



# Degradation of aromatic amines in textile-dyeing sludge by combining the ultrasound technique with potassium permanganate treatment



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## HIGHLIGHTS

- US exhibited apparent sludge disintegration and separated pollutants from sludge.
- Pollutants transferred to the water and reduced competition with aromatic amines.
- US-KMnO<sub>4</sub> was effective in degradation of aromatic amines in textile-dyeing sludge.

## ARTICLE INFO

### Article history:

Received 1 February 2016  
Received in revised form 5 April 2016  
Accepted 9 April 2016  
Available online 20 April 2016

### Keywords:

Textile-dyeing sludge  
Potassium permanganate  
Ultrasound technique  
Aromatic amines  
Degradation

## ABSTRACT

This paper reports, for the first time, a combined technique of ultrasound (US) with KMnO<sub>4</sub> degradation of aromatic amines in a textile-dyeing sludge. The reaction mechanisms and the degradation kinetics of aromatic amines at various operating parameters (KMnO<sub>4</sub> dosage, US power density and pH) were systematically examined by the combined system of US-KMnO<sub>4</sub>. The results indicated that there was a synergistic effect between US and KMnO<sub>4</sub>, as US greatly enhanced KMnO<sub>4</sub> in the degradation of aromatic amines and exhibited apparent sludge disintegration and separated pollutants from the sludge. In addition to accelerating the Mn(VII) reaction with pollutants in the filtrate, US also caused Mn(VII) to enter the porous sludge and sufficiently facilitated the reaction of the strongly absorbed aromatic amines. The combined treatment of US-KMnO<sub>4</sub> was effective in the degradation of aromatic amines in textile-dyeing sludge. On average, 58.7% of monocyclic anilines, 88.3% of other forms of aromatic amines, and 24.0% of TOC were removed under the optimal operating conditions of a KMnO<sub>4</sub> dosage of 12 mM, an US power density of 1.80 W/cm<sup>3</sup> and pH 5. The present study proposed US-KMnO<sub>4</sub> treatment as a practical method for the disposal of aromatic amines in textile-dyeing sludge.

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## 1. Introduction

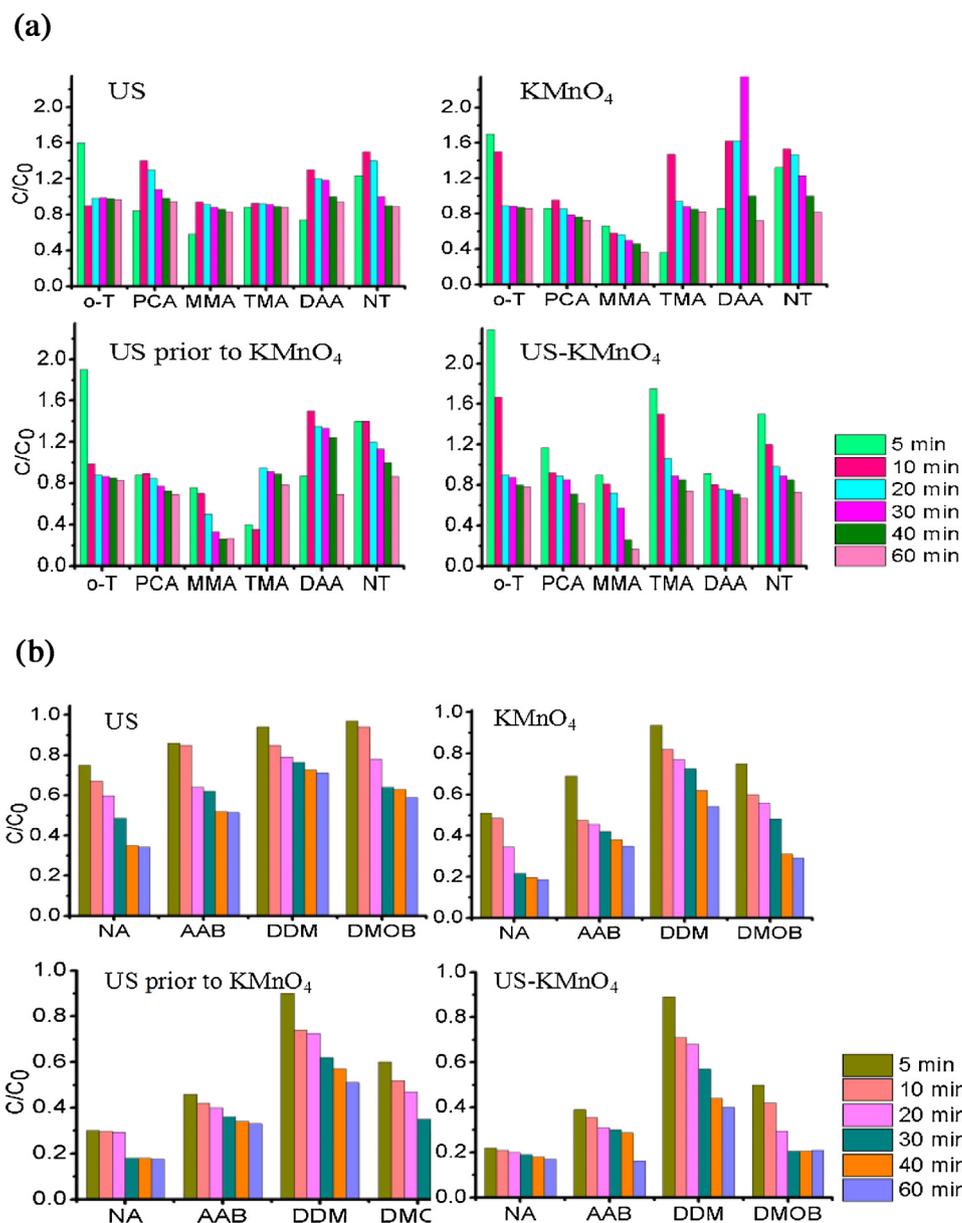
Textile-dyeing sludge has raised serious concerns regarding their adverse effect on environment [1]. According to the China Environment Statistical Yearbook, the amount of textile-dyeing sludge in China was up to approximately 5.38 million tons (80% moisture content) in 2013 in China [2]. Aromatic amines are primarily intermediates and are widely used as components of azo dyes in the textile-dyeing industry [3]. Due to their toxic, carcinogenic and mutagenic characteristics, 22 aromatic amines have been listed as banned pollutants in the European Union 1907/2006 and 24 have been banned in China [4]. Although significant amounts of aromatic amines can be removed via multiple physical,

chemical and biological adsorption/oxidation processes in industrial wastewater treatment plants, considerable quantities still remain in textile-dyeing sludge due to the sorption of aromatic amines to the sludge [5–8]. One recent study elucidated that trace levels of aromatic amines in textile-dyeing sludge may pose a high risk to the soil ecosystem after being discarded into soil or in a landfill [2]. Other methods, such as incineration and heat treatment, will produce strong toxic-persistent organic pollutants (e.g., tetrachlorodibenzo-*p*-dioxin) [9,10]. It is therefore quite imperative to remove aromatic amines from textile-dyeing sludge via either the currently used water treatment technology or via new effective techniques under development.

Various chemical oxidants, such as Fenton reagents [11], ferrate [12], ozone [13], free chlorine [14], chlorine dioxide [15], sulfate radicals [16] and potassium permanganate (KMnO<sub>4</sub>) [17], are commonly used to degrade organic contaminants in aqueous solutions. Among these oxidants employed to degrade aromatic amines in

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**Fig. 1.** Comparison of US, KMnO<sub>4</sub>, US prior to KMnO<sub>4</sub> and US-KMnO<sub>4</sub> on the degradation of monocyclic anilines (a) and other forms of aromatic amines (b). Reaction conditions: [KMnO<sub>4</sub>] = 2.4 mM, pH = 6.0 and US power density = 1.80 W/cm<sup>3</sup>.

textile-dyeing sludge, KMnO<sub>4</sub> was found to be an attractive oxidant, with the advantages of comparative stability over a wide pH range, ease of handling and relatively low cost [17–19]. In addition, as the insoluble reduction product of KMnO<sub>4</sub>, manganese dioxide (MnO<sub>2</sub>) not only can significantly accelerate the oxidation kinetics of pollutants but also avoid secondary pollution in sludge [20,21]. KMnO<sub>4</sub> has been demonstrated to be fairly effective in the degradation of various phenolic compounds [22], antibiotics [23], endocrine disrupting chemicals [24] and other related micro-pollutants that contain electron-rich moieties, including amino, olefin, thiol, aldehyde, ether and ketone groups [25,26]. However, these studies primarily focused on the water-soluble chemicals in synthetic or real wastewater. To date, very limited information is available for the KMnO<sub>4</sub> reaction of hydrophobic aromatic amines in sludge. In particular, textile-dyeing sludge is a very complex mixture, containing dyes, polycyclic aromatic hydrocarbons [9], heavy metal ions [1], surfactants, solvents, detergents and other recalcitrant compounds [26–29]; the sludge is listed as a Strict Control Waste

in Guangdong Province, China. Whether KMnO<sub>4</sub> is appropriate for the treatment of aromatic amines in textile-dyeing sludge and the reaction mechanism still remain unclear.

Among the methods that have potential for the combination with KMnO<sub>4</sub> to be used in sludge, ultrasound (US) is highlighted due to its versatility. Zhou et al. [30] confirmed that an obvious synergistic effect was observed in the degradation of 2,4-dichlorophenol after introduction of US into the Fe/EDTA system. Some studies [31,32] discovered US could eliminate the mass transfer resistance and accelerate the decomposition of pollutants. Chakma and Moholkar [33] have also demonstrated that US could enhance Fenton in the degradation of textile dyes in water. Our recent study [34] also found that US could enhance the Fenton efficiencies for the degradation of PAHs in textile-dyeing sludge. Interestingly, the combined US-Fenton treatment was observed to be efficient not only at the surface of sludge but also in the sludge interior. Okitsu et al. [35] indicated that the sonochemically formed H<sub>2</sub>O<sub>2</sub> and H<sub>2</sub> molecules as well as H atoms played an important role in

MnO<sub>4</sub><sup>-</sup> reduction. It seems likely that the combination of US and KMnO<sub>4</sub> exhibited a promising enhancement in the removal of contaminants from textile-dyeing sludge; however, further studies are required to verify this enhancement.

The objective of this study was to systematically assess the ability of the US-KMnO<sub>4</sub> system to degrade aromatic amines in textile-dyeing sludge, and the role of US was also explored in this combination system. Next, a reasonable reaction mechanism between KMnO<sub>4</sub> and US was also tentatively proposed. Finally, the degradation effectiveness of aromatic amines was evaluated under various conditions for example KMnO<sub>4</sub> dosage, US power density and pH conditions.

## 2. Materials and methods

### 2.1. Materials

A stock solution of KMnO<sub>4</sub> was prepared by dissolving the crystals of KMnO<sub>4</sub> (GR grade, Hengyang, China) in deionized water and standardized spectrophotometrically by the absorbance peak at 525 nm. Selected aromatic amines including *o*-toluidine (*o*-T), *p*-chloroaniline (PCA), 2-methoxy-5-methylaniline (MMA), 2,4,5-trimethylaniline (TMA), 2,4-diaminoanisole (DAA), 5-nitro-*o*-toluidine (NT), 2-naphthylamine (NA), 4-aminoazobenzol (AAB), 4,4'-diamino diphenyl methane (DDM) and 3,3'-dimethoxybenzidine (DMOB) (see Table S1 for their chemical structures and contents in textile-dyeing sludge) were obtained from O<sub>2</sub>si Smart Solutions (Charleston, SC, USA) with a purity >99.5%. High-performance liquid chromatography (HPLC)-grade methanol and methyl *tert*-butyl ether were purchased from Fisher Scientific (USA). Textile-dyeing sludge samples were collected from a representative textile wastewater treatment (Dongguan, Guangdong Province, China), where the treating capacity is 9000 m<sup>3</sup>/day using an anaerobic/aerobic (A/O) activated sludge process. Based on the equal amount of dry sludge, a large amount of high-moisture-content sludge was required but was harder to store and transport than the dewatered sludge. Thus, the sludge samples taken after being dewatered using a belt filter press were collected from the final storage container. The dewatered textile-dyeing sludge characteristics are given in Table S2.

### 2.2. Batch experiments

Based on textile-dyeing sludge with a 98% moisture content prior to being dewatered, the experimental sludge was prepared by mixing the dewatered sludge samples with deionized water. The experiments on the degradation of aromatic amines by US-KMnO<sub>4</sub> were conducted in a 0–1800 W sonicator (Scientz JY99-IIDN, China) equipped with a sealed converter and a titanium probe tip (25 mm in diameter and 320 mm in length) operated at 20 kHz. A structure diagram of experimental apparatus and actual experimental set-up are shown in Fig. S1. The ultrasonic generator provides direct sonication, which will not cause energy loss due to the reaction matrix is in direct contact with the mechanical vibration. The same experimental set-up has also been used by Weng et al. [36]. Sodium acetate was used as a buffer for the reactions at pH 5, while no buffer was employed for those at pH ≥ 7, whose pH was maintained at an almost constant level (±0.1) by the addition of HClO<sub>4</sub> or NaOH. Each reaction was initiated by quickly spiking KMnO<sub>4</sub> while the mixture was being stirred or sonicated. Samples were periodically collected and quenched with hydroxylamine, while the samples of determining Mn(VII) concentration were analyzed quickly without quenching. The slurry of samples was centrifuged at 4000 rpm for 10 min, and the supernatant was filtered through a 0.22-μm membrane and then quickly analyzed with UV detection at 525 nm.

The sludge matrix was freeze-dried using an LGJ-12 vacuum freeze dryer (Songyuan Huaxing Technology Development Co., Ltd., Beijing, China) and stored in a refrigerator at -20 °C until analysis.

### 2.3. Analytical methods

The extraction procedure was performed according to our previous study [2]. Briefly, approximately 1.00 g dry weight of each sample was extracted with methanol using a microwave-assisted extractor (MARS, USA). Thereafter, the methanol extract was filtered and concentrated to approximately 1 mL, redissolved in citrate buffer solution at pH 6 and then subjected to cleanup using an Extrelut liquid-liquid extraction column. The column was eluted with methyl *tert*-butyl ether, and then the eluate was concentrated to 0.2 mL; the final extract was injected into an Agilent 7890A gas chromatograph-5975C mass spectrometer (GC-MS, Agilent, USA) for quantification. Chromatographic separation was achieved by a HP-5MS column (30 m × 0.25 mm, film thickness of 0.25 μm, Agilent, USA) with the instrumental analysis conditions being the same as those reported in our previous study [2]. The procedural blanks, spiked blanks and sample duplicates were routinely analyzed for every batch of samples.

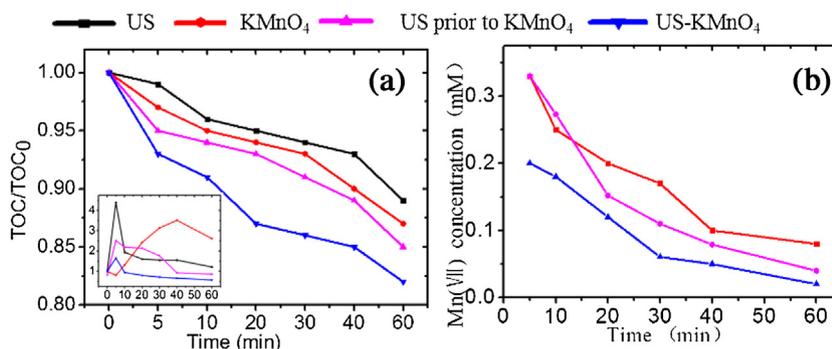
The pH was measured using a digital pH-meter (pHS-3C, Leici, China). The total organic carbon (TOC) of the sample filtrate was determined using a TOC-VCPH analyzer (Shimadzu, Japan). The TOC in the sludge was measured using the potassium dichromate oxidation spectrophotometric method. The KMnO<sub>4</sub> concentration was determined by UV detection at 525 nm. The sludge surface morphologies of multiple sludge samples were performed using a scanning electron microscope (SEM) (S-3400N, Hitachi, Japan). The sludge particle size distributions within the sludge samples were examined using a laser particle size analyzer (Eye Tech, Ankersmid, Netherlands).

All experiments were conducted at 25 ± 1 °C in triplicate, and the averaged data were presented with a standard deviation of <20%.

## 3. Results and discussion

### 3.1. Role of US in the US-KMnO<sub>4</sub> combined treatment of aromatic amines in textile-dyeing sludge

According to Fig. 1a, the degradation of aromatic amines undergoing KMnO<sub>4</sub> treatment was significantly enhanced with the introduction of 1.8 W/cm<sup>3</sup> US at a fixed pH 6.0. The average degradation efficiencies of monocyclic anilines (*o*-T, PCA, MMA, TMA, DAA and NT) was 38.21% in US-KMnO<sub>4</sub> treatment at 60 min, which was somewhat higher than that in US treatment (9.2%), KMnO<sub>4</sub> treatment (28.0%) and US treatment for 20 min prior to KMnO<sub>4</sub> treatment (31.2%). However, no aromatic amines were detected in the filtrate in any instance, suggesting that aromatic amines were rarely transferred to the water due to their hydrophobic characteristics. This could also indicate that the degradation of monocyclic anilines in the US for 20 min prior to KMnO<sub>4</sub> treatment were lower than that in the US-KMnO<sub>4</sub> treatment. Furthermore, KMnO<sub>4</sub> could enter into the porous sludge under US condition and sufficiently reacted with the strongly absorbed aromatic amines. However, the trend was very surprising that monocyclic anilines in textile-dyeing sludge were not degraded but increased dramatically as the reaction time prolonged and reached a maximum at 5–10 min. Different results were obtained compared with the degradation of other forms of aromatic amines (NA, AAB, DDM and DMOB) in multiple treatments (Fig. 1b). The degradation of other forms of aromatic amines decreased progressively as the reaction time prolonged, and US-KMnO<sub>4</sub> treatment achieved the highest



**Fig. 2.** Comparison of US, KMnO<sub>4</sub>, US prior to KMnO<sub>4</sub> and US-KMnO<sub>4</sub> on the removal of TOC in the sludge (a), Mn(VII) concentration in filtrate (b). The inset shows the TOC in the filtrate. Reaction conditions: [KMnO<sub>4</sub>] = 2.4 mM, pH = 6.0 and US power density = 1.80 W/cm<sup>3</sup>.

degradation (76.5%), which was considerably higher than those achieved by US treatment (46.1%), KMnO<sub>4</sub> treatment (65.9%), and US treatment for 20 min prior to KMnO<sub>4</sub> treatment (67.7%). Thus, it can be concluded that other forms of aromatic amines were degraded into monocyclic anilines prior to simultaneous degradation. Compared with the degradation rate constants of aromatic amines in multiple treatments (Table S3), the rate constants in KMnO<sub>4</sub> treatment were significantly increased relative to the US treatment because of the strong oxidizing property of KMnO<sub>4</sub> and the resulting MnO<sub>2</sub> formed played a significant role in KMnO<sub>4</sub> reduction as a mild oxidant [19] or catalyst [21]. Sivasankar and Moholkar [37] have explained in detail that the exact degradation mechanism of different amines depends on their relative hydrophilicity/hydrophobicity. The initial degradation of amines occurs through hydroxylation-attack of •OH radicals. As successive hydroxylation leads to the products becoming hydrophilic and move away from bubble interface. In the present case, however, greater contribution to the degradation is through KMnO<sub>4</sub> oxidation. Hence, the rate of degradation increases with time. Thus, synergy between US and KMnO<sub>4</sub> is of physical nature. Such synergy has also been demonstrated in the research work on US-Fenton technique mentioned earlier [33]. The synergy indexes of o-T, MMA, TMA and DDM that undergo the combination treatment of US and KMnO<sub>4</sub> were higher than 1, suggesting that US could stimulate KMnO<sub>4</sub> reaction and exhibit a synergistic effect on the degradation of aromatic amines as well as their derivatives. This phenomenon is consistent with the synergistic mechanism of US-KMnO<sub>4</sub> treatment for the pollutants degradation in synthetic water [35,38]. While synergy indexes of other aromatic amines were less than 1, indicating that US and KMnO<sub>4</sub> might have no synergistic effect on the degradation of them.

The removal of the TOC in the sludge and the filtrate in multiple treatments was also studied (Fig. 2a). Eighteen percent of TOC was removed from the sludge within 60 min by US-KMnO<sub>4</sub> treatment. The TOC increased rapidly at 5 min and decreased steadily afterwards in the filtrate, but the TOC increased until 40 min in the KMnO<sub>4</sub> treatment and then decreased slightly, as shown in the insert of Fig. 2a, suggesting that US was favorable for the degradation of the TOC in the filtrate. The decay of Mn(VII) is shown in Fig. 2b; the Mn(VII) concentration in the filtrate was slowly consumed upon prolonging the reaction time in every treatment, but the decay of Mn(VII) in US treatment for 20 min prior to KMnO<sub>4</sub> and US-KMnO<sub>4</sub> treatments was much faster. A possible explanation was that various electron-rich hydrophilic moieties were transferred to the water and the US could accelerate Mn(VII) reaction with those moieties in the filtrate.

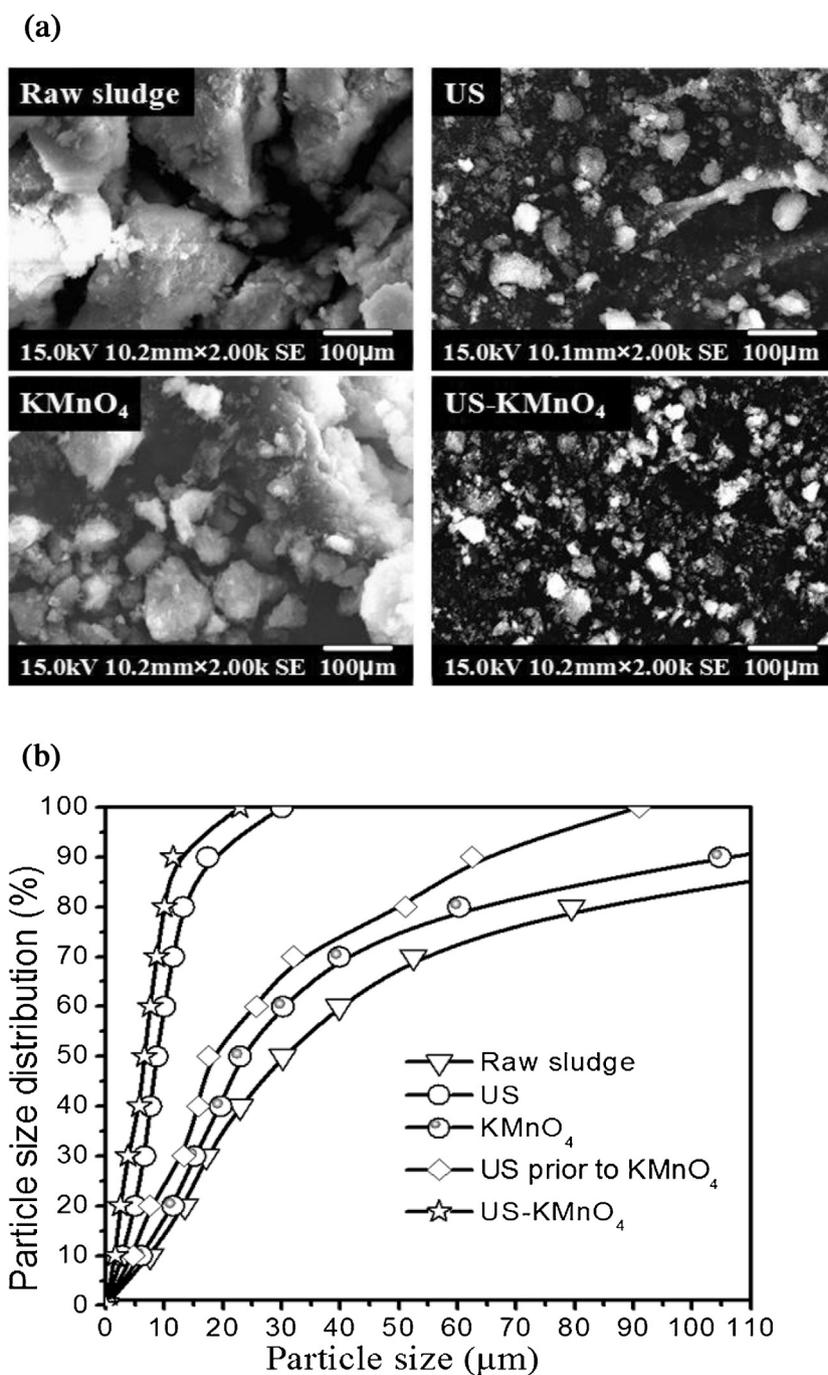
Fig. 3a shows the SEM images (magnification is 2000×) of the multiple samples to confirm the morphological changes of sludge. The raw sludge exhibited that clusters of flocs were aggre-

gated together and uneven, whereas sludge flocs were partially crushing in KMnO<sub>4</sub> treatment, indicating that KMnO<sub>4</sub> treatment did not exhibit an apparent effect on the disruption of sludge flocs without the US enhancement. Compared to the raw sludge sample, significant morphological changes of the sludge sample occurred following the US and US-KMnO<sub>4</sub> treatment due to the nearly completed breakage of sludge flocs. There was no apparent morphological change of the US treatment for 20 min prior to KMnO<sub>4</sub> compared with the KMnO<sub>4</sub> treatment (the result is not shown). This result was consistent with the sludge particle size distribution in Fig. 3b. The sludge particles observed in the four treatments were smaller than that of the raw sludge samples. Sludge treated with US or the US-KMnO<sub>4</sub> treatment exhibited an appreciable increase in the number of smaller sludge particles, which may be due to the cavitation phenomenon in US system. Similar conclusions were drawn by Nalajala and Moholkar [39] as well as our previous study [40].

### 3.2. Effect of operational parameters on the degradation of aromatic amines

#### 3.2.1. Effect of KMnO<sub>4</sub> dosage

The degradation of aromatic amines in textile-dyeing sludge at multiple KMnO<sub>4</sub> dosages was investigated at a fixed pH 6.0 and US power density of 18 W/cm<sup>3</sup>. Fig. 4a displays the degradation of monocyclic anilines (o-T, PCA, MMA, TMA, DAA and NT) in textile-dyeing sludge, which was found to be strange when the KMnO<sub>4</sub> dosage increased from 2.4 to 240 mM o-T, MMA and NT could be completely removed and the highest degradation efficiencies of PAC reached 47.0% at KMnO<sub>4</sub> dosage of 120 mM. However, TMA and DAA increased to some extent from 2.4 to 240 mM at 60 min. Overall, the amount of each of the monocyclic anilines increased marginally as the reaction proceeded and thereafter decreased gradually. DAA and NT were even a few more times than the original value at 5–20 min. Among the selected aromatic amines, DAA and NT were more susceptible to be generated, but NT was easier to be degraded. TMA and DAA were the most difficult species to degrade. The average of the highest degradation of monocyclic anilines was found to be 67.5% at a KMnO<sub>4</sub> dosage of 240 mM. However, as seen in Fig. 4b, the degradation of other forms of aromatic amines (NA, AAB, DDM and DMOB) in textile-dyeing sludge slightly increased as the KMnO<sub>4</sub> dosage increased from 2.4 to 240 mM. As expected, when the oxidant dose was relatively low, the level of aromatic amines decreased slightly. This may be attributed to the strong competition between aromatic amines and various electron-rich moieties [24,25,41] in textile-dyeing sludge. The average of the highest degradation efficiency of other forms of aromatic amines was 92.6% at a KMnO<sub>4</sub> dosage of 240 mM. One possible reason for this result was that aromatic amines with complex structures were

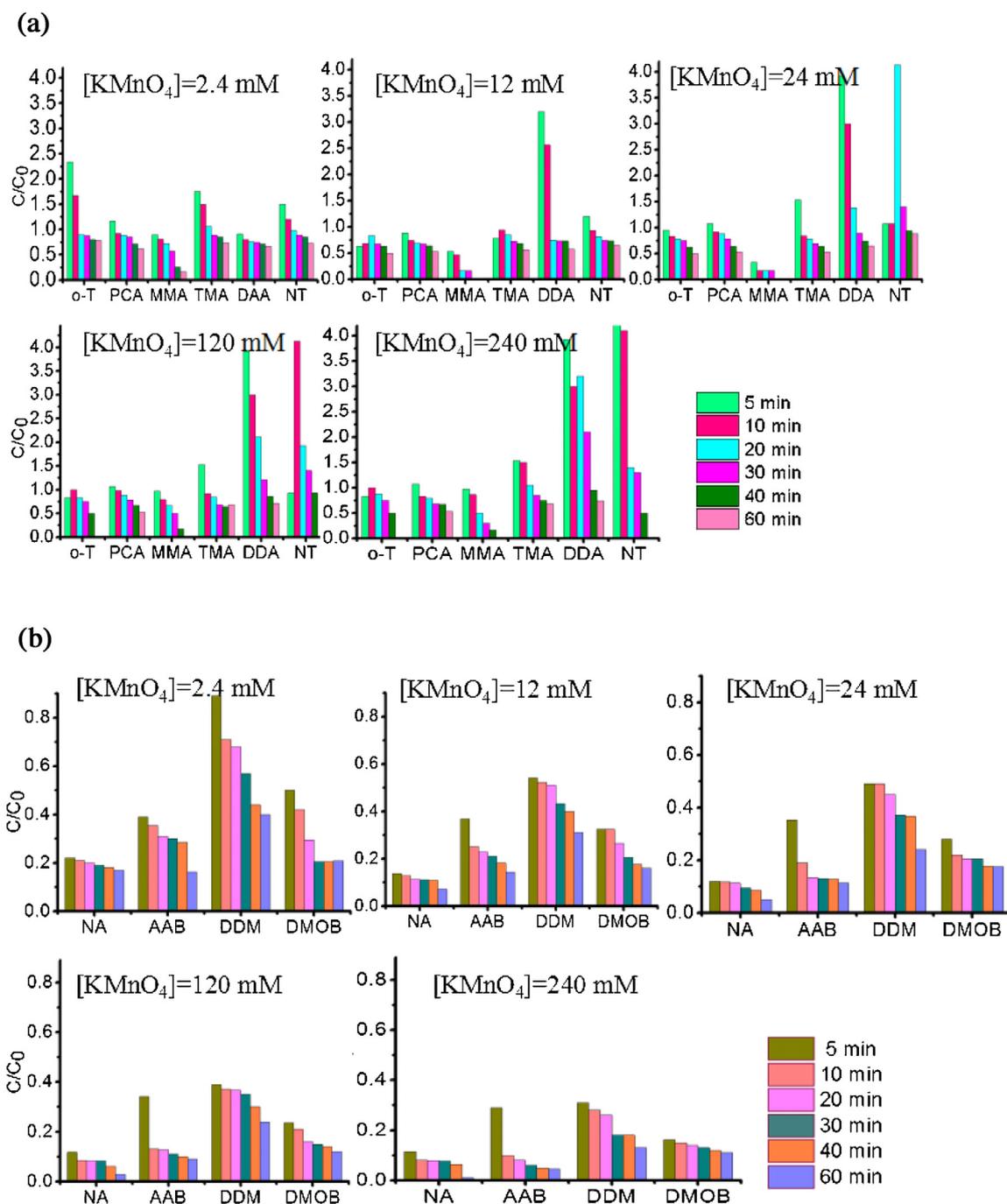


**Fig. 3.** SEM images (a) and particle size distribution of sludge (b). Reaction conditions:  $[\text{KMnO}_4] = 2.4 \text{ mM}$ ,  $\text{pH} = 6.0$  and US power density =  $1.80 \text{ W/cm}^3$ , reaction time = 40 min.

more vulnerable to be degraded into monocyclic anilines, which was the simplest form of aromatic amines [42], whereas another explanation was that an increase in the  $\text{KMnO}_4$  dose led to the depletion of electron-rich moieties in textile-dyeing sludge and the residual concentration of aromatic amines decreased gradually. However, Fig. 4 shows that the trends in the degradation of aromatic amines are not very obvious and the degradation rate of aromatic amines levels off, suggesting that it is a substrate limited reaction. Generally, a dose of  $\text{KMnO}_4$  of 12 mM was sufficient to treat 53.1 and 82.8% of the initial concentration of monocyclic anilines and other forms of aromatic amines in textile-dyeing sludge.

The effect of  $\text{KMnO}_4$  dosage on the TOC is shown in Fig. S2a. A gradual increase in the removal of TOC from 18.0 to 25.0% at 60 min

was observed as the  $\text{KMnO}_4$  dosage increased from 2.4 to 240 mM, whereas a sudden increase in the TOC and a subsequent decrease in the filtrate were observed. The TOC at a  $\text{KMnO}_4$  dosage of 240 mM was less than that at a dosage of 120 mM in the filtrate; a possible reason for this difference is that the degradation efficiencies of TOC are much faster at 240 mM. Fig. S2b shows that the  $\text{Mn(VII)}$  concentration in the filtrate increased and subsequently decreased as the reaction time increased at a  $\text{KMnO}_4$  dosage of 12–240 mM. This could be explained by the transference of  $\text{Mn(VII)}$  in the sludge to water and the reaction with organic pollutants. However, the  $\text{Mn(VII)}$  concentration decreased over time at a  $\text{KMnO}_4$  dosage of 2.4 mM. It is obvious that  $\text{Mn(VII)}$  was not sufficient to react with



**Fig. 4.** Effect of the  $\text{KMnO}_4$  dosage on the degradation of monocyclic anilines (a) and other forms of aromatic amines (b) in the US- $\text{KMnO}_4$  system. Reaction conditions:  $\text{pH}=6.0$  and US power density =  $1.80 \text{ W/cm}^3$ .

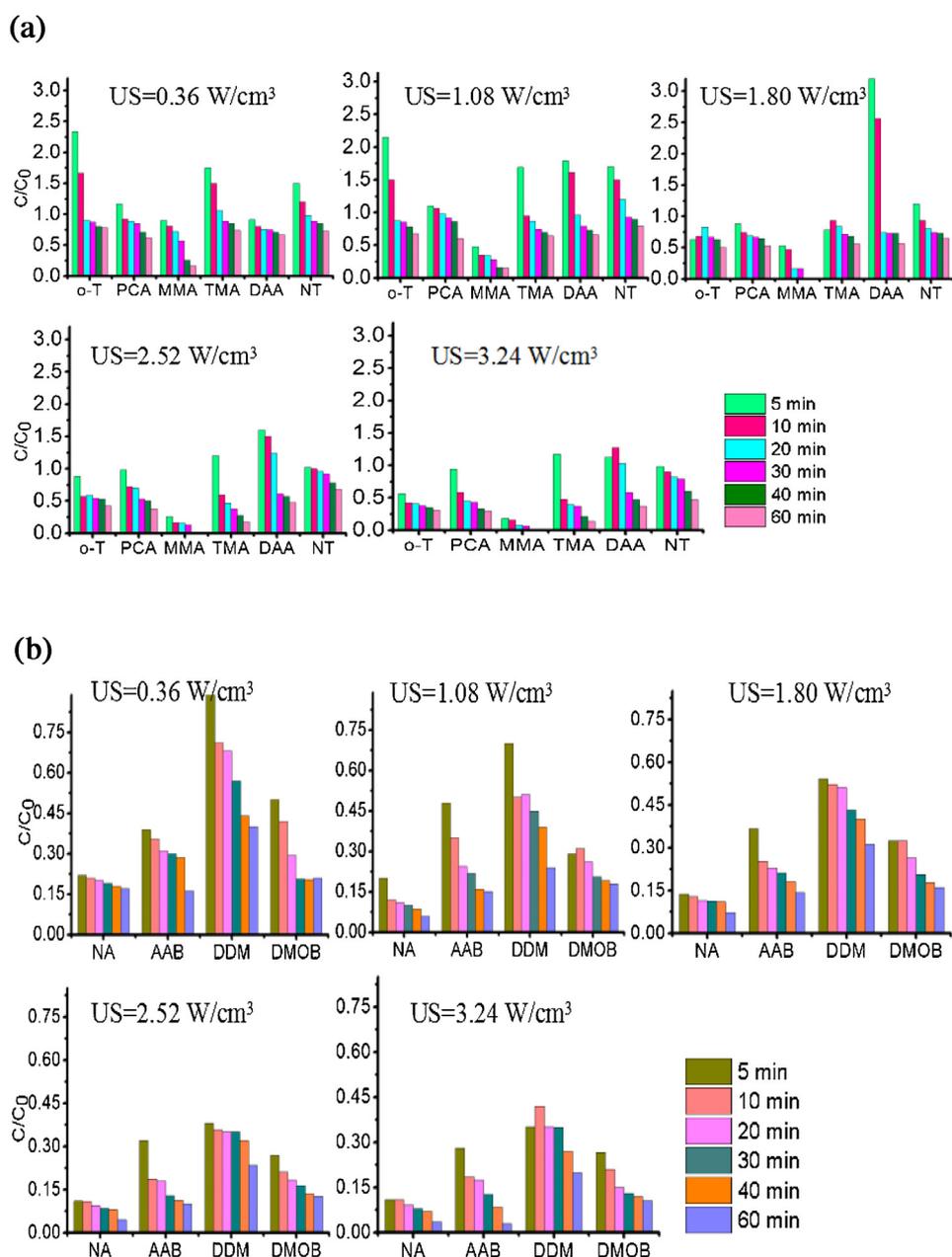
pollutants completely in water. Thus, the  $\text{KMnO}_4$  dosage of 12 mM was used in the next experiments.

The required dosage of  $\text{KMnO}_4$  is relevant to the complexity of the reaction system and the type of pollutants. Hu et al. [23] found that 60% lincomycin and 20% trimethoprim were removed at the  $\text{KMnO}_4$  dosage of 6 mM, and 80% anticonvulsant drug carbamazepine was removed at the  $\text{KMnO}_4$  dosage of 2 mM. Jiang et al. [24] observed that more than 90% of endocrine disrupting chemicals were transformed in synthetic and real waters at the  $\text{KMnO}_4$  dose of 0.012 mM. However, the background matrix in real water was found to accelerate the oxidation dynamics. Pang et al. [25] reported that the degradation of tetrabromobisphenol was more than 80% in the treatment of real waters at the  $\text{KMnO}_4$  dose of

0.006 mM. Zhang et al. [43] discovered the removal of butylparaben increased from 7.7 to 44.1% as  $\text{KMnO}_4$  dosage increased from 0.01 to 0.1 mM because the direct oxidation increased when  $\text{KMnO}_4$  was overdosed. The background matrix of textile-dyeing sludge is so complicated that a higher oxidant demand is required.

### 3.2.2. Effect of US power density

The combined US- $\text{KMnO}_4$  technique was used to treat textile-dyeing sludge with various US power density of 0.36, 1.08, 1.80, 2.52 and  $3.24 \text{ W/cm}^3$  in the raw textile dyeing sludge. The results obtained in Fig. 5a indicated that o-T, PCA, MMA and TMA were simultaneously degraded and their highest degradation achieved 69.0, 70.0, 100.0 and 86.0%, respectively, at an US power density



**Fig. 5.** Effect of US power density on the degradation of different forms of monocyclic anilines (a) and other forms of aromatic amines (b) in the US-KMnO<sub>4</sub> system. Reaction conditions: [KMnO<sub>4</sub>] = 12 mM and pH = 6.

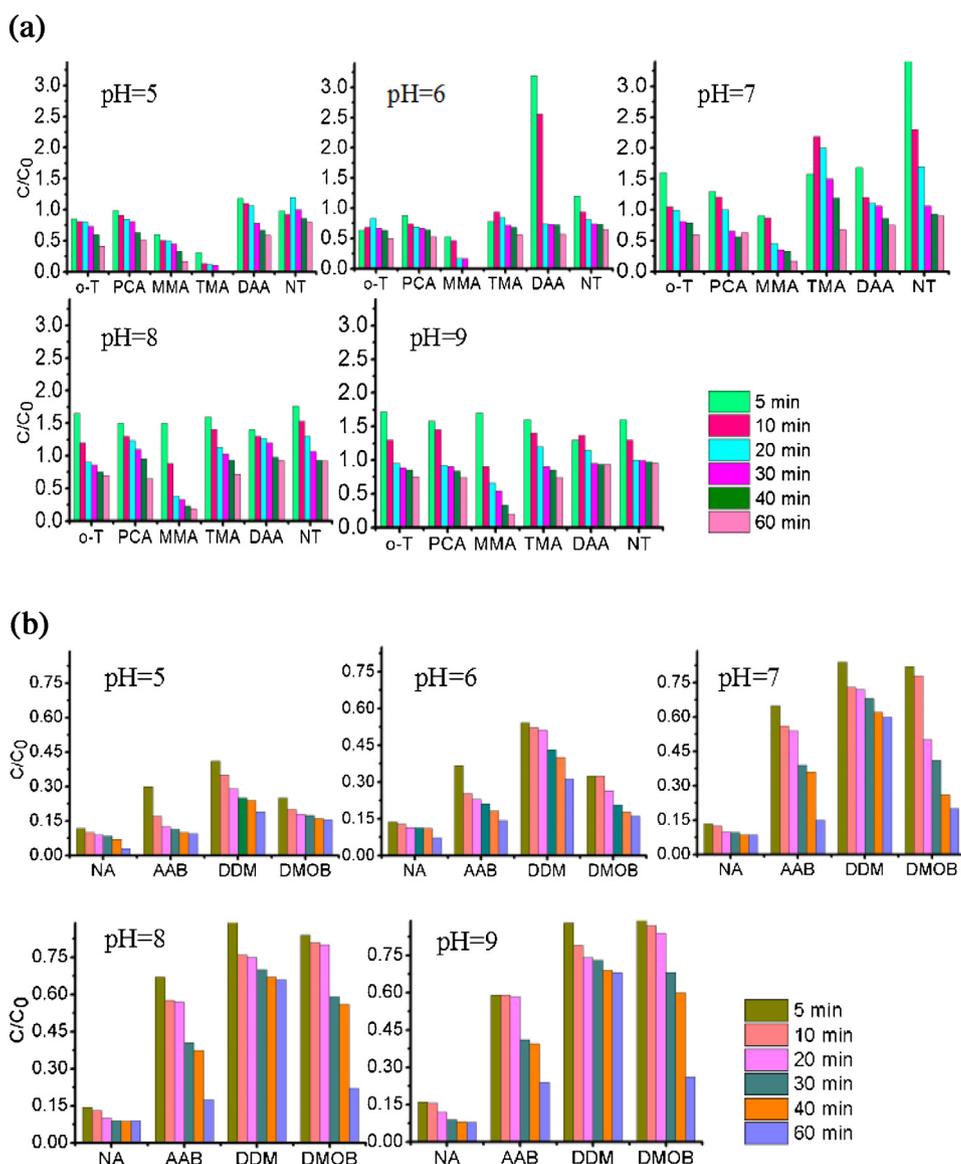
of 3.24 W/cm<sup>3</sup> at 60 min. DAA and NT increased steadily as the US power densities increased, whereas an US power density greater than 1.80 W/cm<sup>3</sup> led to slight decreases. Only 63.0% DAA and 53.0% NT were removed at 3.24 W/cm<sup>3</sup> at 60 min. Fig. 5b displays the degradation of other aromatic amines in textile-dyeing sludge. As US power density increased from 0.36 to 3.24 W/cm<sup>3</sup>, the degradation efficiencies of other aromatic amines significantly increased from 76.5 to 90.8%. Comparatively, the average degradation efficiencies of monocyclic anilines and other forms of aromatic amines at an US power density of 1.80 W/cm<sup>3</sup> were 82.8 and 53.1%, respectively, which were slightly lower than the highest degradation (90.8 and 73.5%, respectively). However, to avoid the high energy consumption, the US power density of 1.80 W/cm<sup>3</sup> was used in the next experiments.

Fig. S3a shows that the removal of TOC in the sludge rose from 16 to 25% as the US power density increased from 0.36 to 3.24 W/cm<sup>3</sup>

within 60 min. The TOC increased steadily in the filtrate as the US power density increased and reached a peak in 2.52 W/cm<sup>3</sup>, whereas the TOC declined suddenly in 3.24 W/cm<sup>3</sup>. This was unsurprising because the TOC in the filtrate was generated and degraded dynamically, and the removal efficiencies of TOC in 3.24 W/cm<sup>3</sup> was much faster than that in 2.52 W/cm<sup>3</sup>. As seen in Fig. S3b, the Mn(VII) concentration in the filtrate increased steadily as the US power density increased because the ultrasonic intensity could increase the number of active cavitation bubbles [44,45] that caused Mn(VII) transfer to water.

### 3.2.3. Effect of pH

pH is another important parameter in the oxidation potential of the US-KMnO<sub>4</sub> treatment. The pH range varied from 5 to 9 were investigated at the fixed KMnO<sub>4</sub> dosage of 12 mM and the US power density of 18 W/cm<sup>3</sup>. No significant shift of the pH



**Fig. 6.** Effect of pH on the degradation of different forms of monocyclic anilines (a) and other forms of aromatic amines (b) in the US-KMnO<sub>4</sub> system. Reaction conditions: [KMnO<sub>4</sub>] = 12 mM and US power density = 1.80 W/cm<sup>3</sup>.

values was observed at the end of each reaction. As demonstrated in Fig. 6, the degradation of monocyclic anilines and other forms of aromatic amines in the textile-dyeing sludge elevated as the pH decreased, with the average of the highest degradation efficiencies of 58.7 and 88.3%, respectively, at conditions of pH 5 and 60 min of reaction time. In particular, the degradation efficiencies of o-T (Table S1,  $pK_a = 4.44$ ), TMA (Table S1,  $pK_a = 5.09$ ) and NA (Table S1,  $pK_a = 4.16$ ) at pH 5 were relatively higher than that of other aromatic amines because KMnO<sub>4</sub> was efficient at the pH range near pollutants'  $pK_a$  values [22,26]. This verified that the degradation of aromatic amines exhibited a strong pH-dependence. However, as seen from Table S1, when  $pK_a$  values (2.35–5.09) were less than pH and the aromatic amines are in ionic form, the contribution of the US to degradation is minimal as the ionic compounds are not likely to stay near cavitation bubble interface and undergo degradation by hydroxylation.

The TOC in the sludge decreased progressively as the pH decreased from 9 to 5, as 14–24% TOC was removed at 60 min (Fig. S4a). The TOC in the filtrate exhibited similar tendencies to that in the sludge. Overall, the acidity was favorable for the degradation of

aromatic amines and the removal of TOC; this finding is probably associated with the increasing oxidation potential of KMnO<sub>4</sub> with decreasing pH. Fig. S4b shows that the Mn(VII) concentration in the filtrate gradually increased as the pH increased; this behavior was because the acidity was more efficient for the Mn(VII) reaction with aromatic amines. However, this did not influence Mn(VII) reaction with other pollutants in the filtrate because Mn(VII) was overdosed and selective [24,40].

In summary, the US-KMnO<sub>4</sub> approach has strong oxidation potential toward aromatic amines in secondary textile-dyeing sludge, and the proposed approach could be used to return the sludge to the hydrolysis-acidification pool for subsequent biochemical treatment because of the incomplete mineralization of pollutants. Furthermore, Barber [46] indicated that the release of extra-cellular material under US condition could catalyze biological reactions and improve the bacterial degradation kinetics, resulting in lower sludge quantities and significantly increased biogas. Therefore, it is hoped that the present research results contribute to improve the treatment efficiency and reduce the treatment cost. The oxidation method described in this study might be considered

as a reference for the disposal of aromatic amines in textile-dyeing sludge. Studies are still required to consider the altered or enhanced toxicological effects of aromatic amine transformation intermediates compared with the original compounds prior to the practical use of this method.

#### 4. Conclusions

The results indicated that the combined US-KMnO<sub>4</sub> treatment had a synergistic effect on degradation of aromatic amines in textile-dyeing sludge. US exhibited significant enhancement on sludge particle disruption and separated pollutants from the sludge. US not only accelerated the reaction of Mn(VII) and pollutants in the filtrate but also sufficiently facilitated the reaction of Mn(VII) with the strongly absorbed aromatic amines under US conditions. Aromatic amines with complex structures were degraded into the monocyclic anilines prior to undergoing complete mineralization. The performance of US-KMnO<sub>4</sub> toward the degradation of aromatic amines was strongly dependent on the KMnO<sub>4</sub> dosage, US power density and pH. The increase in the KMnO<sub>4</sub> dosage and US power density and the decrease in the pH value led to a progressive enhancement in the degradation of aromatic amines in textile-dyeing sludge. The combined US and KMnO<sub>4</sub> treatment possess a great potential for the degradation of aromatic amines in textile-dyeing sludge and offered some useful suggestions to develop the advance oxidation process for the degradation of persistent organic pollutants in sludge.

#### Acknowledgments

This research was supported by the Natural Science Foundation of China (No. 21577027), the Science and Technology Plan of Guangdong Province (No. 2015A020215032), the Special Applied Technology Research and Development of Guangdong Province (major project) (No. 2015B020235013), and the Science and Technology Plan of Guangzhou.

#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jhazmat.2016.04.018>.

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