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ORIGINAL PAPER

Combined ultrasound with Fenton treatment for the degradation of carcinogenic polycyclic aromatic hydrocarbons in textile dying sludge

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Abstract To develop an effective method to remove the toxic and carcinogenic polycyclic aromatic hydrocarbons (CPAHs) from textile dyeing sludge, five CPAHs were selected to investigate the degradation efficiencies using ultrasound combined with Fenton process (US/Fenton). The results showed that the synergistic effect of the US/Fenton process on the degradation of CPAHs in textile dyeing sludge was significant with the synergy degree of 30.4. During the US/Fenton process, low ultrasonic density showed significant advantage in degrading the CPAHs in textile dyeing sludge. Key reaction parameters on CPAHs degradation were optimized by the central composite design as followed: H_2O_2 concentration of 152 mmol/L, ultrasonic density of 408 W/L, pH value of 3.7, the molar ratio of H_2O_2 to Fe^{2+} of 1.3 and reaction time of 43 min. Under the optimal conditions of the US/Fenton process, the degradation efficiencies of five CPAHs were obtained as 81.23% (benzo[a]pyrene) to 84.98% (benz[a]anthracene), and the benzo[a]pyrene equivalent (BaP_{eq}) concentrations of five CPAHs declined by 81.22–85.19%, which indicated the high potency of US/Fenton process for removing toxic CPAHs from textile dyeing sludge.

Keywords Carcinogenic polycyclic aromatic hydrocarbons · Textile dyeing sludge · Ultrasound · Fenton · Central composite design

Introduction

Textile dyeing sludge is the primary solid waste generated during textile dyeing wastewater treatment. In 2013, the amount of textile dyeing sludge discharged in China was 5.38 million tons (80% moisture content) (Ning et al. 2015). A large proportion of the sludge has not been treated appropriately before disposal, which poses a great threat to the ecological system (Feng et al. 2015). In addition, some pollutants were found to be resistant to the conventional wastewater treatment process and are liable to accumulate in sludge. Our previous study showed that polycyclic aromatic hydrocarbons (PAHs) were a type of recalcitrant organic pollutants in textile dyeing sludge (Ning et al. 2014b). In particular, the carcinogenic polycyclic aromatic hydrocarbons (CPAHs), such as benz[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene

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(BkF), benzo[a]pyrene (BaP), dibenz[a,h]anthracene (DBA) and indeno[1,2,3-cd]pyrene (InP), were the main contributors to total carcinogenic potency of textile dyeing sludge, accounting for 97% of the BaP_{eq} concentrations of $\sum_{16}$PAHs (Ning et al. 2014b). It is necessary to develop an effective approach to remove the toxic CPAHs from textile dyeing sludge.

Recently, advanced oxidation processes (AOPs) have been applied as promising methods in the degradation of persistent pollutants (Bocos et al. 2015; Yap et al. 2011). Among AOPs, ultrasound irradiation (US), which has unique physical and chemical effects through the cavitation, is found to be an efficient method to remove recalcitrant chemicals (Carail et al. 2015; David 2009). As has been reported in recent studies, US is capable of degrading various organic compounds, such as chlorinated hydrocarbons (Pera-Titus et al. 2004), PAHs (Psillakis et al. 2004), textile dyes (Berberidou et al. 2007) and phenols (Kobayashi et al. 2011). However, high mineralization efficiencies of organic contaminants using US alone are difficult to obtain.

Fenton process is another widely used AOP for the degradation of organic pollutants. A large amount of ·OH, which are generated through the catalytic decomposition of hydrogen peroxide using ferrous ion as the catalyst, are the key oxidizing species in the Fenton process (Neyens and Baeyens 2003). It is also reported that Fenton process could be applied to remedy contaminated solid matrices (Flotron et al. 2005; Watts et al. 2002; Usman et al. 2012). However, the efficiency of the Fenton treatment in the destruction of hydrophobic contaminants in solid matrices is limited, because some of the pollutants have adsorbed deep into the organic matter and become unavailable or competitive to the ·OH (Lundstedt et al. 2006).

To overcome these disadvantages, the combination of US and Fenton treatment (US/Fenton) has been proposed. Ultrasound has significant effect on sludge particle disruption, which may release the absorbed pollutant from sludge and enhance the degradation efficiency (Ning et al. 2014a; Lin et al. 2016). For example, Zhang et al. (2013) investigated the capability of US/Fenton to eliminate petroleum hydrocarbons in oily sludge and revealed that the US/Fenton process could perform as a more effective method to oily sludge compared with either US or Fenton alone. Furthermore, Virkutyte et al. (2009) also studied the degradation of naphthalene in contaminated soil by the US/Fenton process and found a degradation efficiency of 97%. Li and Song (2009) studied the effect of US/Fenton treatment on the degradation of an AR 97 aqueous solution and observed an improvement in the removal of AR 97 compared with the Fenton process alone. Lan et al. (2012) also reported that the highest removal rate of naproxen in the solution reached 100% within 10 min using US/Fenton process. These studies showed that combined US/Fenton process could utilize the advantages of these two methods to generate more ·OH and could effectively improve the degradation efficiencies of organic pollutants. In our previous studies (Lin et al. 2016), various operating parameters of US process alone and Fenton process alone were optimized and compared by the ultrasound process, Fenton process as well as the simply combined US/Fenton process for the degradation efficiency of $\sum$16 PAHs in textile dyeing sludge. However, the kinetic and the optimal parameters of the combined US/Fenton process for the PAHs degradation were lack of research.

In the present study, five CPAHs in textile dyeing sludge were selected as model organic pollutants to test their degradation efficiencies using US/Fenton process. The specific objectives were as follows: (1) to evaluate kinetics and the synergistic effect between US and the Fenton process for the degradation of five CPAHs in textile dyeing sludge, (2) to investigate the effects of various operating parameters on the degradation of CPAHs during US/Fenton process, (3) to obtain optimal conditions using the central composite design (CCD) model for the US/Fenton treatment of CPAHs in textile dyeing sludge and (4) to evaluate the carcinogenic potency of CPAHs after optimizing US/Fenton process. The study will provide a scientific basis and technological support for upgrading and developing the current industrial wastewater treatment to remove the recalcitrant organic pollutants from industrial wastewater sludge.

Materials and methods

Materials

The standard solution containing five CPAHs including BaA, Chr, BbF, BkF and BaP with each at 2000 mg/L [dissolved in 1:1 benzene and dichloromethane (*v*/*v*)] and an internal standard containing perylene-d12 at a concentration of 2000 mg/L (dissolved in dichloromethane) were provided by O2si Smart Solutions (Charleston, SC, USA). Ferrous sulfate ($FeSO_4{\cdot}7H_2O$), hydrogen peroxide [H_2O_2, 30% (*w*/*w*) in water] and anhydrous sodium sulfate were obtained from Keshi (China). Silica gel (100–200 mesh) obtained from the Qingdao Haiyang Chemical Company (Shandong, China) was activated at 130 °C for 16 h. Alumina (100–200 mesh) supplied by Aladdin (Shanghai, China) was dried at 450 °C for 12 h before use. All organic solvents obtained from Fisher Scientific (USA) were of pesticide analytical grade. Deionized water was used throughout this study.

Sludge samples

The dewatered sludge was collected from a textile wastewater treatment plant in Guangzhou City, Guangdong province, China. With equal amount of dry sludge, large amount of high moisture content sludge was harder to store and transport than the dewatered sludge. So the sludge samples were dewatered by a special plate-frame pressure filtration without addition of any conditioners or polymers. The dewatered sludge was kept at constant temperature (4 °C) prior to analysis, and its characteristics are presented in Table S1.

Experimental apparatus

Ultrasonic reactor was supplied by a 0–1800 W sonicator (Scientz JY99-IIDN, China, 20 kHz) equipped with a sealed converter and a titanium probe tip (25 mm in diameter and 320 mm in length). Reactions were performed in a cylindrical reactor (1 L volume) with a cooling jacket and a circulating temperature controller to keep the reaction temperature constant (25 ± 1 °C) during the US and US/Fenton processes. Additionally, a magnetic mixer controlling the mixing speed of the solution at 200 r/min was used to ensure the sufficient mixing of the chemicals during the Fenton process, but the power of ultrasonic could well mix the water–sludge mixture without the magnetic mixer during the US and US/Fenton process.

Experimental procedure

In this study, sludge samples (each 500 mL, 98% moisture content) were prepared by stirring the ground dewatered sludge samples with the corresponding amount of deionized water for 2 h. The initial pH of the sludge samples was adjusted by using diluted sulfuric acid and sodium hydroxide. During the US/Fenton process, $FeSO_4{\cdot}7H_2O$ was added in advance into the sludge samples and the reactions were initiated by adding H_2O_2 and turning on the ultrasound at the same time. For Fenton or US alone, the sludge samples were treated with only Fenton's reagent or US at the above-mentioned experimental procedure, respectively. All experiments were performed in triplicate.

Analytical methods

After the treatment, the sludge samples were separated by the centrifugation at 4000 rpm for 5 min. After the centrifugation, the solid residue was freeze-dried in the vacuum freeze dryer (12 h, −60 °C) before further extraction and detection. The supernatant was filtered by means of 0.45 µm filter for further analysis. The extraction of PAHs was carried out in an ultrasonic bath (40 kHz, KQ300D, China) at 400 W, and the extraction process was accomplished following the method of Oturan et al. (2008) with proper modifications. Two grams of sludge sample mixed with 2 g of anhydrous sodium sulfate was placed into an Erlenmeyer flask (100 mL) and extracted with a 20 mL of a hexane/acetone (1:1 *v*/*v*) solution for 5 min. The mixtures were centrifuged at 4000 rpm for 5 min, and the supernatant was collected. The extraction process was repeated three times. The collected extraction solution was concentrated to approximately 1 mL using a rotary vacuum evaporator and solvent-exchanged with 10 mL *n*-hexane twice. The extracts were cleaned up through a glass chromatography column with anhydrous sodium sulfate and alumina/silica (1:2 by volume), and then, the fraction containing CPAHs was eluted by 70 mL of a hexane/dichloromethane (7:3, *v*/*v*) solution, followed by reduction to 1 mL with a rotary vacuum evaporator and a gentle flow of nitrogen with an NEVAP 112 (Organomation, USA). Perylene-D12 was used as internal standard to determine the concentrations of CPAHs. The analysis of CPAHs concentrations was carried out using an Agilent 7890A gas chromatograph-5975C mass spectrometer (GC–MS, Agilent, USA) equipped with a 30 m × 0.25 mm—i.d.—(0.25 µm film thickness) HP-5MS column (Agilent, USA). The instrumental conditions for sample analysis were described elsewhere (Ning et al. 2014b).

The pH value of the sludge was measured by using a digital pH meter (pHS-3C, Leici, China). The dissolved organic carbon (DOC) in the filtrate of the sample was measured using a total organic carbon analyzer (TOC-V_{CPH}, Shimadzu, Japan), and the solid total organic carbon (STOC) content of the residue of the sample was measured based on a modified potassium dichromate oxidation method.

CCD method based on the response surface methodology (RSM) was employed to optimize the ultrasonic density (W/L), reaction time (min), molar ratio of H_2O_2 to Fe^{2+}, pH value and H_2O_2 dosage (mmol/L) for the degradation of $\sum_5$CPAHs in textile dying sludge. The analysis of the experimental data was performed using the free Design-Expert software (trail version 9, Stat-Ease, Inc., MN, USA).

Quality assurance and quality control (QA/QC)

All the samples were analyzed in triplicate, and the results took the average. Because there is no suitable standard reference material, the accuracy and precision of the method were determined using six spiked (2.00 mg/kg of each CPAHs) replicate sludge samples. The recoveries of BaA, Chr, BbF, BkF and BaP standards were 99.52 ± 2.16, 95.38 ± 0.39, 98.10 ± 0.75, 113.05 ± 0.94 and $83.52 \pm 0.36\%$, respectively.

Result and discussion

Study of synergistic effects

Three different processes including US alone (360 W/L), Fenton treatment alone (H_2O_2 concentration of 100 mmol/L, 5:2 molar ratio of H_2O_2 to Fe^{2+} and an initial pH of 3.0), and the US/Fenton combined process were compared via the effectiveness of five CPAHs degradation.

Figure S1 shows five CPAHs degradation efficiencies as a result of treatment with different processes. For ultrasound alone process, the result of degradation was not remarkable. However, as reported previously, the US process had significant effect on sludge particle disruption (Ning et al. 2014a; Lin et al. 2016), which may release the adsorbed PAHs from sludge to the aqueous phase. The combination of US with Fenton could notably enhance the process efficiency due to a synergistic effect. As a consequence, higher degradation efficiencies of all five CPAHs were achieved in US/Fenton process than in US or Fenton process. The pseudo-first-order rate constants of US (k_{US}), Fenton (k_{Fenton}), and US/Fenton oxidation ($k_{US/Fenton}$) as well as the regression coefficient (R^2) were calculated, and the degree of synergy (S) was determined according to Eq. (1) (Weng et al. 2013):

$$\%S = \frac{k_{US/Fenton} - (k_{US} + k_{Fenton})}{k_{US/Fenton}} \times 100 \tag{1}$$

As shown in Table 1, the k [apparent rate constant (min^{-1})] of five CPAHs by US and Fenton alone processes were achieved as 0.0042–0.0071 min^{-1} and 0.0043–0.0111 min^{-1}, respectively. An enhancement in CPAHs degradation was achieved in the combined system, i.e., US/Fenton process, and the k values of 0.0141–0.0207 min^{-1} were obtained. It was observed that the synergy factors were larger than zero. The synergy factors of individual CPAHs were 19.0–47.6, and the synergy factor of $\sum_5$CPAHs was 30.4, indicating the significant synergistic effect of the US/Fenton process for CPAHs degradation in textile dyeing sludge. Among five CPAHs, BbF obtained the highest synergy factors. The synergistic mechanism of the US/Fenton process could attribute to the increase in ·OH radical concentration production and the sludge disintegration, resulting from the influence of ultrasound.

The removal of STOC and the release of DOC also proved the advantage of the combined US/Fenton process in this study. It is observed that both the US and Fenton processes could destroy the sludge structure and release the organic matter from sludge into the aqueous phase or mineralize the organic matter (Gong et al. 2015; Ning et al. 2014a). Figure S2 shows the changes of STOC and DOC in the sludge systems during different processes with the treatment time. As shown in Fig. S2a, during 0–40 min, the STOC in sludge solid matrices decreased from about 8500 to 8000, 7300 and 6600 mg/L with time after US, Fenton and US/Fenton treatments, respectively. In Fig. S2b, the DOC in the aqueous phase increased from about 130 to 190, 340 and 380 mg/L with time after US, Fenton and US/Fenton treatments, respectively. By comparing Fig. S2a with Fig. S2b, the mineralization

Table 1 Synergy degree of the combined ultrasound with Fenton process for the degradation of CPAHs as well as STOC in sludge

Compounds	k_{US}	R^2 $_{ultrasound}$	k_{Fenton}	R^2 $_{Fenton}$	$k_{US/Fenton}$	R^2 $_{US/Fenton}$	S (%)
BaA	0.0043	0.9809	0.0093	0.9685	0.0175	0.9545	22.3
Chr	0.0071	0.9809	0.0096	0.9505	0.0207	0.8867	19.3
BbF	0.0033	0.7991	0.0043	0.7550	0.0145	0.9294	47.6
BkF	0.0047	0.8161	0.0058	0.9274	0.0141	0.7991	25.5
BaP	0.0042	0.9606	0.0111	0.9640	0.0189	0.9768	19.0
$\sum_5$CPAHs	0.0044	0.9354	0.0068	0.9503	0.0161	0.9252	30.4
STOC	0.0007	0.7837	0.0022	0.9830	0.0044	0.9794	34.1

of sludge organic matter was obtained. The mineralization amount of organic matter was about 440, 990 and 1650 mg/L after 40 min treated by US, Fenton and US/Fenton, respectively. It indicated the great enhancement of combined US/Fenton process for degradation of organic matter in textile dyeing sludge. The degree of synergy of STOC was obtained as 34.1, which also proved the significant synergistic effect of the US/Fenton process on the degradation efficiencies of organic matter in textile dyeing sludge (Table 1).

Effects of reaction parameters of the US/Fenton process

Effect of the ultrasonic intensity

Generally, the increase in ultrasonic intensity would accelerate cavitation effect by increasing the number of active cavitation bubbles and also the size of the individual bubbles during the US/Fenton process (Kanthale et al. 2008; Lai et al. 2013). Nevertheless, high ultrasonic intensity would result in the insufficient collapse of the cavitation bubbles (Zhong et al. 2011). Figure 1 shows the effects of different ultrasonic densities on the degradation of five CPAHs with time at an initial pH of 3.0, H_2O_2 concentration of 100 mmol/L, and H_2O_2 to Fe^{2+} molar ratio of 5:2.

As seen in Fig. 1, the CPAHs removal efficiencies increased along with the reaction time for all of the ultrasonic densities except for BaP at the ultrasonic density of 1080 W/L. The highest removal efficiencies of BaA, Chr, BbF, BkF and BaP were 66.1, 69.4, 62.8, 63.4 and 68.7%, respectively, at the lowest ultrasonic density of 360 W/L within 40 min. The removal efficiencies of $\sum_5$CPAHs also reached the highest (64.97%) at the ultrasonic density of 360 W/L at 40 min. However, the removal efficiencies of these CPAHs in textile dyeing sludge decreased by increasing the ultrasonic density from 360 to 1800 W/L. This result seemed different from the previous report that the production of ·OH radicals could be enhanced by increasing the ultrasonic density because of the enhancement of cavitational activity, which would promote the removal efficiencies of contaminants (Golash and Gogate 2012). Zhong et al. (2011) found that the degradation efficiency of C.I. Acid Orange 7 increased with an increase in the ultrasound intensity until the ultrasound density reached to 400 W/L. Chen and Su (2012) investigated

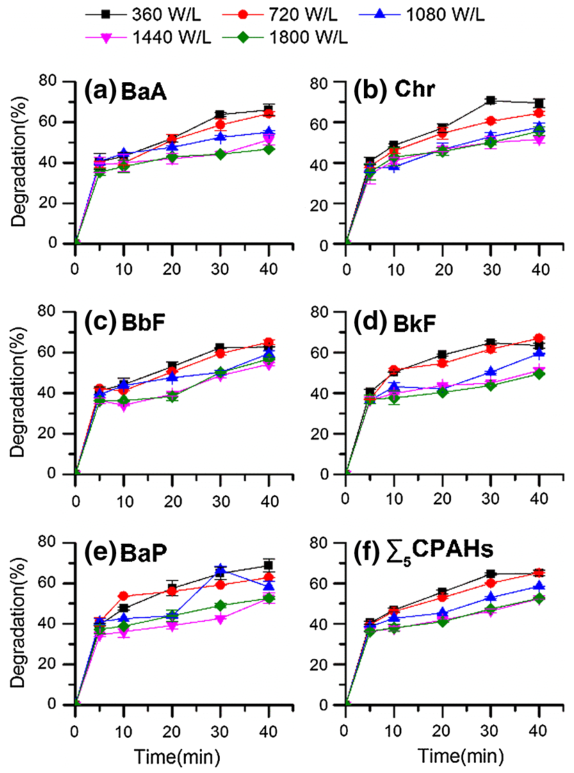

Fig. 1 Effect of ultrasonic density on the degradation efficiencies of CPAHs

the degradation of dinitrotoluenes by sono-activated persulfate oxidation, and the degradation efficiency reached to a maximum at approximately 1260 W/L. However, it also reported that coalescence of the cavitation bubbles would be produced by a high ultrasonic intensity, and large bubble field would block the energy transmission from the probe to the medium at higher ultrasound intensity (Chen and Su 2012; Wang et al. 2012). Moreover, when the ultrasonic intensity was too high, a large amount of gas bubbles could be generated and easily absorb the sound waves, resulting in less energy focused on the pollutants (Wang et al. 2012). The increasing of the ultrasonic intensity can result in the generation of an acoustic screen (Zhong et al. 2011). In the textile dyeing sludge reaction system, excessively high ultrasound intensity might result in the disruption of sludge particles and releasing the absorbed contaminants rather than degrading more pollutants. Therefore, low ultrasonic intensity was more appropriate for the degradation of CPAHs in textile dyeing sludge.

Effect of the pH

It is known that the pH value is usually considered to be an important factor for US/Fenton process (Bagal and Gogate 2014). Therefore, the effects of initial pH values of 2.0, 3.0, 4.0, 5.0, and 7.3 on the degradation of five CPAHs in textile dyeing sludge were investigated at initial H_2O_2 concentration of 100 mmol/L, H_2O_2 to Fe^{2+} molar ratio of 5:2, reaction time of 40 min and ultrasonic density of 360 W/L. The results are shown in Fig. 2. Obtained results indicated that the removals of CPAHs were significantly affected by the pH value, and the highest removal rates were obtained at an initial pH of 3.0–4.0. The highest removal efficiencies of BaA, Chr and BaP were 66.1, 69.4 and 68.7%, respectively, at an initial pH of 3.0, while the highest removal efficiencies of BbF (64.2%) and BkF (63.8%) were obtained at an initial pH of 4.0. The highest removal efficiencies of $\sum_5$CPAHs were obtained as 64.97% at pH of 3.0. The degradation efficiencies of five CPAHs sharply decreased by 17.6–23.8% when the pH value increased. In the US/Fenton process, when the pH of solution was greater than 4.0, the formation of Fe(II) complexes also reduced the generation of free radicals, and the ferrous ion inhibited by the precipitation of ferric oxyhydroxides, which would decrease the degradation of pollutants (Gogate and Pandit 2004). On the other hand, ·OH could be eliminated by the scavenging effects of the high concentration of H^+ ions in solution at low pH values (<2.5) (Yang et al. 2005). Additionally, under such conditions, the formation of $[Fe(H_2O)_2]^{2+}$ occurred and the amount of ·OH produced was smaller, which would limit the degradation rate (Gogate and Pandit 2004; Yang et al. 2005).

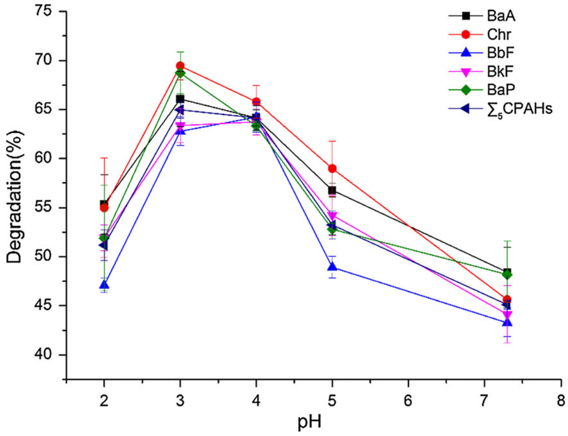

Fig. 2 Effect of the initial pH on the degradation efficiencies of CPAHs

Effect of the initial H_2O_2 concentration

Considering that the H_2O_2 dosage will also affect the performance of the US/Fenton process, the effects of this variable on the degradation of five CPAHs in textile dyeing sludge were investigated with pH of 3.0, reaction time of 40 min, ultrasound density of 360 W/L and H_2O_2 and Fe^{2+} molar ratio of 5:2. As illustrated in Fig. 3, the degradation efficiencies of five CPAHs increased when the H_2O_2 dosage increased from 20 to 140 mmol/L. However, the degradation efficiencies of CPAHs decreased when the H_2O_2 dosage further increased from 140 to 180 mmol/L. The degradation efficiencies of five CPAHs at an initial H_2O_2 concentration of 140 mmol/L were obtained as 24.4–29.4% higher than that at an initial H_2O_2 concentration of 20 mmol/L. It suggested that the degradation of CPAHs in textile dyeing sludge was significantly affected by H_2O_2 dosage during the US/Fenton process. The highest removal efficiencies of BaA, Chr, BbF, BkF, BaP and $\sum_5$CPAHs were obtained as 72.7, 74.8, 70.5, 70.7, 73.7 and 71.8%, respectively. Previous studies reported that H_2O_2 dosage played an

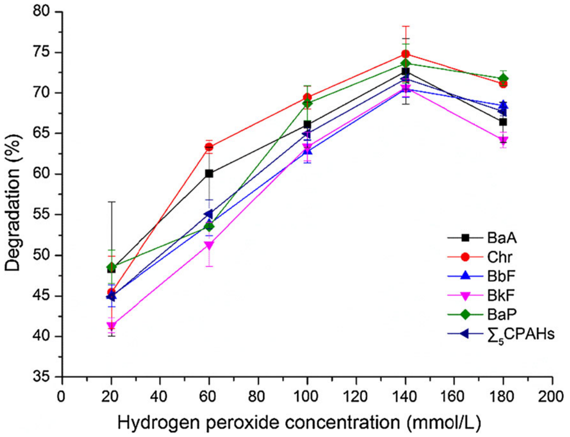

Fig. 3 Effect of hydrogen peroxide concentration on the degradation efficiencies of CPAHs

important role in acting as a source of free radicals through the decomposition process in the presence of ferrous iron and ultrasonic irradiations, which could enhance the extent of the elimination of contaminants (Bagal and Gogate 2014). However, H_2O_2 is also a scavenger of the free radicals when a high H_2O_2 dosage is used (Bagal and Gogate 2014). A similar result has been reported by Hou et al. (2016) who used a coupled ultrasound/heterogeneous Fenton process to degrade tetracycline over Fe_3O_4 catalyst. An increase in H_2O_2 concentration from 10 to 150 mmol/L could enhance the tetracycline degradation efficiency, but a further increase led to a slight decrease in the tetracycline degradation efficiency.

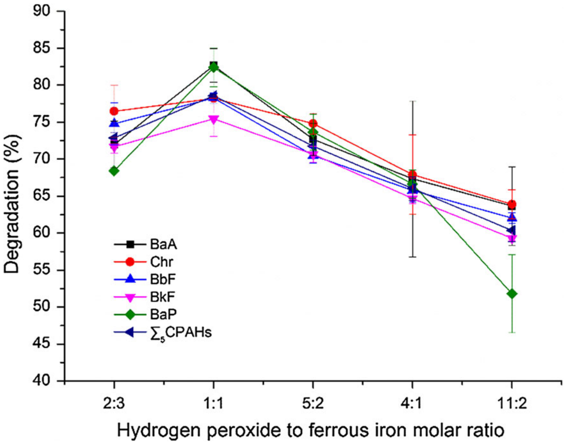

Fig. 4 Effect of molar ratio of hydrogen peroxide to ferrous iron on the degradation efficiencies of CPAHs

Effect of the molar ratio of H_2O_2 to Fe^{2+}

The loading of Fe^{2+} is also another important parameter in determining the degradation efficiencies of CPAHs in textile dyeing sludge during the US/Fenton process. The effects of the H_2O_2 to Fe^{2+} molar ratios in the range of 2:3–11:2 on the degradations of five CPAHs in textile dyeing sludge were investigated during the US/Fenton process. The H_2O_2 concentration was fixed at 140 mmol/L, and the reactions were also proceed with pH of 3.0, reaction time of 40 min and ultrasound density of 360 W/L. The results are presented in Fig. 4. The highest degradation efficiencies of BaA (82.7%), Chr (78.2%), BbF (78.3%), BkF (75.5%), BaP (82.4%) and $\sum_5$PAHs (78.57%) were obtained when the molar ratio of H_2O_2 to Fe^{2+} was 1:1. However, the degradation efficiencies of PAHs decreased sharply when the molar ratio of H_2O_2 to Fe^{2+} increased from 1:1 to 11:2. Moreover, when the molar ratio of H_2O_2 to Fe^{2+} was 2:3, the degradation efficiencies of PAHs were 3.4–14.0% lower than the highest degradation efficiencies. An overdose of iron sulfate would produce too many ferrous ions in solution, resulting in the scavenging of the ·OH and a reduced degradation efficiency (Özdemir et al. 2011). C. Wang and Liu (2014) found that the excessive addition of Fe^{2+} could produce Fe^{3+} which would react with ·OH to inhibit the reaction between ·OH and the organic pollutant.

Multivariable experimental design

CCD method was adopted to obtain an optimal response from a minimal number of experiments and to explore the effects of independent variables and their interactions on the response variables according to early reported references (An et al. 2011; Hammi et al. 2015). Five experimental variables [i.e., ultrasonic density (X_1), reaction time (X_2), pH value (X_3), H_2O_2 to Fe^{2+} molar ratio (X_4), and H_2O_2 dosage (X_5)] were selected in the CCD method. One response was selected as the degradation efficiency of $\sum_5$CPAHs (Y). Accordingly, a central composite rotatable design was composed of 50 experiments with eight replicates at the central points, and Table S2 summarizes the variables and levels involved in the design strategy.

The operating conditions and corresponding experimental data in the CCD for the US/Fenton degradation of CPAHs are summarized in Table S3.

Table 2 Experimental degradation efficiencies of CPAHs during optimized US/Fenton process

Compounds	BaA	Chr	BbF	BkF	BaP	$\sum_5$CPAHs
Degradation efficiency (%)	84.98	84.07	81.78	82.21	81.23	82.53

Table 3 BaP_{eq} concentrations of CPAHs before and after the optimized US/Fenton treatment

Compounds	TEF	BaP_{eq} concentrations (mg/kg)		Reduction percentage (%)
		Before the treatment	After the treatment	
BaA	0.10	0.0270	0.0040	85.19
Chr	0.01	0.0025	0.0004	84.00
BbF	0.10	0.0670	0.0122	81.79
BkF	0.10	0.0600	0.0107	82.17
BaP	1.00	0.2700	0.0507	81.22
$\sum_5$CPAHs		0.4265	0.0780	81.71

Equation (2) presents the response regression equation which represented the relationship between the five independent variables and response of $\sum_5$CPAHs degradation.

$$\begin{aligned} Y = 10.10 &- 0.02X_1 + 1.01 + 13.82X_3 - 1.91X_4 \\ &+ 0.38X_5 - 1.03 \times 10^{-4}X_1X_2 + 1.60 \\ &\times 10^{-4}X_1X_3 - 3.46 \times 10^{-4}X_1X_4 - 1.69 \\ &\times 10^{-5}X_1X_5 - 0.10X_2X_3 - 4.17 \times 10^{-4}X_2X_4 \\ &- 6.72 \times 10^{-5}X_2X_5 - 0.10X_3X_4 + 2.34 \\ &\times 10^{-4}X_3X_5 - 6.43 \times 10^{-3}X_4X_5 + 2.84 \\ &\times 10^{-6}X_1^2 - 3.88 \times 10^{-3}X_2^2 - 2.03X_3^2 + 0.08X_4^2 \\ &- 7.83 \times 10^{-4}X_5^2 \end{aligned} \tag{2}$$

To reveal the significance of the five variables of the model, the p values and the F values are listed in Table S4. In this design, the p value of the model was <0.0001, which meant that the model was highly significant. As shown in Table S4, most of the linear coefficients were significant ($p < 0.01$) for the response factor (Y). Moreover, the lack of fit of the model was not significant, which indicated that the model fitted the experimental results. Two-dimensional contours and response surface plots, which present the interaction among all of the significant independent variables, were plotted and are shown in Fig. S3.

The optimized $\sum_5$CPAHs degradation efficiency was 81.96% at the optimized conditions of a H_2O_2 concentration of 152 mmol/L, an ultrasonic density of 408 W/L, a pH value of 3.7, a H_2O_2 to Fe^{2+} molar ratio of 1.3 and a reaction time of 43 min. To validate the accuracy of the model, the experiments were performed at the optimal reaction parameters. As shown in Table 2, the experimental $\sum_5$CPAHs degradation efficiency was obtained as 82.53%, which is very similar to the predicted value, indicating the validity of the acquired model to optimize the reaction parameters of US/Fenton process for the degradation of CPAHs in textile dyeing sludge. The degradation efficiency of the most highly carcinogenic BaP was 81.23%. The highest degradation efficiency of CPAHs was BaA which reached 84.98%. In addition, Table 3 shows the change of the carcinogenic potency of CPAHs with the benzo[a]pyrene equivalent (BaP_{eq}) concentrations. The BaP_{eq} for sludge samples was calculated by multiplying the concentration of each CPAH by its benzo[a]pyrene toxic equivalency factors (TEF) (Nisbet and LaGoy 1992). The BaP_{eq} concentrations of five CPAHs declined by 81.22–85.19% after the optimized US/Fenton treatment. Thus, these results suggested that the US/Fenton process may strongly reduce the toxicity concentration of textile dyeing sludge by effectively degrading the carcinogenic compounds.

Conclusion

A significant synergistic effect of the US/Fenton process on the CPAHs degradation in textile dyeing sludge was achieved. The degrees of synergy of the $\sum_5$CPAHs and STOC removal were obtained as 30.4

and 34.1, respectively. The single factor studies revealed that low ultrasonic density had an advantage in degrading the CPAHs during the US/Fenton process. The H_2O_2 dosage, the molar ratio of H_2O_2 to Fe^{2+} and pH value also had significant effect on the degradation efficiencies of CPAHs during the US/Fenton process. The reaction parameters of the US/Fenton process were further optimized by CCD, and the results were as followed: H_2O_2 concentration of 152 mmol/L, ultrasonic density of 408 W/L, pH value of 3.7, H_2O_2 to Fe^{2+} molar ratio of 1.3 and reaction time of 43 min. Under the optimal conditions, the degradation efficiencies of $\sum_5$CPAHs in textile dyeing sludge reached to 82.53%, which was similar to the predicted value (81.96%) by CCD method. Also the BaP_{eq} concentrations of five CPAHs declined by 81.22–85.19% after the optimized US/Fenton treatment. These results suggested that the US/Fenton process was able to efficiently remove the toxic CPAHs from textile dyeing sludge.

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