corrosion. Thus, less $\cdot\text{OH}$ was generated in the S1 + Mg(OH)₂ system. Mg(OH)₂ is an inhibitor that reduces the oxidation efficiency by competing for trivalent iron ions. The same was true for other hydroxides with a smaller dissolution constant than ferric hydroxide. During the adsorption tests, the adsorption of 2–4 and 3-ring PAHs was promoted by Mg(OH)₂ and SO₄²⁻, respectively. Because the total pore volume of S1 + Na₂SO₄ and S1 + Mg(OH)₂ was much smaller than the BET surface area, the amount of low-ring PAHs adsorbed on the surface of simulated sludge was higher than that in the micropores. The low-ring PAHs on the simulated sludge surface were more susceptible to oxidative degradation by $\cdot\text{OH}$. Thus, the degradation rate of the 3 and 4 ring PAHs was increased, and that of the $\Sigma 16$ PAHs was decreased by Mg(OH)₂ and SO₄²⁻. In general, Mg(OH)₂ and SO₄²⁻ have inhibitory effects on the degradation of PAHs by the US/ZEA system.

The concentration of $\cdot\text{OH}$ in US/ZEA(S1 + Na₂HPO₄) was 66.25% higher than US/ZEA(S1). Under common environmental conditions (pH 6–8), the rate of reaction between divalent iron and dissolved oxygen in aqueous solutions can be enhanced by phosphate (Guan et al., 2011). Thus, a possible explanation for the promotion of PAH degradation by HPO₄²⁻ is the reaction of the ligand ([Fe^{II}(-EDTA)]) with O₂, producing H₂O₂, which was promoted by HPO₄²⁻. The concentration of $\cdot\text{OH}$ in US/ZEA(S1 + Na₂SiO₃) was 42.39% higher than US/ZEA(S1). SiO₃²⁻ was adsorbed onto the surface of

ZVI and inhibited the dissolution of ZVI (Kohn et al., 2003). However, in this test, because of the limited contact of SiO₃²⁻ with ZVI, the inhibitory effect was not apparent. In contrast, similar to phosphate, dissolved oxygen can accelerate the rate of [Fe^{II}(EDTA)] oxidation by silicate (Guan et al., 2011). Therefore, more $\cdot\text{OH}$ was generated in US/ZEA(S1 + Na₂SiO₃), which promoted the degradation of PAHs. SiO₃²⁻ and HPO₄²⁻ are auxiliary oxidising species that promote the production of $\cdot\text{OH}$. From the adsorption tests, the adsorption of 2–4 ring PAHs was promoted by SiO₃²⁻ and HPO₄²⁻. Moreover, the degradation rate of the 3 and 4 ring PAHs in SiO₃²⁻ and HPO₄²⁻ were significantly higher than that of 5–6 ring PAHs. In general, the PAHs whose adsorption was promoted by inorganic salts were more readily degraded by US/ZEA.

Different inorganic salts had different influences and mechanisms on the adsorption and degradation processes, and the adsorption process affected subsequent degradation. The properties of the PAHs were also one of the factors affecting adsorption and US/ZEA degradation. Therefore, to improve the adsorption of organic matter by sludge and the subsequent treatment of sludge, the amount of added sulfate should be reduced, and the content of phosphorus and silicon in the sludge should be increased.

3.4. Mechanism of the effect of inorganic salts via different flocculants

Through the study of different flocculants (PAC and PAFC), the effect of other inorganic salts on the degradation of PAHs can be explored. A comparison of the 16 PAHs adsorbed by S1 and S2 is presented in Fig. 5a. Under the same conditions, the adsorption rate of 16 PAHs in S2 was 0.21% to 24.44% higher than that of S1. Based on the SEM observations of the particles of S1 and S2, it was found that those of S2 were relatively smooth. The BET surface area of S2 was 1.54 m²/g. Nevertheless, more PAHs were adsorbed by S2 than S1. This may be that calcium ions competed with PAHs, occupying adsorption sites on S1 (Song et al., 2014). Thus, more PAHs were adsorbed by S2 than S1.

As shown in Fig. 5b, compared with S1, the removal efficiency of fourteen PAHs in S2 increased by 1.05% to 48.28%, and the degradation efficiency for 3–5 ring PAHs were more obvious. The concentration of $\cdot\text{OH}$ in US/ZEA(S2) was 147.05 ± 0.72 µg/L, which is 38.35% lower than that of US/ZEA(S1). The TFe in US/air (S2) was

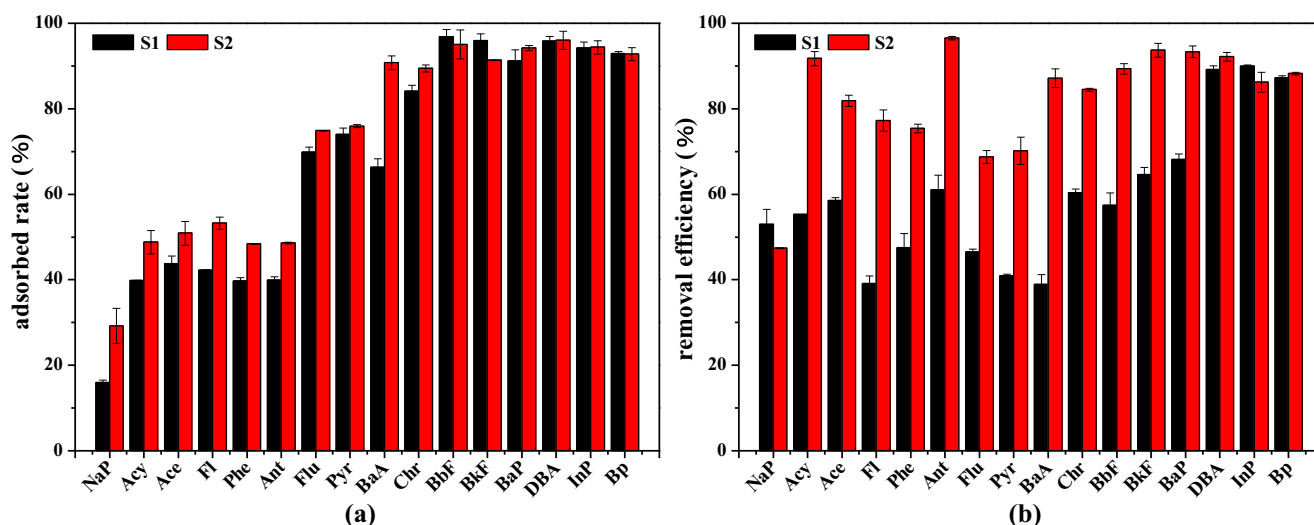


Fig. 5. (a) Adsorption of 16 PAHs by S1 and S2, (b) US/ZEA degradation of 16 PAHs in S1 and S2.

4.07 ± 0.21 mg/L, which was 3.75 times that of US/air (S1). It is known that the stability coefficient of $[\text{Fe}^{\text{III}}(\text{EDTA})]$ is higher than that of $[\text{Fe}^{\text{II}}(\text{EDTA})]$. Thus, the Fe^{3+} from S2 bound to EDTA, and less $\cdot\text{OH}$ was generated. However, S2 was relatively smooth and the average pore diameter of S2 was 41.73 nm. It seems that PAHs were adsorbed on the surface and larger mesoporous of S2. Thus, PAHs may be more readily degraded in S2. In summary, the degradation ability of the ZEA system will be reduced by ferric coagulants and trivalent iron salt. Calcium ions had no noticeable effect on the US/ZEA degradation, but the adsorption of PAHs in water by sludge could be inhibited by it.

4. Conclusion

Most refractory organics in textile dyeing sludge such as PAHs are adsorbed on the surfaces of sludge particles and their inner cavities. The composition and physicochemical properties of the inorganic particles play an essential role in the degradation of PAHs. The effects of inorganic compounds that were typically rich in textile dyeing sludge on PAH adsorption and degradation were studied in a simulated system. The adsorption of PAHs by sludge was promoted by Na_2SiO_3 , Na_2HPO_4 , and $\text{Mg}(\text{OH})_2$. This was because the particle size of sludge was decreased and the specific surface area of sludge was increased. More low-ring PAHs were adsorbed by sludge with a larger specific surface area, which is favourable for the degradation of low-ring PAHs. The generation of $\cdot\text{OH}$ was promoted by SiO_3^{2-} and HPO_4^{2-} , which promoted the degradation of PAHs in the sludge by US/ZEA. The opposite was true for SO_4^{2-} , $\text{Mg}(\text{OH})_2$ and trivalent iron salts. Therefore, the degradation of persistent organic matter was facilitated by the generation of $\cdot\text{OH}$, which was promoted by inorganic compounds, but depressed by the inhibition corrosion of ZVI or the consumption of EDTA by the inorganic compounds. According to this work, the influence of inorganic salts in textile dyeing sludge and wastewater on Fenton-like oxidation system can be prejudged, and the adverse influence of inorganic salts on Fenton-like system can be reduced by pretreatment, reducing the concentration of SO_4^{2-} , $\text{Mg}(\text{OH})_2$ and trivalent iron salts.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.wasman.2019.01.009>.

References

- Bogan, B.W., Trbovic, V., 2003. Effect of sequestration on PAH degradability with Fenton's reagent: roles of total organic carbon, humin, and soil porosity. *J. Hazard. Mater.* 100, 285–300.
- Chen, B.L., Xuan, X.D., Zhu, L.Z., Wang, J., Gao, Y.Z., Yang, K., Shen, X.Y., Lou, B.F., 2004. Distributions of polycyclic aromatic hydrocarbons in surface waters, sediments and soils of Hangzhou City, China. *Water Res.* 38, 3558–3568.
- Crini, G., Peindly, H.N., Gimbert, F., Robert, C., 2007. Removal of Cl Basic Green 4 (Malachite Green) from aqueous solutions by adsorption using cyclodextrin-based adsorbent: Kinetic and equilibrium studies. *Sep. Purif. Technol.* 53, 97–110.
- Dong, J., Ding, L.J., Wen, C.Y., Hong, M., Zhao, Y.S., 2013. Effects of geochemical constituents on the zero-valent iron reductive removal of nitrobenzene in groundwater. *Water Environ. J.* 27, 20–28.
- Eren, Z., 2012. Ultrasound as a basic and auxiliary process for dye remediation: a review. *J. Environ. Manage.* 104, 127–141.
- Fu, F.L., Lu, J.W., Cheng, Z.H., Tang, B., 2016. Removal of selenite by zero-valent iron combined with ultrasound: $\text{Se}(\text{IV})$ concentration changes, $\text{Se}(\text{VI})$ generation, and reaction mechanism. *Ultrason. Sonochem.* 29, 328–336.
- Gao, B., Yue, Q., Miao, J., 2003. Evaluation of polyaluminum ferric chloride (PAFC) as a composite coagulant for water and wastewater treatment. *Water Sci. Technol.* 47, 127–132.
- Gao, Y.Y., Gu, G.W., Zou, Q., 2007. *Water Pollution Control Engineering*, third ed. Beijing, China.
- Guan, X.H., Dong, H.R., Ma, J., 2011. Influence of phosphate, humic acid and silicate on the transformation of chromate by $\text{Fe}(\text{II})$ under suboxic conditions. *Sep. Purif. Technol.* 78, 253–260.
- Haritash, A.K., Kaushik, C.P., 2009. Biodegradation aspects of Polycyclic Aromatic Hydrocarbons (PAHs): a review. *J. Hazard. Mater.* 169, 1–15.
- Huang, D.L., Xue, W.J., Zeng, G.M., Wan, J., Chen, G.M., Huang, C., Zhang, C., Cheng, M., Xu, P.A., 2016. Immobilization of Cd in river sediments by sodium alginate modified nanoscale zero-valent iron: Impact on enzyme activities and microbial community diversity. *Water Res.* 106, 15–25.
- Iwamori, S., Nishiyama, N., Oya, K., 2016. A colorimetric indicator for detection of hydroxyl radicals in atmosphere using a methylene blue dye based on nafion film. *Polym. Degrad. Stab.* 123, 131–136.
- Jonsson, S., Persson, Y., Frankki, S., van Bavel, B., Lundstedt, S., Haglund, P., Tysklind, M., 2007. Degradation of polycyclic aromatic hydrocarbons (PAHs) in contaminated soils by Fenton's reagent: a multivariate evaluation of the importance of soil characteristics and PAH properties. *J. Hazard. Mater.* 149, 86–96.

- Jr, A.E.H., Smart, J.A., Amis, E.S., 1955. Simultaneous spectrophotometric determination of iron(II) and total iron with 1,10-phenanthroline. *Anal. Chem.* 27, 26–29.
- Ke, Y.W., Ning, X.A., Liang, J.Y., Zou, H.Y., Sun, J., Cai, H.L., Lin, M.Q., Li, R.J., Zhang, Y.P., 2018. Sludge treatment by integrated ultrasound–Fenton process: characterization of sludge organic matter and its impact on PAHs removal. *J. Hazard. Mater.* 343, 191–199.
- Keenan, C.R., Sedlak, D.L., 2008. Factors affecting the yield of oxidants from the reaction of nanoparticulate zero-valent iron and oxygen. *Environ. Sci. Technol.* 42, 5378.
- Kohn, T., Livi, K.J.T., Roberts, A.L., Vikesland, P.J., 2005. Longevity of granular iron in groundwater treatment processes: corrosion product development. *Environ. Sci. Technol.* 39, 2867–2879.
- Kohn, T., Kane, S.R., Fairbrother, D.H., Roberts, A.L., 2003. Investigation of the inhibitory effect of silica on the degradation of 1,1,1-trichloroethane by granular iron. *Environ. Sci. Technol.* 37, 5806–5812.
- Liang, J.Y., Ning, X.A., Kong, M.Y., Liu, D.H., Wang, G.W., Cai, H.L., Sun, J., Zhang, Y.P., Lu, X.W., Yuan, Y., 2017. Elimination and ecotoxicity evaluation of phthalic acid esters from textile-dyeing wastewater. *Environ. Pollut.* 231, 115–122.
- Liang, X., Ning, X.A., Chen, G.X., Lin, M.Q., Liu, J.Y., Wang, Y.J., 2013. Concentrations and speciation of heavy metals in sludge from nine textile dyeing plants. *Ecotoxicol. Environ. Saf.* 98, 128–134.
- Lin, M.Q., Ning, X.A., An, T.C., Zhang, J.H., Chen, C.M., Ke, Y.W., Wang, Y.J., Zhang, Y.P., Sun, J., Liu, J.Y., 2016. Degradation of polycyclic aromatic hydrocarbons (PAHs) in textile dyeing sludge with ultrasound and Fenton processes: effect of system parameters and synergistic effect study. *J. Hazard. Mater.* 307, 7–16.
- Liu, Y., Phenrat, T., Lowry, G.V., 2007. Effect of TCE concentration and dissolved groundwater solutes on NZVI-promoted TCE dechlorination and H₂ evolution. *Environ. Sci. Technol.* 41, 7881–7887.
- Man, X.Y., Ning, X.A., Zou, H.Y., Liang, J.Y., Sun, J., Lu, X.W., Sun, J.K., 2018. Removal of polycyclic aromatic hydrocarbons (PAHs) from textile dyeing sludge by ultrasound combined zero-valent iron/EDTA/Air system. *Chemosphere* 191, 839–847.
- Ning, X.A., Lin, M.Q., Shen, L.Z., Zhang, J.H., Wang, J.Y., Wang, Y.J., Yang, Z.Y., Liu, J.Y., 2014. Levels, composition profiles and risk assessment of polycyclic aromatic hydrocarbons (PAHs) in sludge from ten textile dyeing plants. *Environ. Res.* 132, 112–118.
- Pignatello, J.J., Oliveros, E., MacKay, A., 2006. Advanced oxidation processes for organic contaminant destruction based on the Fenton reaction and related chemistry. *Crit. Rev. Env. Sci. Technol.* 36, 1–84.
- Ribeiro, A.R., Nunes, O.C., Pereira, M.F.R., Silva, A.M.T., 2015. An overview on the advanced oxidation processes applied for the treatment of water pollutants defined in the recently launched Directive 2013/39/EU. *Environ. Int.* 75, 33–51.
- Seibig, S., Eldik, R.V., 1997. Kinetics of [Fe(II)(edta)] oxidation by molecular oxygen revisited. New evidence for a multistep mechanism. *Inorg. Chem.* 36, 4115–4120.
- Song, X.C., Liu, D.F., Zhang, G.W., Frigon, M., Meng, X.R., Li, K.X., 2014. Adsorption mechanisms and the effect of oxytetracycline on activated sludge. *Bioresour. Technol.* 151, 428–431.
- Sudoh, R., Islam, M.S., Sazawa, K., Okazaki, T., Hata, N., Taguchi, S., Kuramitz, H., 2015. Removal of dissolved humic acid from water by coagulation method using polyaluminum chloride (PAC) with calcium carbonate as neutralizer and coagulant aid. *J. Environ. Chem. Eng.* 3, 770–774.
- Sun, D.Z., Li, X.Q., Lou, L.S., 2010. On the research of adsorption of polycyclic aromatic hydrocarbons (phenanthrene) in soil-groundwater in Zhangshi Irrigation District. *Procedia Environ. Sci.* 2, 824–831.
- Sun, Y.K., Li, J.X., Huang, T.L., Guan, X.H., 2016. The influences of iron characteristics, operating conditions and solution chemistry on contaminants removal by zero-valent iron: a review. *Water Res.* 100, 277–295.
- Vanhulle, S., Trovaslet, M., Enaud, E., Lucas, M., Taghavi, S., Van Der Lelie, D., Van Aken, B., Foret, M., Onderwater, R.C.A., Wesenberg, D., Agathos, S.N., Schneider, Y.J., Corbisier, A.M., 2008. Decolorization, cytotoxicity, and genotoxicity reduction during a combined ozonation/fungal treatment of dye-contaminated wastewater. *Environ. Sci. Technol.* 42, 584–589.
- Wei, F., Cao, J.P., Zhao, X.Y., Ren, J., Gu, B., Wei, X.Y., 2018. Formation of aromatics and removal of nitrogen in catalytic fast pyrolysis of sewage sludge: a study of sewage sludge and model amino acids. *Fuel* 218, 148–154.
- Weng, S.P., 2010. *Fourier Transform Infrared Spectroscopy Analysis*, third ed. Beijing, China.
- Xu, L.J., Wang, J.L., 2011. A heterogeneous Fenton-like system with nanoparticulate zero-valent iron for removal of 4-chloro-3-methyl phenol. *J. Hazard. Mater.* 186, 256–264.
- Yu, J., Liu, W., Zeng, A., Guan, B., Xu, X., 2013. Effect of SO on 1,1,1-trichloroethane degradation by Fe(0) in aqueous solution. *Ground water* 51, 286–292.
- Zhang, H.D., Gao, Z.P., Ao, W.Y., Li, J., Liu, G.Q., Fu, J., Ran, C.M., Mao, X., Kang, Q.H., Liu, Y., Dai, J.J., 2017a. Microwave pyrolysis of textile dyeing sludge in a continuously operated auger reactor: char characterization and analysis. *J. Hazard. Mater.* 334, 112–120.
- Zhang, J.H., Liu, J.L., 2015. Study on processing desulfurization waste water of power plant using polymeric flocculant. *Chem. Eng. Trans.* 46, 1129–1134.
- Zhang, J.H., Zou, H.Y., Ning, X.A., Lin, M.Q., Chen, C.M., An, T.C., Sun, J., 2017b. Combined ultrasound with Fenton treatment for the degradation of carcinogenic polycyclic aromatic hydrocarbons in textile dyeing sludge. *Environ. Geochem. Health* 1, 1–10.
- Zhou, H.Y., Sun, Q., Wang, X., Wang, L.L., Chen, J., Zhang, J.D., Lu, X.H., 2014. Removal of 2,4-dichlorophenol from contaminated soil by a heterogeneous ZVI/EDTA/Air Fenton-like system. *Sep. Purif. Technol.* 132, 346–353.
- Zhou, T., Lim, T.T., Li, Y.Z., Lu, X.H., Wong, F.S., 2010. The role and fate of EDTA in ultrasound-enhanced zero-valent iron/air system. *Chemosphere* 78, 576–582.
- Zhou, T., Lu, X.H., Wang, J., Wong, F.S., Li, Y.Z., 2009. Rapid decolorization and mineralization of simulated textile wastewater in a heterogeneous Fenton like system with/without external energy. *J. Hazard. Mater.* 165, 193–199.
- Zhou, X.X., Lai, C., Huang, D.L., Zeng, G.M., Chen, L., Qin, L., Xu, P., Cheng, M., Huang, C., Zhang, C., Zhou, C.Y., 2018. Preparation of water-compatible molecularly imprinted thiol-functionalized activated titanium dioxide: Selective adsorption and efficient photodegradation of 2, 4-dinitrophenol in aqueous solution. *J. Hazard. Mater.* 346, 113–123.