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Degradation of polycyclic aromatic hydrocarbons (PAHs) in textile dyeing sludge with ultrasound and Fenton processes: Effect of system parameters and synergistic effect study

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HIGHLIGHTS

- Ultrasound–Fenton process can degrade PAHs in the surface and interior of sludge.
- The degradation of HMW PAHs was close to or even higher than those of LMW PAHs.
- The disruption of sludge would increase the amount of PAHs in the reaction system.
- The degradation efficiency of PAHs would be inhibited by organic matter.

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ABSTRACT

To establish an efficient oxidation process for the degradation of polycyclic aromatic hydrocarbons (PAHs) in textile dyeing sludge, the effects of various operating parameters were optimized during the ultrasound process, Fenton process and the combined ultrasound–Fenton process. The results showed that the ultrasonic density of 1.80 w/cm^3, both H_2O_2 and Fe^{2+} dosages of 140 mmol/L and pH 3 were favorable conditions for the degradation of PAHs. The degradation efficiency of high molecular weight PAHs was close to or even higher than that of light molecular weight PAHs. The highest degradation efficiencies of Σ16 PAHs were obtained within 30 min in the order of: Fenton (83.5%) >ultrasound–Fenton (75.5%) >ultrasound (45.5%), then the efficiencies were decreased in the other of: ultrasound–Fenton (73.0%) >Fenton (70.3%) >ultrasound (41.4%) in 60 min. The extra PAHs were released from the intracellular substances and the cavities of sludge due to the disruption of sludge during the oxidation process. Also, the degradation of PAHs could be inhibited by the other organic matter in the sludge. The combined ultrasound–Fenton process showed more efficient than both ultrasound process and Fenton process not only in the surface of sludge but also in the sludge interior.

1. Introduction

Textile dyeing sludge is one of the most critical environmental problems in China. Textile dyeing sludge has been listed as Strict Control Waste (HY02) with reference to hazardous waste by local government, Guangdong Province, China. In 2013, the amount of textile dyeing sludge in China has been up to 5.38 million tons (80% moisture content) [1]. There are different kinds of dyes and auxiliary chemicals used in textile industry. Polycyclic aromatic hydrocarbons (PAHs) are the minor components and the transformation intermediates of dyes [2]. PAHs are characterized as toxic, mutative and carcinogenic to human. The hydrophobic PAHs are found to be resistant to conventional treatment process. Thus, considerable amount of PAHs are absorbed onto the sludge particles during the wastewater treatment process and are difficult to degrade once released into aquatic or soil system [3]. In previous studies [4], 10 textile dyeing plants were comprehensively investigated to evaluate PAHs level in textile dyeing sludge. PAHs are one of the characteristic pollutants in textile dyeing sludge and may pose a threat to environment during the process of sludge disposal. Therefore, it is necessary to develop an effective method to

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treat textile dyeing sludge containing PAHs before discharge into the environment.

Selection of a suitable elimination technology for textile dyeing sludge is one of the most challenging tasks due to the complexity of sludge chemistry and aquifer characteristics as well as limited rule-of-thumbs for textile dyeing sludge decontamination. A great deal of research efforts have been expanded to find effective techniques for PAHs removal in solid matrix (such as soil, sediment and sludge) [5,6]. During the past few decades, advanced oxidation processes (AOPs) have been extensively developed for degrading many toxic and recalcitrant contaminants. Amongst AOPs, Fenton process, which is characterized by production of highly oxidative hydroxyl ($^{\bullet}OH$) radical as the primary oxidant, has been well believed as an effective method for the destruction of organic pollutants [7]. It was reported that the $^{\bullet}OH$ addition is very well known pathway to initiate aromatic ring opening [8].

Sonolysis is also one of the most promising AOPs for organic substances degradation. Sonochemical effects generally based on the formation of short-lived radical species generated in transient cavitational bubble collapses, which leads to localized high temperatures ($T \sim 5000$ K) and pressures ($P \sim 500$ bar) [9,10]. These radical species and extreme conditions provide the main driving mechanism for the degradation of pollutants. A number of studies has reported the use of ultrasound for the degradation of various organic pollutants, such as chlorinated hydrocarbons [11], aromatic compounds [12–14] and textile dyes [15–17]. However, the total mineralization of these recalcitrant contaminants is difficult to obtain with ultrasound alone [18].

Recently, considerable efforts have determined that combining Fenton process with sonolysis is effective in enhancing the degradation of recalcitrant contaminants in aqueous system. Ma et al. [19] investigated the degradation of carbofuran in aqueous solution by ultrasound and Fenton processes and found that more than 99% of the carbofuran was degraded by the combined ultrasound–Fenton process within short reaction time periods. Liang et al. [20] and Sun et al. [21] also reported that the combined ultrasound–Fenton process could accelerate the degradation and mineralization of organic compounds. In addition, the ultrasound–Fenton process is not limited to wastewater treatment. Zhang et al. [22] used the ultrasound–Fenton process to treat oily sludge and high removal efficiency of petroleum hydrocarbon was obtained. Qiu et al. [23] and our previous group [24] also used the ultrasound–Fenton process to enhance the efficiency of sludge reduction and dewaterability. In a word, the combination of ultrasound with the Fenton process is a meritorious technology that has improved the efficiency of both the ultrasound and Fenton process. However, to our knowledge, no study has reported on the degradation of PAHs in textile dyeing sludge by the combined ultrasound–Fenton process.

Therefore, in the present study, the effects of ultrasonic densities, dosages of H_2O_2, Fe^{2+} and pH on PAHs degradation in textile dyeing sludge were investigated and compared by the ultrasound process, Fenton process as well as the combined ultrasound–Fenton process. The synergistic mechanism of ultrasound–Fenton process on the PAHs degradation in textile dyeing sludge matrix was also discussed. The study will offer some useful suggestions for AOPs development for the degradation of persistent organic pollutants (POPs) in sludge.

2. Materials and methods

2.1. Materials

Mixed standard solutions (2000 mg/L in benzene/menthylene chloride 1:1) of 16 PAHs were obtained from O2si Smart Solutions (Charleston, SC, USA): 2-ring PAH (naphthalene), 3-ring PAHs (acenaphthylene, acenaphthene, fluorine, phenanthrene, anthracene), 4-ring PAHs (fluoranthene, pyrene, benz[*a*]anthracene, chrysene), 5-ring PAHs (benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, dibenz[*a,h*]anthracene) and 6-ring PAHs (indeno[1,2,3-cd]pyrene, benzo[ghi]perylene). Perylene-D12 at the concentration of 2000 mg/L was used as internal standards. Hydrogen peroxide (H_2O_2, 30% (w/w) in water), ferrous sulfate ($FeSO_4 \cdot 7H_2O$, purity >99.5%) and anhydrous sodium sulfate were supplied by Keshi (China). Silica gel (100–200 mesh) was purchased from Qingdao Haiyang Chemical Company (Shangdong, China), and alumina (100–200 mesh) was purchased from Aladdin (Shanghai, China). All organic solvents of pesticide analytical grade were obtained from Fisher Scientific (USA). The textile dyeing sludge samples were collected from a textile wastewater treatment station in Panyu District, Guangzhou, Guangdong Province, China. Based on the equal amount of dry sludge, large amount of high moisture content sludge was required and harder to store and transport than the dewatered sludge. So the dewatered sludge samples which were dewatered without any conditioner or polymers by a special plate-frame pressure filtration were collected. The textile dyeing sludge characteristics are presented in Table 1.

Table 1
Characteristics of dewatered dry sludge sample.

Parameters	Average value
pH	6.82
Moisture content (%)	65.53
Organic matter content (%)	32.00
2 ring PAHs (mg/kg)	0.09
3 ring PAHs (mg/kg)	1.07
4 ring PAHs (mg/kg)	1.49
5 ring PAHs (mg/kg)	1.48
6 ring PAHs (mg/kg)	0.32
Σ16 PAHs (mg/kg)	4.45
Σ7 CarPAHs (mg/kg)	2.18

2.2. Experimental apparatus

A 0–1800 W sonicator (Scientz JY99-IIDN, China) equipped with a sealed converter and titanium probe tip (25 mm in diameter and 320 mm in length) operated at 20 kHz was used in this study. Reactions were performed in a cylindrical reactor (1 L working volume) with a cooling jacket and a circulating temperature controller to maintain the reaction temperature at $25 \pm 1\,^{\circ}C$ during the ultrasound, Fenton and ultrasound–Fenton process. A magnetic mixer controlled the mixing speed of the water-sludge system at 200 rpm during Fenton process, but the power of ultrasonic could well mix the water-sludge mixture without the magnetic mixer during the ultrasound and ultrasound–Fenton process.

2.3. Experimental procedure

We considered that the ultrasound–Fenton process would be in conjunction with the unit of sludge conditioning where the moisture content of sludge is about 98%. Accordingly, 98% moisture content sludge was prepared by mixing the dewatered sludge samples with the right amount of deionized water. For ultrasound–Fenton process, the 98% moisture content sludge samples of 500 mL were initially adjusted to the required pH value by sulfuric acid (H_2SO_4) and were transferred to the cylindrical reactor of the sonicator. $FeSO_4 \cdot 7H_2O$ was added into the sludge samples and Fenton reaction was then initiated after adding H_2O_2. The ultrasonic irradiation exposed to the sludge samples immediately, and the samples were collected at desired time intervals. For Fenton process or ultrasound process, the sludge samples were treated

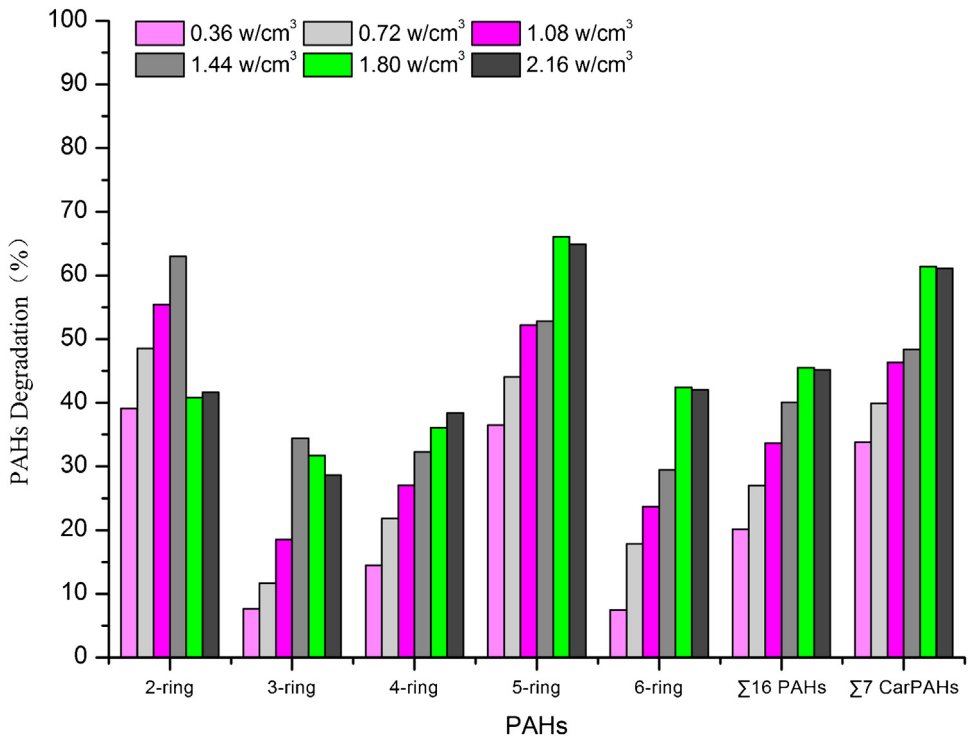

Fig. 1. Effect of various ultrasonic densities on PAHs degradation in textile dyeing sludge.

with only Fenton's reagent or ultrasonic irradiation at the above mentioned experimental procedure, respectively.

2.4. Analytical methods

After ultrasound, Fenton and ultrasound–Fenton oxidation in sludge-aqueous suspensions, the sludge matrix was separated from the aqueous phase by centrifugation (10 min, 4000 rpm). The aqueous supernatant was discarded. The sludge matrix was freeze-dried in the vacuum freeze dryer (12 h, −60 °C) before being extracted. The extraction of PAHs was a modification of the method used by Song et al. [25] and Li et al. [26]. About 2 g of each sample were extracted with a 20 mL hexane/acetone (1:1 in volume) solution using a 240 W ultrasonic bath (KQ300D, China) in a 250 mL Erlenmeyer flask for 5 min. The slurry was centrifuged at 4000 rpm for 10 min and the supernatant was collected. The extraction procedure was repeated three times, using fresh solvent each time. The supernatants were combined and concentrated by rotary vacuum evaporation to approximately 1 mL, and then loaded into a cleanup column with alumina/silica (1:2 by volume) and anhydrous sodium sulfate. The fraction containing PAHs was eluated with 70 mL hexane/menthylene chloride (7:3 in volume) and was concentrated to 1 mL under a gentle flow of nitrogen with an NEVAP 112 (Organomation, USA). Instrumental analysis was conducted after internal standard was added. PAHs concentrations were analyzed by an Agilant 7890A gas chromatograph–5975C mass spectrometer (GC–MS, Agilant, USA) equipped with a 30 m × 0.25 mm-i.d. (0.25 μm film thickness) HP-5MS column (Agilant, USA). The instrumental analysis conditions were performed as our previous study [4]. The procedural blanks, spiked blanks, sample duplicates were routinely analyzed with sludge samples. The recovery of the PAHs was 96 ± 23%.

The pH was measured using a digital pH-meter (pHS-3C, Leici, China). Sludge particle size distributions within sludge samples were examined by a laser particle size analyzer (Eye Tech, Ankersmid, Netherlands). To determine the loss-on-ignition, which is a measure of the organic matter in sludge, about 10 g wet sludge matrix samples were dried overnight at 105 °C, weighted, then baked in an oven for 2 h at 550 °C and reweighed.

All experiments were done in triplicate and the average values were obtained.

3. Results and discussion

3.1. Degradation of PAHs in textile dyeing sludge by the ultrasound process

In the present study, the ultrasonic process was used to treat the textile dyeing sludge containing PAHs with various ultrasonic densities of 0.36, 0.72, 1.08, 1.44, 1.80 and 2.16 w/cm^3 at pH 3 within reaction period of 30 min. It is worth to mention that ultrasound irradiation could increase the temperature up to 50–60 °C depending on the power and frequency applied, this will help the degradation of PAHs. However, for comparing the ultrasonic process with other technologies without ultrasound, the reaction temperature was controlled at 25 ± 1 °C by circulating water in this study. So the effect of the temperature on PAHs degradation during the ultrasound process would not be discussed herein.

The results of the PAHs degradation in textile dyeing sludge in Fig. 1 show that the degradation of the 4-,5- and 6-ring PAHs (high-molecular weight (HMW) PAHs) increased from 14.5% to 36.0%, 36.5% to 66.0% and 7.4% to 42.5%, respectively, with increasing ultrasonic densities of 0.36–1.80 w/cm^3. Ultrasonic density greater than 1.80 w/cm^3 led to slight increase in the degradation of 4-ring PAHs to around 2.0%. The degradations of Σ16 PAHs and Σ7 CarPAHs also obtained similar results with increasing ultrasonic densities from 0.36 to 2.16 w/cm^3. The highest degradations of Σ16 PAHs and Σ7 CarPAHs were 45.5% and 61.3% at the ultrasonic density of 1.08 w/cm^3. It suggested that high ultrasonic density was favorable to the degradations of HMW PAHs and CarPAHs in textile

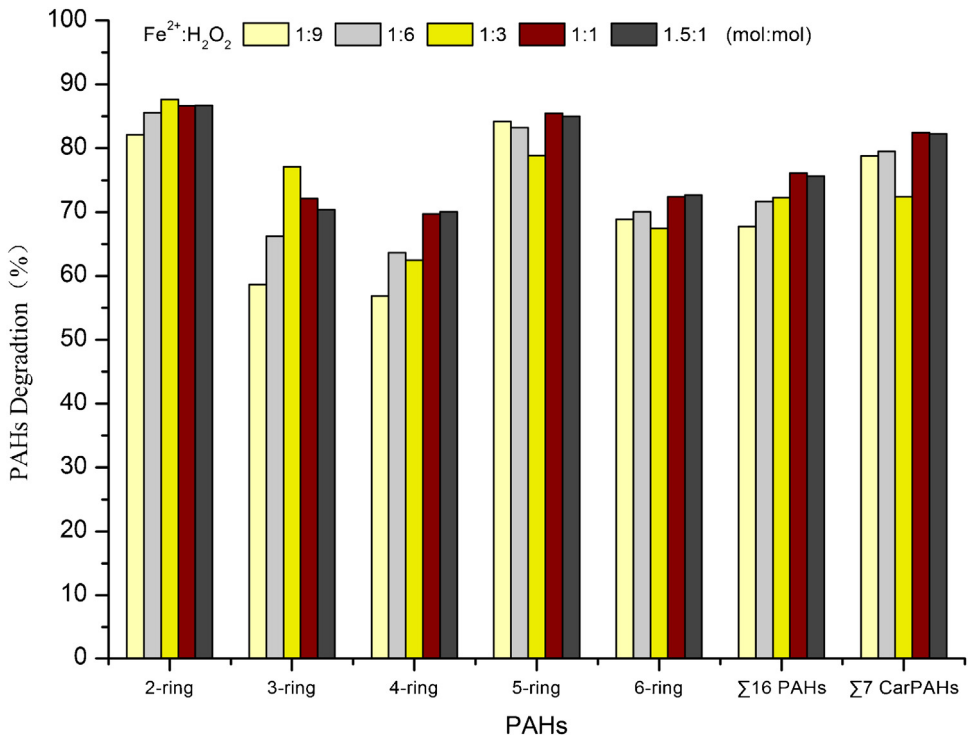

Fig. 2. Effect of various Fe^{2+}:H_2O_2 moral ratios on PAHs degradation in textile dyeing sludge.

dyeing sludge. And the increase of the total amount of LMW PAH at high ultrasonic density might also be achieved due to the HMW PAH was degrade into many intermediates for example LMW PAH. However, the highest degradation of the light-molecular weight (LMW) PAHs obtained at the ultrasonic density of 1.44 w/cm^3. The ultrasonic density greater than 1.44 w/cm^3 led to sharp decreases in the degradations of 2- and 3-ring PAHs from 63.0% to 41.0% and 34.4% to 28.6%, respectively, which suggested that the high ultrasonic density had negative influence on LMW PAHs degradation in textile dyeing sludge.

As we know, higher ultrasonic intensity in the reaction system would accelerate the reactions. The increase in the ultrasonic intensity could increase the number of active cavitation bubbles and also the size of the individual bubbles. Both increases can be expected to result in an increase in the maximum collapse temperature [27]. Moreover, the ultrasound was conductive to release PAHs from textile dyeing sludge to the bulk solution. The solubility of PAHs in water decreases with the increase of molecular weight [28]. The hydrophobic organic pollutants can undergo high-temperature pyrolysis in the gas-phase inside the bubbles and hydrophilic compounds can be degraded by $^{\bullet}OH$ at the bubble surface or in the bulk solution [29,30]. Thus, in this study, more HMW PAHs would easily enter into the amplified bubbles and be degraded by high-temperature pyrolysis under the higher ultrasonic density. On the other hand, the competition of $^{\bullet}OH$ radicals between LMW PAHs and HMW PAHs occurred. The HMW PAHs have more oxidation potential [31]. and would be more easily to be attacked and degraded under the higher ultrasonic density where large number of $^{\bullet}OH$ radicals were produced by decomposing H_2O. As a result, LMW PAHs obtained relatively low degradation efficiency in the high ultrasonic density reaction system. Take the detoxification of textile dyeing sludge consideration, 1.80 w/cm^3 was optimized as the optimal ultrasonic densities for PAHs degradation in textile dyeing sludge during the ultrasound process.

3.2. Degradation of PAHs in textile dyeing sludge by the Fenton process

3.2.1. Effect of hydrogen peroxide to ferrous iron moral ratio

During the Fenton process, the removal efficiency of target organic compounds may be marginal when the concentration of Fe^{2+} or H_2O_2 is too high. Excess iron would produce too many ferrous ions, which would scavenge hydroxyl radicals resulting in reduced degradation efficiency [32]. In the textile dyeing sludge system, overdose of H_2O_2 results in sludge flotation due to O_2 off-gassing caused by autodecompostion of excess H_2O_2 [33,34], and residual H_2O_2 may also scavenge hydroxyl radicals [35]. Thus, determining optimal dosages involves the consideration of both their relative ratio and absolute levels.

Fig. 2 shows the degradation of PAHs in textile dyeing sludge at fixed H_2O_2 concentration of 100 mmol/L and the varying concentration of ferrous ion which yield Fe^{2+} to H_2O_2 molar ratio in the range of 1:9–1.5:1, pH 3 and stirring rate of 200 r/min of a reaction period of 30 min. The degradation of 4-ring PAHs as well as Σ16 PAHs increased with increasing molar ratio of Fe^{2+}:H_2O_2 and reached a maximum value at 1:1 and 1.5:1. The 5-,6-ring PAHs and Σ7 CarPAHs also reached the maximum degradation rate at 1:1 and 1.5:1, but their lowest degradation efficiencies were obtained at 1:3. The degradations of 5-,6-ring PAHs and Σ7 CarPAHs at Fe^{2+}:H_2O_2 molar ratio of 1:3 were 6.0%, 6.0% and 10.0% lower than that of 1:1 or 1.5:1, respectively. However, 1:3 is the optimal Fe^{2+}:H_2O_2 molar ratio for the degradation of LMW PAHs. This observation suggested that the optimal Fe^{2+}:H_2O_2 molar ratio is based on the type of pollutant. The efficacy of the Fenton process is dependent on the utilization of free radicals and its reactivity with the PAHs molecules in textile dyeing sludge [36]. An optimal molar ratio of Fe^{2+}:H_2O_2 required could be theoretically calculated for some individual organic compounds in pure water. For example, Tang and Huang [37,38] calculated that the optimal molar ratio of Fe^{2+}:H_2O_2 was 1:11 for TCE and 1:10 for 2,4-Dichlorophenol.

Table 2
Results of first-order kinetic constants in the degradations of PAHs in textile dyeing sludge by ultrasound, Fenton and ultrasound–Fenton processes in 30 min.

PAHs	$k_{ultrasound}$ (min^{-1})	$R^2{}_{ultrasound}$	k_{Fenton} (min^{-1})	$R^2{}_{Fenton}$	$k_{ultrasound-Fenton}$ (min^{-1})	$R^2{}_{ultrasound-Fenton}$
2-Ring	0.007	0.952	0.027	0.975	0.031	0.973
3-Ring	0.003	0.674	0.007	0.997	0.016	1.000
4-Ring	0.005	0.867	0.016	0.872	0.021	0.955
5-Ring	0.013	0.789	0.048	0.779	0.021	0.996
6-Ring	0.021	0.999	0.053	0.881	0.040	0.832
Σ16 PAHs	0.007	0.975	0.026	0.830	0.022	0.972
Σ7 CarPAHs	0.012	0.913	0.040	0.765	0.027	0.967

However, such calculation is not possible for PAHs in textile dyeing sludge due to its complex texture. The textile dyeing sludge contained organic and inorganic matter that may interfere with PAHs degradation by scavenging reaction transients. In this study, 1:1 was selected as the optimal Fe^{2+}:H_2O_2 molar ratio for PAHs degradation in textile dyeing sludge.

3.2.2. Effect of Fenton reagents dosages

The degradation of PAHs in textile dyeing sludge at different Fenton reagents dosages were investigated with a fixed Fe^{2+}:H_2O_2 molar ratio of 1:1, pH of 3 and stirring rate of 200 r/min for a reaction period of 30 min. As seen in Fig. 3, the degradations of PAHs in textile dyeing sludge increased with increasing the dosage of Fenton reagent of 20–140 mmol/L. The highest degradations of all kinds of PAHs obtained at Fenton reagent dosage of 140 mmol/L except for the 5- and 6-ring PAHs. The highest degradation of Σ16 PAHs and Σ7 CarPAHs reached 83.0% and 86.5%, respectively. When the Fenton reagent dosage > 140 mmol/L, the degradations of 2-, 3- and 4-ring PAHs decreased but the degradations of 5- and 6-ring PAHs slightly increased. The loading of Fenton reagents which used for PAHs degradation in treating textile dyeing sludge was required much more than that for other pollutants degradation in simulated wastewater.

The required dosage of Fenton reagents is relevant to the complexity of reaction system and the type of pollutant [39]. Taylor et al. [40] reported that the degradation rates of PAHs were significantly retarded in the natural water samples though the loss of PAHs in pure water was rapid during the oxidation process. Ma et al. [41]. investigated the degradation of carbofuran in an aqueous system using Fenton process and observed that more than 90% of the carbofuran was removed from an initial carbofuran concentration of 10 mg/L within 5 min using 0.09 mmol/L of Fe^{2+} and 2.9 mmol/L of H_2O_2. Catalkaya and Kargi [42] also applied the Fenton process to the degradation of diuron in an aqueous system, and the results obtained that 98.5% of the diuron was removed using 0.68 mmol/L of Fe^{2+} and 8.9 mmol/L of H_2O_2. Pérez et al. [43] applied Fenton process to the degradation of the organic content of a bleaching Kraft mill effluent. Levels of TOC removal over 80% were obtained using 1.79 mmol/L of Fe^{2+} and 294.10 mmol/L of H_2O_2 for a reaction period of 15 min. In the treatment of textile dyeing sludge with Fenton oxidation, the •OH radicals are short-lived and relatively non-specific species that they oxidize most organic compounds while the target compounds (PAHs) sometimes exhibit minimal reactivity with •OH radicals [44]. Thus, a higher oxidant demand is required. Thus, the optimal Fenton reagents dosage was optimized as 140 mmol/L of both Fe^{2+} and H_2O_2 in the system of textile dyeing sludge.

3.2.3. Effect of pH

pH is one of the most important aspects on the oxidation potential in the Fenton process. It is well known that Fenton oxidations are efficient in the acidic range from pH 3–4 by directly increasing the concentration of Fe^{2+} in the solution and the availability of •OH radicals for the desired reaction of oxidation of the pollutant [45,46]. In the textile dyeing sludge system, the investigated pH values were 6.8 (pH of raw textile dyeing sludge), 5, 4, 3 and 2 at fixed Fe^{2+} and H_2O_2 concentrations of 140 mmol/L and stirring rate of 200 r/min for a reaction period of 30 min. It can be seen from Fig. 4 that the degradations of PAHs in textile dyeing sludge increased with decreasing pH and reached a maximum degradation rates at pH 3 after which the rates decreased. In particular, the degradations of 3- and 4-ring PAHs at pH 3 were significant higher than other pH values. However, the 5-,6-ring PAHs and Σ7 CarPAHs obtained relatively high degradation rates in the range from pH 3–5. It suggested that the degradations of 3- and 4-ring PAHs were more sensitive to pH value.

During the Fenton process, the degradation efficiency of HMW PAHs was close to or even higher than that of LMW PAHs. This result was different from the study of Jonsson et al. [47] who reported that the degradation efficiency of LMW PAHs (up to 89 and 59% degradation) was greater than that of HMW PAHs (0–38% degradation) during the Fenton process. This difference could be attributed to the matrix characteristics and the PAH physic-chemical properties [47]. As to exactly why the difference occurred, further investigation is needed to study how the chemical degradability of PAHs in textile dyeing sludge is influenced by sludge characteristics and PAH physic-chemical properties.

3.3. Treatment of PAHs in textile dyeing sludge by the ultrasound–Fenton process

From the above, the optimal operating parameters of ultrasound process and Fenton process for PAHs degradations were attained (ultrasonic density of 1.80 w/cm^3, H_2O_2 concentration of 140 mmol/L, Fe^{2+}:H_2O_2 molar ratio of 1:1 and pH of 3) by taking the detoxification of textile dyeing sludge consideration. In the present study, the effect of combining these operating parameters of ultrasound process and Fenton process which termed the ultrasound–Fenton process on the degradation of PAHs in textile dyeing sludge was investigated within a reaction time of 5–60 min. In addition, the result of ultrasound–Fenton process was compared with the results of ultrasound process and Fenton process alone at the correspondence operation parameters (as seen in Fig. 5).

Fig. 5 shows that the degradations of PAHs in textile dyeing sludge increased with the time and reached a maximum degradation rates at 30 min after which the rates decreased during the three processes except the 2-,3- and 4-ring PAHs in ultrasound process. At 30 min, the degradations of Σ16 PAHs and Σ7 CarPAHs in the Fenton process (83.5% and 86.7%, respectively) were higher than that in the ultrasound processes (45.5% and 57.0%, respectively) and the combined ultrasound–Fenton process (75.5% and 80.4%, respectively). Comparing with PAHs degradation rate constants in different processes in 30 min (Table 2) also obtained the similar results. The degradation rate constants of every group of PAHs in Fenton process were significant greater than that in ultrasound process, even the degradation rate constants of HMW PAHs, Σ16 PAHs and Σ7 CarPAHs in the Fenton process were greater than those in the combined ultrasound–Fenton process. It seemed that the synergistic effect of combined ultrasound–Fenton process failed to reflect in PAHs degradation in textile dyeing sludge. This

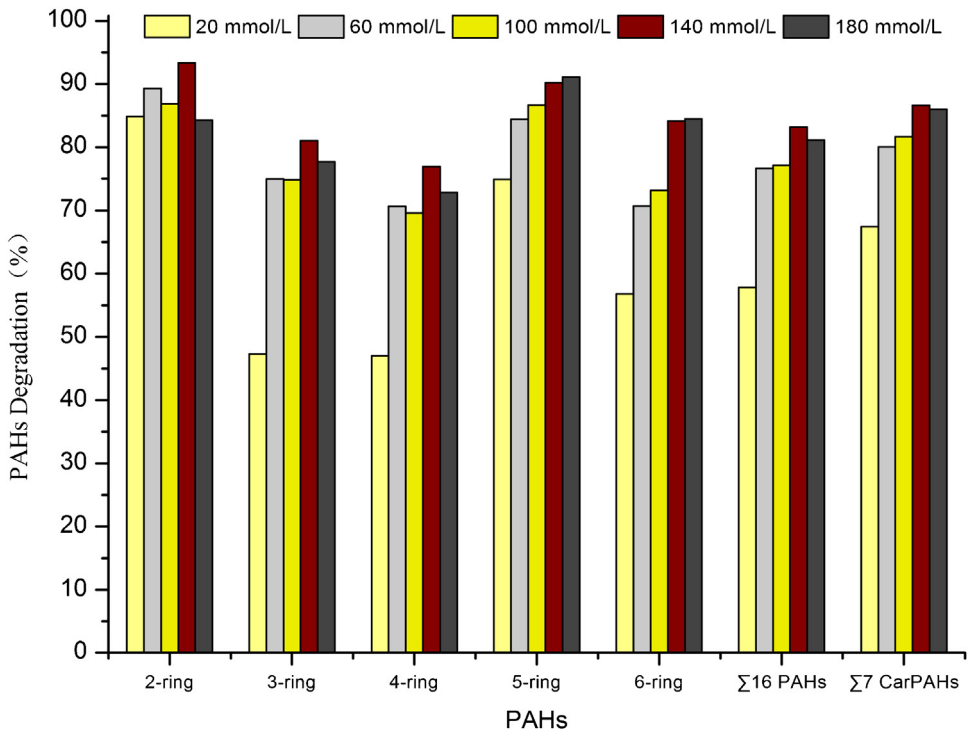

Fig. 3. Effect of various H_2O_2 dosages on PAHs degradation in textile dyeing sludge.

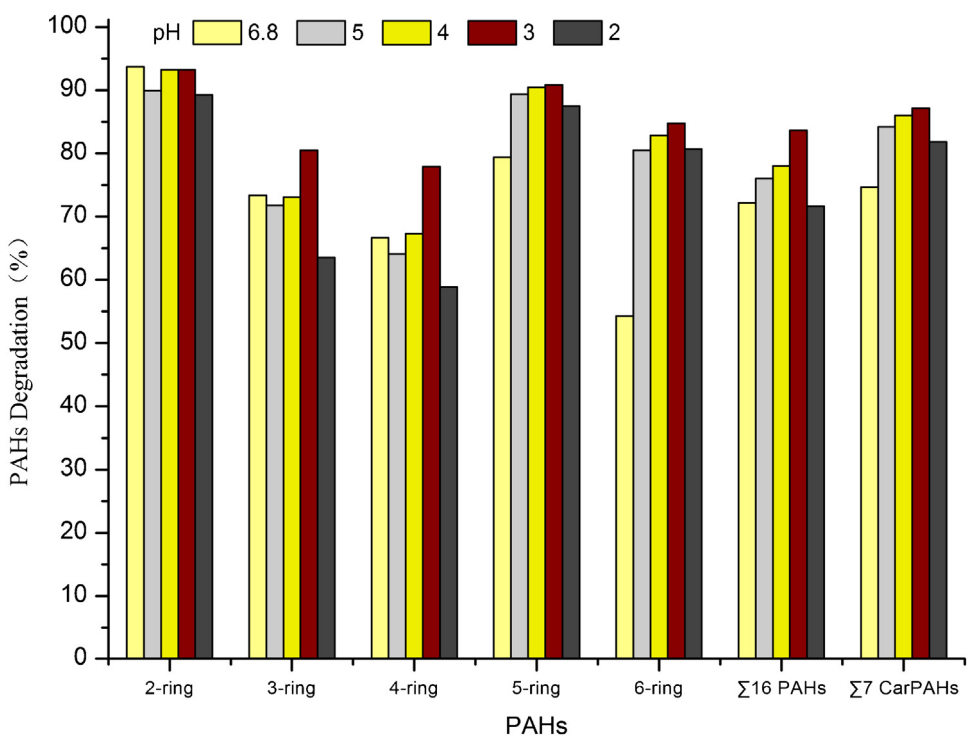

Fig. 4. Effect of various pH on PAHs degradation in textile dyeing sludge.

phenomenon was disagreed with the synergistic mechanism of ultrasound–Fenton process for the pollutants degradation in pure water. The researches from Weng et al. [48], Ma et al. [19] and Zhou et al. [49] suggested that the ultrasound–Fenton process could achieve synergistic degradation of pollutants in aqueous system.

Textile dyeing sludge is a complex matrix which contains many kinds of contaminants including metals, pathogens as well as organic compounds [4,50–52]. PAHs could be efficiently adsorbed onto the surface of the sludge organic matter and slowly penetrate into cavities [47]. During the oxidation process, the sludge structure would be disrupt and partial contaminants would be converted into the soluble phase (hydrophilic compounds) or the surface of sludge organic matter (hydrophobic compounds) [24]. Fig. 6 shows the changes of particle size by ultrasound, Fenton

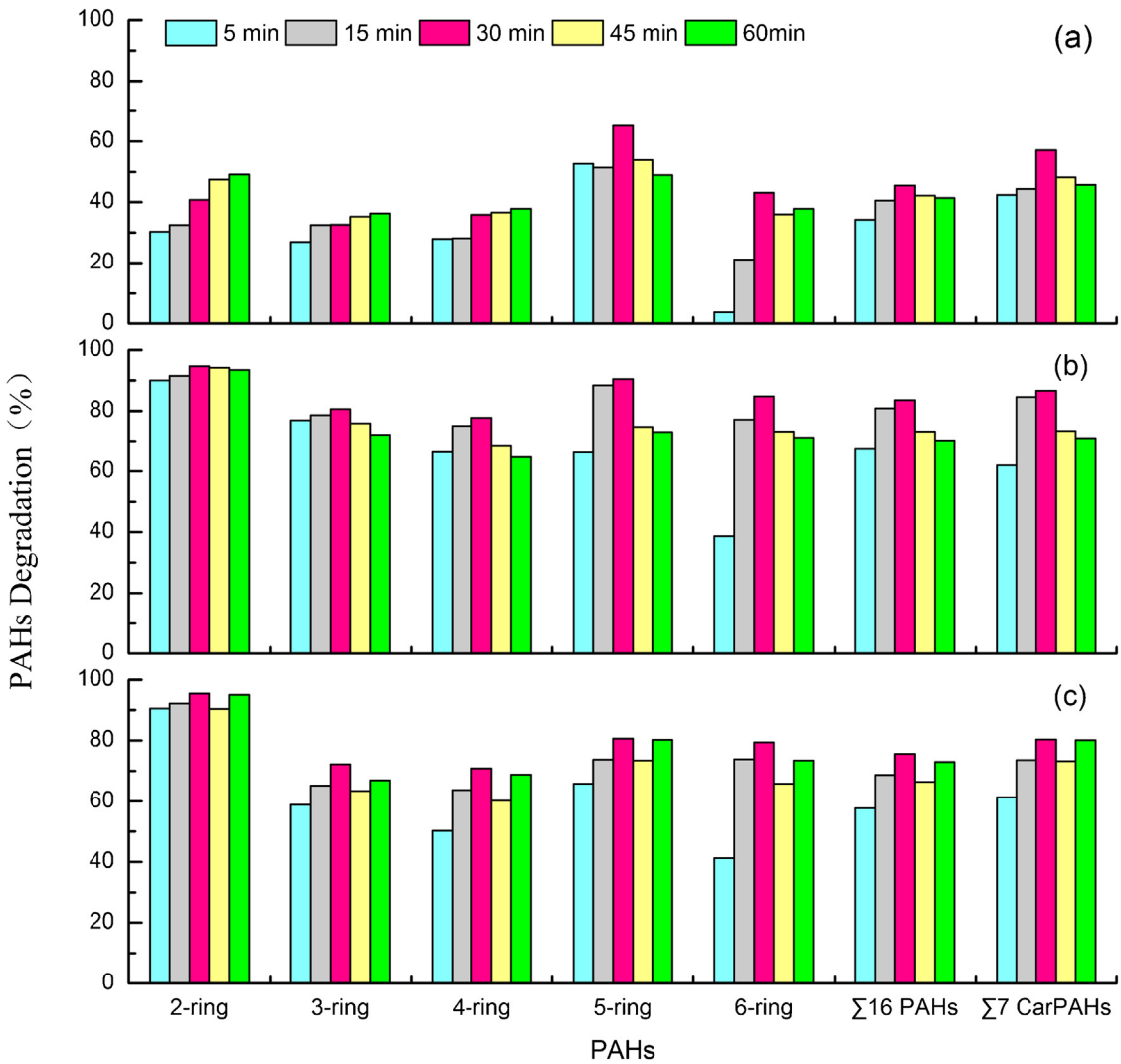

Fig. 5. Comparison of (a) ultrasound, (b) Fenton and (c) combined ultrasound–Fenton process of PAHs degradation in textile dyeing sludge.

and ultrasound–Fenton processes, respectively. The median particle size (dp_{50}) and effective size (dp_{10}) were determined to confirm the observation mentioned following. The textile dyeing sludge particles observed in the ultrasound and ultrasound–Fenton process were similar and were about ten times smaller than that of raw sludge and that in the Fenton process. For Fenton-treated sludge and raw sludge, dp_{50} and dp_{10} were similar, approximately 43 μm and 22 μm, respectively. It suggested that Fenton process had insignificant effect on sludge disruption. So the Fenton process just oxidized the PAHs which adsorbed onto the surface of sludge. And the PAHs which strongly entrapped within the sludge cavities tended to be less susceptible to Fenton oxidation. However, the microturbulence and shock waves which were created by the cavitation in ultrasonic system had significant effect on sludge particle disruption. Large amount of organic compounds including PAHs could be released from cavities of sludge particles during the oxidation process. Therefore, more contents of PAHs needed to be degraded in the ultrasound system than the Fenton alone system, which led to the efficiency of combined ultrasound–Fenton process superficially being lower than those of the Fenton process for PAHs degradation in textile dyeing sludge. Moreover, the oxidizing conditions in the textile dyeing sludge were never pristine due to the nature of sludge heterogeneity and numerous competing reactions that occur during the oxidation of contaminants.

In addition, after 30 min, the degradations of PAHs in ultrasound, Fenton and ultrasound–Fenton processes decreased with the time (as seen in Fig. 5), namely the amount of PAHs increase in textile dyeing sludge during the oxidation processes. Apart from the explanation of sludge disruption and extra PAHs releasing above, the additional PAHs might be formed from the intermediate of the oxidation of macromolecular compounds such as dyes due to the non-specific of the reactive radicals [44]. Meanwhile, the efficiency of these three processes would be reduced with the time due to the consumption of oxidant and the reactive radicals. It suggested that the majority of reactions of the three processes in textile dyeing sludge almost finished within 30 min, which was consistent with the result of the study of Sun and Yan [53]. Therefore, the oxidizing capabilities of the systems were too weak to degrade the additional PAHs after 30 min. However, the degradation of PAHs by ultrasound–Fenton process at 60 min increased again and almost reached to the levels of the PAHs degradation at 30 min, while the degradation of PAHs by ultrasound and Fenton alone process still decreased. It indicated that the combined ultrasound–Fenton process could revive and strength the oxidation of PAHs in textile dyeing sludge in the later stage.

The changes of organic matter contents in textile dyeing sludge by the three processes also confirmed the explanation above. As seen in Fig. 7, the initial organic content of textile dyeing

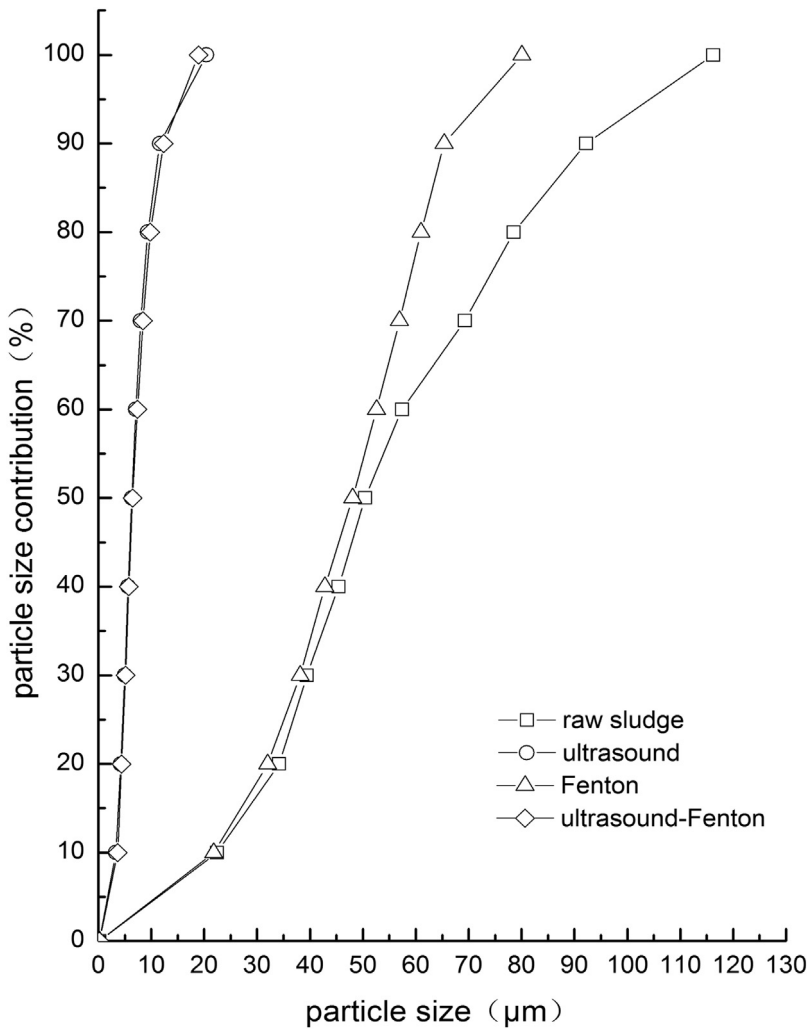

Fig. 6. Changes of particle size distribution of textile dyeing sludge by different processes within 30 min.

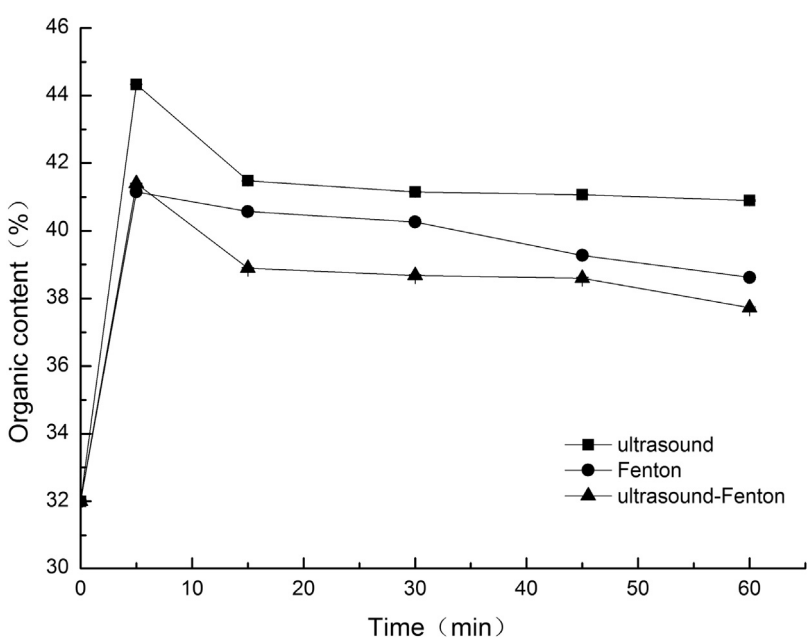

Fig. 7. Changes of organic matter contents in textile dyeing sludge by different processes.

sludge was about 32%. At 5 min, the organic contents of sludge increased to 44.3%, 41.2% and 41.4% by the ultrasound, Fenton and ultrasound–Fenton process, respectively. The relative organic contents in sludge increased after the treatments, because the oxidation processes changed the constituent of organic and inorganic matter in sludge. It is reported that there are large amount of metallic oxide, such as Al_2O_3 and CaO, in textile dyeing sludge [54]. The metal speciation existed in the form of hydroxide or oxide precipitation in primary sludge (pH 6.8) would leave from the sludge in the form of soluble ions during the ultrasound, Fenton or ultrasound–Fenton processes (pH 3). As a result, the total mass of sludge decreased. Comparatively, the relative mass of organic matter decreased fewer than the inorganic matter. Amongst the three processes, ultrasound process could result in the highest degree of sludge disintegration and released large amount of organic compounds. When the ultrasound process combined with the Fenton process, their synergistic effect could enhance the oxidizing capacity of the reaction system and remove some of released organic compounds during the process. After 30 min, the organic contents in textile dyeing sludge decreased (Fig. 7) while the PAHs contents in textile dyeing sludge increased (Fig. 5b) during the Fenton process. This evidence confirmed the possible competitive effects between PAHs and organic matter in textile dyeing sludge. Thus, above data clearly demonstrated that the organic matter significantly reduced the Fenton oxidation degradation efficiency of PAHs in textile dyeing sludge due to the non-specific of the reactive radicals. However, during the combined ultrasound–Fenton process, both the organic contents and PAHs contents in textile dyeing sludge decreased after 45 min. It suggested that the ultrasound–Fenton process could achieve synergistic degradation of the additional PAHs in textile dyeing sludge at the later stage.

All above, the conventional synergistic mechanism of ultrasound–Fenton process was not found in this PAHs degradation system of textile dyeing sludge matrix. The synergistic mechanism of the combined ultrasound–Fenton process in PAHs degradation in the complex textile dyeing sludge matrix could be concluded that (1) the ultrasound–Fenton process could highly disrupt sludge and release large amount of organic compounds including PAHs; (2) ultrasound–Fenton process could enhance the oxidation capacity to degrade the target contaminant (the extra PAHs) at the later reaction stage though there were many kinds of contaminants in the reaction system.

4. Conclusion

The results of this study indicated that the degradation of target contaminant (PAHs) in textile dyeing sludge could be inhibited by other organic matter due to the complexity of the matrix. The Σ16 PAHs degradation efficiencies of three processes were Fenton (83.5%) >ultrasound–Fenton (75.5%) >ultrasound (45.5%) within the reaction period of 30 min, and the order of ultrasound–Fenton (73.0%) >Fenton (70.3%) >ultrasound (41.4%) within 60 min for the ultrasonic density of 1.80 w/cm^3, with both H_2O_2 and Fe^{2+} dosages of 140 mmol/L, respectively, and at pH 3. The ultrasound process had significant effect on sludge particle disruption but low efficiency of oxidizing PAHs. The effect of Fenton process was in contrast to the ultrasound process. However, the combined ultrasound–Fenton process had both advantages in sludge disruption and effective PAHs degradation in textile dyeing sludge matrix. In other words, the combined ultrasound–Fenton process was found to be an efficient approach for the degradations of PAHs not only in the surface of sludge but also in the cavities and intracellular substances of sludge. Further researches still need to be done to deeply study the competing reaction between PAHs and other organic compounds in textile dyeing sludge and their intermediate.

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