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FULL PAPER

Degradation of polycyclic aromatic hydrocarbons (PAHs) in textile dyeing sludge by O_3/H_2O_2 treatment

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The degradation of polycyclic aromatic hydrocarbons (PAHs) in textile dyeing sludge by O_3/H_2O_2 treatment was investigated. Fluorene (Fl), phenanthrene (Ph), anthracene (An) and dibenz[a, h]anthracene (DBA) were selected to represent typical PAHs. The effect of radical inhibitors, H_2O_2, O_3 flow rate, pH and reaction time on the degradation of the four types of PAHs were examined to determine the optimal conditions for degradation and to clarify the mechanism(s) of PAHs degradation. The results indicated that the combined O_3/H_2O_2 treatment resulted in high removal rates of the selected PAHs: 89% for Fl, 66% for Ph, 71% for An and 81% for DBA. These results correspond to the optimal conditions of an O_3 flow rate of 0.4 L/min, a H_2O_2 concentration of 0.60 mol/L, a reaction time of 15 min and pH 7. The removal rate (within 30 min) increased by 5% for Fl, 27% for Ph, 21% for An and 5% for DBA through the addition of H_2O_2 to the O_3 process. The O_3 flow rate, reaction time and pH were the key parameters affecting PAHs degradation with multiple interacting factors ($p < 0.05$) by the O_3/H_2O_2 treatment. The degradation of the PAHs can be well fit by pseudo-first-order kinetics ($R^2 = 0.9656$). The combined O_3/H_2O_2 treatment is demonstrated to be an efficient approach for the degradation of PAHs in textile dyeing sludge.

Introduction

With the growth of the textile dyeing industry in the Pearl River Delta of Guangdong province, China, large quantities of textile dyeing sludge are generated during the physicochemical (e.g., coagulation/flocculation) and biological treatment of textile dyeing wastewater [1-3]. Some contaminants that cannot be degraded and removed are likely to accumulate in the sludge, such as polycyclic aromatic hydrocarbons (PAHs). The fate of carcinogenic, teratogenic and mutagenic effect on organisms and humans [4-6]. Therefore, the remediation of PAHs in textile dyeing sludge should be conducted immediately.

Recent studies have shown that Fenton reagents can be used to eliminate PAHs adsorbed in sludge, soil and sediment [7-8]. However, Fenton reagents have the drawbacks of forming sludge, a harsh pH control and the need for high concentrations of H_2O_2, all of which limit the practical application of Fenton technology [9-10]. Ultrasonic irradiation has also been reported to be an efficient treatment for the degradation of PAHs [11-12]. However, the total mineralization of organic pollutants by ultrasound irradiation alone is energy consuming because the intermediate products (e.g., alcohols, carboxylic acids, etc.) are generally more hydrophilic than the parent compounds [13].

O_3 might serve as an effective and promising alternative to remove PAHs from textile dyeing sludge because of its high oxidation capacity and broad pH adaptability [14-15]. Many studies have proposed the use of O_3 for PAH removal from water and sediment [16-17]. In general, O_3 fragments PAHs into simple, soluble and biodegradable compounds through direct oxidation and reactions involving radical intermediates [18]. Additionally, the performance of ozonation depends on several key factors, including O_3 concentration, PAHs concentration, surface-active impurity, O_3 mass transfer and several other operating variables such as O_3 flow rate, pH and reaction time [16, 19, 20]. H_2O_2, which is a strong oxidation agent, coupled with O_3 can increase the efficiency of PAH oxidation by generating additional hydroxyl radicals [21] to contribute to the combined action of direct ozonation, radical ($\cdot OH$, $HO_2\cdot$ or $O_3^- \cdot$) oxidation and H_2O_2 oxidation. The main advantage of O_3/H_2O_2 treatment lies in the

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acceleration of the O_3 transformation process by the addition of H_2O_2. According to Staehelin and Hoigné [22], the reaction of O_3 with H_2O_2 begins with the deprotonated form of H_2O_2. As shown in Eqs. (1) and (2), O_3 decomposition can be artificially improved by increasing the pH or by adding H_2O_2. Furthermore, Von Gunten U [23] has demonstrated that the oxidation of para-chlorobenzoic acid by conventional ozonation and O_3/H_2O_2 led to a complete depletion of O_3 at a dose of 1 mg L^{-1}. To the best of our knowledge, there have been no investigations reported on the degradation of PAHs in textile dyeing sludge by a combined O_3/H_2O treatment.

$$O_3 + HO^- \rightarrow HO_2\cdot + O_2 \qquad (1)$$

$$O_3 + HO_2^- \rightarrow \cdot OH + O_2 + O_2\cdot^- \qquad (2)$$

The present study aims to investigate the feasibility and mechanism(s) of PAH degradation in textile dyeing sludge using an O_3/H_2O_2 treatment. Fluorene (Fl), phenanthrene (Ph), anthracene (An) and dibenz[a, h]anthracene (DBA) were selected to represent typical PAHs. The degradation kinetics of the four PAHs were calculated based on dynamics equations, and the optimal conditions for PAH degradation was determined using a Central Composite Design (CCD) model.

Results and discussion

Effect of Radical Inhibitors

The mechanism of the reactions of O_3 with PAHs refers to whether ozone attacks PAHs directly or whether the radical(s) react indirectly with the PAHs. Thus, a series of ozonation reactions at various pH values (i.e., 3, 7, 9) were conducted with and without isopropanol, which is a strong hydroxyl radical scavenger [24]. The ~~dimensionless~~ concentrations of Fl, Ph, An and DBA versus time at different pH values corresponding to ozonation reactions with and without isopropanol are shown in Figures1a–d. The results show that the ozonation of all PAHs was retarded to some extent. It has been recognized that PAHs degradation occurs through two mechanisms: (1) direct degradation of the target PAHs by O_3 (Eq. (3)); and (2) indirect degradation by $\cdot OH$, $HO_2\cdot$ or $O_3^-\cdot$ produced from O_3 and H_2O_2 transformation (Eqs. (4)-(8)) [17,23]. Indirect degradation by $\cdot OH$ is undoubtedly interfered in the presence of isopropanol in the reaction system which are clearly observed in the Figure 1a–c.

$$O_3 + \mathrm{PAHs} \rightarrow \mathrm{PAHs_{ox}} \qquad (3)$$

$$O_3 + H_2O_2 \rightarrow O_2 + HO_2\cdot + \cdot OH \qquad (4)$$

$$HO_2\cdot \rightarrow O_2^-\cdot + H^+ \qquad (5)$$

$$O_3 + O_2^-\cdot \rightarrow O_2 + O_3^-\cdot \qquad (6)$$

$$O_3^-\cdot + H^+ \rightarrow HO_3\cdot \qquad (7)$$

$$HO_3\cdot \rightarrow O_2 + \cdot OH \qquad (8)$$

The ozonation of Fl, Ph and An, especially in reaction time of 15 min and 20 min, was significantly retarded when isopropanol was added in the reaction system. However, the ozonation of DBA was only slightly retarded in the presence of isopropanol during the whole reaction period. These results indicated that Fl, Ph and An were partially oxidized by hydroxyl radicals, whereas DBA was likely oxidized by O_3. This is because that isopropanol is a strong hydroxyl radicals scavenger which can eliminate the $\cdot OH$. Thus the degradation of Fl, Ph and An was slowed down due to lack of $\cdot OH$ but the degradation rate of DBA was not affected because it was directly degraded by O_3. In particular, the ozonation of Ph, An and Fl were clearly affected, with the extent of attenuation following the order: pH 9 < pH 7 < pH 3 (average data of the whole reaction time). It is clear that the presence of isopropanol resulted in a decrease in the oxidation rate, which indicates that reactions involving hydroxyl radicals were operative during the ozonation process. The results mentioned above may result from the self-decomposition of O_3, which would induce the formation of hydroxyl (or other) radicals from a direct attack of O_3 in alkaline conditions [23]. Both types of radicals were likely involved in consuming O_3. For this reason, the attenuation of the oxidation rate of DBA at different pH values follows the order: pH 7 <pH 3< pH 9 in figure 1.

Figure 1

An accurate O_3 concentration could not be measured in agitated ozonation reactors of the four types of PAHs because of its fast consumption in the reactions. We note that the oxidation rate could be accelerated in an agitated reactor because of the higher volumetric mass transfer coefficient than that in a reactor without agitation. This result was consistent with the study of Beltran [25], who made a comparison of ozonation of Fl in agitated tank and photochemical tank, and found that the total O_3 efficiency is lower in the photochemical reactor probably than that in agitated tank due to lower volumetric mass transfer coefficient.

Effect of pH

pH has a significant influence on the ozonation of PAHs in the textile dyeing sludge. The effect of pH on PAH decomposition is presented in Figure 2. The results show that the dimensionless concentrations of Ph and An decreased when the pH increased from 3 to 7. The concentrations reached a valley point at pH = 7, and then it increased when the pH increased from 7 to 11. However, the dimensionless concentrations of Fl and DBA underwent continuous decreases when the pH increased from 3 to 11. This was likely caused by the high O_3 concentration at acidic and neutral pH values for the rapid degradation of Fl, Ph and An. Furthermore, as the pH increased, the O_3 decomposition occurred via the five chain reactions shown in Eqs. (9)–(13) [26]. More hydroxyl radicals ($\cdot OH$), superoxide ($O_2\cdot^-$) and ozonide ions ($O_3\cdot^-$) were formed as the O_3 concentration decreased because it

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decomposed in an alkaline environment. Therefore, the degradation of Ph and An decreased under alkaline conditions, whereas the degradation of DBA increased throughout the entire pH range from 3 to 11. The reaction of DBA appeared to occur directly, which is consistent with the results involving radical inhibitors that also showed that DBA was likely oxidized by O_3 directly. Furthermore, pH has a positive effect on the Fl degradation rate, which has been demonstrated by Beltran [25]. Furthermore, the concentration of dissolved ozone in the higher pH (pH 12) were always lower than those observed in the presence of tert-butyl alcohol and decreased as pH increased during the ozonation of Fl.

$$O_3 + H_2O \rightarrow 2HO\cdot + O_2 \qquad (9)$$

$$O_3 + HO^- \rightarrow HO_2\cdot + O_2\cdot^- \qquad (10)$$

$$O_3 + HO\cdot \rightarrow HO_2\cdot + O_2 \leftrightarrow O_2\cdot^- + H^+ \qquad (11)$$

$$O_3 + HO_2\cdot \rightarrow 2O_2 + HO\cdot \qquad (12)$$

$$2HO_2\cdot \rightarrow O_2 + H_2O_2 \qquad (13)$$

Figure 2

Effect of H_2O_2

The degradations of the PAHs in the presence and absence of H_2O_2 during the O_3 process are shown in Figure 3. The results show that the addition of H_2O_2 to the O_3 process accelerated the degradation of the four PAHs. The removal rate increased by approximately 5% for Fl, 27% for Ph, 21% for An and 5% for DBA. Moreover, the removal rate of Fl, Ph, An and DBA reached 70%, 99%, 90% and 70%, respectively, as the reaction time increased to 30 min.

Figure 3

Coupling H_2O_2 to ozonation is an effective way to improve the removal rate because of cumulative, or synergistic effects. The pseudo-first-order rate constants of ozonation (k_{O3}), H_2O_2 (k_{H2O2}), and O_3/ H_2O_2 oxidation ($k_{O3/H2O2}$) were used to assess the degree of synergy, S, according to Eq. (14) [27].

$$\%S = \frac{k_{O_3/H_2O_2} - (k_{O_3} + k_{H_2O_2})}{k_{O_3/H_2O_2}} \qquad (14)$$

It can be observed from Table 1 that S is larger than zero, ranging from 2.12 to 30.37. These data indicate that a synergistic effect of the individual processes is operative. That is, the effect is not simply a summation of the individual processes; rather, there exists a mutual synergy between the processes. It is well known that the accepted pathways for the decomposition of organic pollutants by O_3/H_2O_2 treatment occur via direct reactions and via hydroxyl radical reactions. Two types of active oxidizing species that result from the decomposition of O_3 have been proposed (i.e., hydroxyl radicals and atomic oxygen) [28]. Furthermore, it has been demonstrated that atomic oxygen could serve as the source of hydroxyl radicals in an instantaneous reaction [29]. Additionally, H_2O_2 could increase the efficiency of ozonation by generating more hydroxyl radicals [30]. In general, PAHs can undergo direct ozonation, radical ($\cdot OH$, $HO_2\cdot$ or $O_3^-\cdot$) oxidation and/or H_2O_2 oxidation when they are introduced into an O_3/H_2O_2 treatment system. However, on the basis of the high S values, the reactions of Ph and An may occur via two-way reactions. In contrast, the reactions of ~~Fl and~~ DBA theoretically undergo direct ozonation, as indicated by the low values of S. And Fl was least reactive PAHs among the O_3 degradation of the target PAHs in our study. These results may be indicative of the unique degradation characteristics of ~~Fl,~~ Ph and An. Indeed, these two PAHs possess relatively few rings, which may enhance the ozonation reactions by generating activated radicals from H_2O_2. Further, uneven charge distributions between π-electrons above and below the face of the ring (i.e., the π-electron system) and sp^2-hybridized C atoms may occur [31]. Moreover, the addition of electron density to aromatic rings may induce large quadrupole moments such that the electron-rich π-system can serve as a π-donor. In addition, the removal of electron density from aromatic structures can invert the quadrupole moments causing them to behave such as electron-deficient π-acceptors [32]. From these perspectives, Ph and An were readily degraded because π-donors and electron-deficient π-acceptors were generated. However, the K_{OC} values of DBA increased as the number of aromatic moieties increased, which resulted in the faster removal rate of Ph and An relative to DBA [33].

Table 1

Oxidation kinetics of PAHs by O_3/H_2O_2 treatment

The pseudo-first-order reaction shown in Eq. (19) was investigated to assess the process of oxidation of PAHs by O_3/H_2O_2 treatment. Several parameters such as the reaction rate, $t_{1/2}$ of PAHs and R^2 were used to characterize the degradation kinetics of the four kinds PAHs at their respective initial concentrations, and the results are presented in Table 2. The results show that the degradation of PAHs within the first 30 minutes follows pseudo-first-order kinetics, with a high R^2 value of 0.9656. In addition, Ph and An were more easily degraded because they possess higher reaction rate constants (0.0959 ng mL^{-1} min^{-1} for Ph and 0.0715 ng mL^{-1} min^{-1} for An). The results of Ph and An degradation suggested that Ph was easier to be degraded than An at their own initial concentrations of the two PAHs. The dissolved O_3 concentration was on the order of mg L^{-1}, which is dramatically higher than that of the target PAHs (i.e., ng mL^{-1}). Moreover, it was demonstrated that the gas-liquid two-phase flow that occurs in an agitated reactor could improve the volumetric mass transfer coefficient between the target PAHs (liquid phase) and O_3 (gas phase) [27]. Additionally, the ozonation activity can be promoted rapidly in the presence of H_2O_2 because $\cdot OH$, $HO_2\cdot$ and/or $O_3^-\cdot$ radicals are generated [27].

Table 2

Central composite design

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A CCD model with 30 runs was conducted to demonstrate the influence of O_3 flow rate, pH, reaction time and H_2O_2 dose on the removal of PAHs from the textile dyeing sludge and to determine the optimal conditions for PAH degradation by the O_3/H_2O_2 treatment. The results are presented in Table 3 and Figure 4.

Table 3

Figure 4

Based on the CCD model, Table 3 shows that the optimal conditions for PAH degradation by a combined O_3/H_2O_2 treatment includes an O_3 flow rate of 0.4 L/min, a reaction time of 15 min, pH = 7 and H_2O_2 doses of 0.60 mol/L. Using these optimal conditions, up to 89% for Fl, 66% for Ph, 71% for An and 81% for DBA were removed from the textile dyeing sludge.

It is noteworthy that almost all extractable Fl and DBA can be degraded under certain conditions from the textile dyeing sludge. It has been suggested that PAHs with more rings have increased reactivity [31]. In contrast, others have instead suggested that a decrease in reactivity of PAHs occurs as the number of rings increases [34]. Although the number of PAH rings clearly affects the O_3/H_2O_2 reaction, it is instructive to first consider the variables that have the greatest impact on the process. For instance, PAHs are hydrophobic compounds that readily accumulate on the surface of textile dyeing sludge. Thus, gaseous O_3 might preferentially react with the PAHs on the surface of the textile dyeing sludge according to Eq. (15). Additionally, O_3 can react with other active substances in the sludge (e.g., amine and nitro-compounds, heavy metal, reactive dye, etc.) to produce hydroxyl radicals according to Eq. (16), which presents yet another mechanism of PAH degradation via the radical reaction given in Eq. (17) [16].

$$O_3 + Sludge - PAH \rightarrow Sludge - PAHs_{ox}(eventually + CO_2 + H_2O) \tag{15}$$

$$O_3 + Sludge \rightarrow Sludge - HO\cdot + O_2 \tag{16}$$

$$Sludge - HO\cdot + Sludge - PAHs \rightarrow Sludge - PAHs_{ox}(eventually + CO_2 + H_2O) \tag{17}$$

A second-order model involving other factors could clarify the mechanism(s) involved in the degradation of PAHs by O_3/H_2O_2 treatment (Table 4). Furthermore, calculated p values of the coefficients (not shown) indicated that the O_3 flow rate, reaction time and pH were the factors that most affect PAH degradation. In addition, a p value above 0.05 for the target PAHs investigated in the model indicates that their corresponding variables play a comparably subordinate role in the O_3/H_2O_2 reaction.

Table 4

Experimental

Sludge samples

The sludge samples were obtained from a textile dyeing wastewater treatment plant in Dongguan City, Guangdong Province, China. The sludge samples were gravitationally thickened to approximately 98% moisture content. The samples were then stored in a refrigerator at 4°C to minimize microbial activity. The characteristics of the sludge are presented in Table 5.

Table 5

Standards and chemicals

Four PAHs characterized as priority pollutants by the US Environmental Protection Agency were analyzed in this study, including fluorene (Fl), phenanthrene (Ph), anthracene (An) and dibenz[a, h]anthracene (DBA), each at a concentration of 2000 mg L^{-1}. The internal standards included perylene-D12, chrysene-D12, naphthalene-D8, acenaphthene-D10 and phenanthrene-D10, each at a concentration of 2000 μg mL^{-1}. Fluorine-D10 and pyrene-D10, each at a concentration of 2000 μg mL^{-1}, were employed as the surrogate standards. All chemical standards were purchased from O2si Smart Solutions (Charleston, SC, USA). The silica gel (100–200 mesh) was purchased from Qingdao Haiyang Chemical Company (Shangdong, China) and the alumina (100–200 mesh) was purchased from Aladdin (Shanghai, China). Silica gel was baked at 130°C for 16 h, whereas alumina and anhydrous sodium sulfate were baked at 450°C for 12 h and 4 h, respectively. These materials were then stored in sealed containers until further use. All organic solvents were of analytical grade and were obtained from Fisher Scientific (USA).

Other reagents, such as sulfuric acid (H_2SO_4), sodium hydroxide (NaOH), H_2O_2 and isopropanol, were of analytical grade and were used without further purification. All solutions were prepared with deionized water.

O_3/H_2O_2 operation

O_3 production

The ozonation experiments were performed in semi-batch mode. O_3 was continuously bubbled into the solutions through a diffuser placed at the bottom of the reactor. O_3 was steadily produced from pure oxygen using a CY-H500 Laboratory O_3 Generator (Honghuan Electrical Technology Ltd. Co., Guangzhou, China). Once the ozonator was stabilized, O_3 was fed into a 1 L borosilicate glass reactor with a 500 ml sludge sample. Figure 5 shows a schematic representation of the experimental design.

Figure 5

Batch experiment

Effect of Radical Inhibitors

Sludge samples (500 ml) were initially adjusted to the desired pH value (i.e., 3, 7, 9) by either 3 mol/L H_2SO_4 or 4 mol/L NaOH, and then the samples were transferred to a 1 L borosilicate glass reactor. A series of ozonation reactions at various pH values (i.e., 3, 7, 9) were conducted for a designated time interval. Concurrently, isopropanol was fed into the reactor so that the effect of radical inhibitors on the degradation of PAHs could be examined.

Effect of pH

The effect of pH on PAH degradation was investigated according to the experiments performed involving radical inhibitors. However, in this case the pH range was varied from 3 to 11.

Effect of H_2O_2

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To determine the effect of H_2O_2 on the degradation of PAHs, sludge samples of 500 ml were first transferred to 1 L borosilicate glass reactors. Then, the experiment was performed at an O_3 flow rate of 0.4 L/min, pH 6.58–6.72 and with 7.5 mL H_2O_2 for different time intervals.

Central Composite Design (CCD)

For the CCD test, the gas flow rate, reaction time, pH and H_2O_2 dose were ranged from 0.32 to 0.48 L min^{-1}, 13–19 min, 5–9 and 5–9 mL (0.60 mol/L), respectively, through a single-factor experiment, and then the optimal conditions for PAH degradation was determined.

Degradation kinetics of PAHs by O_3/H_2O_2 treatment

First, the sludge samples (500 ml) were transferred to 1 L borosilicate glass reactors. Then, the degradation of PAHs by individual O_3 and H_2O_2 treatments were conducted for designated time intervals. Pseudo-first-order kinetics was used to investigate the degradation kinetics of PAHs, as shown in Eq. (3). Here, k is an apparent rate constant that is equivalent to the sum of the specific rate constants for O_3, H_2O_2 and ·OH (Eq. (4)). C_t is the target PAHs concentration at time t, and C_0 is the initial concentrations of the target PAHs. The half-life of the PAHs degradation ($t_{1/2}$, min) was measured based on Eq. (5) [26].

$$-\frac{dC_t}{dt} = k \times C_t \Leftrightarrow -\ln\frac{C_t}{C_0} = kt \qquad (18)$$

$$k = k_{o_3} + k_{H_2O_2} + k_{\cdot OH} \qquad (19)$$

$$t_{½} = \frac{0.693}{k} \qquad (20)$$

Sample preparation

After the O_3/H_2O_2 treatment, the supernatant and solid substances were separated by centrifugation. The PAH samples were then freeze-dried by a LGJ-12 vacuum freeze dryer (Songyuan Huaxing Technology Development Co., Ltd., Beijing, China), homogenized and sorted with a 100-mesh (mesh size: 0.15 mm) stainless steel sieve before further extraction and detection.

The freeze-dried PAH samples were then extracted in triplicate using a JY92-IIN high intensity ultrasonic processor (Scientz Biotechnology, Ningbo, China). The extraction procedures were based on the method of Li et al. [35], with appropriate modifications. Approximately 2 g of each sample uniformly mixed with 2 g of anhydrous sodium sulfate was placed into a conical flask and spiked with surrogate standards. The mixtures were then ultrasonic-extracted with 50 mL of dichloromethane/acetone (1:1 in volume) for 5 min. The ultrasonic power was fixed at 640W. After extraction, the extract was decanted and filtered in a round-bottom flask. The extraction process was performed in duplicate to ensure complete extraction. Subsequently, the filtered PAH extracts were combined and concentrated by a RE52A rotary vacuum evaporator (Yarong biochemical instrument factory, Shanghai, China) to approximately 1 mL, solvent-exchanged in duplicate to n-hexane (by adding 10 mL n-hexane to the extract and shaking), and then further concentrated to approximately 1 mL. The concentrated extract was transferred into a glass chromatography column (12 mm i.d.) packed with 1:2 (by volume) alumina/silica gel, followed by 1 cm anhydrous sodium sulfate for the chromatographic separation. 70 mL of a mixed solution of hexane and dichloromethane (7:3 by volume) was used as the elution solvent to obtain the PAH eluent. The eluent was then concentrated to 0.5 mL under a gentle flow of nitrogen with an N-EVAP 112 (Organomation, USA). After evaporation, 0.5 mL of hexane and 10 µL of internal standards were added to the sample before gas chromatograph/mass spectrometer (GC/MS) analysis.

Instrumental analysis

The analysis of PAHs was conducted with an Agilant 7890 A gas chromatograph-5975C mass spectrometer (GC/MS, Agilant, USA) in selected ion monitoring mode and using electron impact ionization. The GC/MS was equipped with a 30 m×0.25 mm-i.d. (0.25 µm film thickness) HP-5 MS column (Agilant, USA) for separating the analytes. The column temperature was programmed to hold at 50°C for 2 min, heated to 200°C at a rate of 20°C min^{-1}, held at 200°C for 2 min, heated to 240°C at a rate of 5°C min^{-1}, held at 240°C for 2 min, and heated to 290°C at a rate of 3°C min^{-1}, then held at 290°C for 5 min. A 1 µL sample was injected into an automatic sampler in splitless mode for analysis, and helium was used as the carrier gas at a rate of 1.0 mL min^{-1}.

Conclusion

A combined O_3/H_2O_2 treatment was demonstrated to be an efficient approach for the degradation of PAHs in textile dyeing sludge. The O_3/H_2O_2 treatment presented synergistic advantages over individual O_3 and H_2O_2 treatments for PAH degradation. The removal rate increased by 27% for Ph and 21% for An through the addition of H_2O_2 to the O_3 process. Further, the addition of isopropanol resulted in a decrease of the oxidation rate of the PAHs. Ph, An and Fl were partially oxidized by hydroxyl radicals, whereas DBA was oxidized by O_3. Ph, An and Fl achieved high oxidation rates in both acidic and neutral conditions. The optimal parameters of the O_3/H_2O_2 treatment include an O_3 flow rate of 0.4 L/min, a reaction time of 15 min, pH 7 and H_2O_2 doses of 0.60 mol/L. These optimal conditions led to a removal rate of 89% for Fl, 66% for Ph, 71% for An and 81% for DBA. The flow rate and reaction time exert a large positive effect on the degradation of the target PAHs. The degradation of the PAHs can be well fit by pseudo-first-order kinetics.

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Table captions

Table 1 Degree of synergy by coupling H_2O_2 to ozonation in the O_3/ H_2O_2 process.

Table 2 Degradation kinetic parameters for the PAHs by the O_3/H_2O_2 treatment.

Table 3 CCD for PAH removal from textile dyeing sludge by the O_3/H_2O_2 treatment.

Table 4 Second-order and interaction model of PAH degradation in textile dyeing sludge by the O_3/H_2O_2 treatment.

Table 5 Characteristics of the raw sludge samples.

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Figure captions

Figure 1. Ozone concentration (dimensionless) of the PAHs at different pH values over time during PAH degradation by O_3/ H_2O_2 treatment with and without isopropanol. Fl: (a). Ph: (b). An: (c). DBA: (d).

Figure 2. Effect of pH on PAH degradation by the O_3/ H_2O_2 treatment.

Figure 3. The degradation rate of PAHs with and without H_2O_2 in the O_3 system. Fl: (a). Ph: (b). An: (c). DBA: (d).

Figure 4. Response surface of the O_3/ H_2O_2 treatment of the PAHs in the textile dyeing sludge.

Figure 5. Experimental design: 1. oxygen cylinder; 2. O_3 generator; 3. flowmeter; 4. reactor; 5. electromagnetic agitator; 6. security trap.

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Table 1

PAHs	K_{O3}	k_{H2O2}	$k_{O3/H2O2}$	S%
Fl	0.0356	0.0018	0.0378	2.96
Ph	0.0433	0.0235	0.09594	30.37
An	0.0433	0.01614	0.07154	16.91
DBA	0.0346	0.00425	0.04010	2.12

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Table 2

PAHs	Initial concentration(ng mL^{-1})	k (ng mL^{-1} min^{-1})	$t_{1/2}$ (min)	R^2
Fl	31.32	0.0378	18.3333	0.9878
Ph	107.15	0.0959	7.2233	0.9297
An	132.35	0.0715	9.6869	0.9586
DBA	2.64	0.0401	17.2818	0.9863

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Table 3

O_3 flow rate(L/min)	Time(min)	pH	H_2O_2(mL)	Fl(%)	Ph(%)	An(%)	DBA(%)
0.4	15	7	5	57.92	47.57	47.57	71.07
0.4	19	7	7	60.89	64.87	64.87	67.77
0.36	13	6	8	55.04	42.81	42.81	90.08
0.36	17	6	8	30.32	5.34	5.34	90.08
0.4	15	7	7	29.61	13.55	13.54	80.17
0.4	11	7	7	22.59	5.28	5.29	57.85
0.36	17	8	6	45.45	28.45	28.45	62.81
0.44	17	8	6	51.61	43.48	43.48	89.26
0.44	13	8	8	64.37	38.76	38.76	40.50
0.4	15	7	7	29.61	13.55	13.54	80.17
0.4	15	9	7	76.78	67.16	67.16	29.75
0.4	15	7	7	29.61	13.55	13.54	80.17
0.32	15	7	7	45.51	35.11	35.11	53.72
0.44	17	6	8	66.68	63.58	63.59	75.21
0.44	13	6	8	69.08	43.38	53.95	13.22
0.4	15	7	7	29.61	13.55	13.54	80.17
0.36	13	8	8	46.11	38.06	38.06	62.81
0.48	15	7	7	69.46	50.90	71.17	80.17
0.44	13	8	6	53.43	29.72	29.73	41.32
0.4	15	5	7	62.17	57.88	57.88	60.33
0.44	17	8	8	65.32	49.76	49.76	42.98
0.36	13	8	6	14.56	11.39	11.38	19.01
0.36	17	6	6	47.14	27.24	27.24	75.21
0.44	13	6	6	65.54	45.59	45.59	71.90
0.36	13	6	6	66.14	40.26	40.26	53.72
0.36	17	8	8	56.10	27.05	27.04	68.60
0.4	15	7	7	29.61	13.55	13.54	80.17
0.44	17	6	6	67.46	72.18	65.63	77.78
0.4	15	7	7	29.61	13.55	13.54	80.17
0.4	15	7	9	88.73	65.98	71.13	81.26

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Table 4

$$\% Fl \quad removal = \alpha_0 + \alpha_1 \times Q + \alpha_2 \times t + \alpha_3 \times pH + \alpha_4 \times H_2O_2 + \alpha_5 \times Q \times \mathrm{t} + \alpha_6 \times Q \times pH + \alpha_7 \times Q \times H_2O_2 + \alpha_8 \times t \times pH + \alpha_9 \times t \times H_2O_2 + \alpha_{10} \times pH \times H_2O_2 + \alpha_{11} \times Q^2 + \alpha_{12} \times t^2 + \alpha_{13} \times pH^2 + \alpha_{14} \times H_2O_2{}^2$$

$$\% Ph \quad revomal = \alpha_0 + \alpha_1 \times Q + \alpha_2 \times t + \alpha_3 \times pH + \alpha_4 \times H_2O_2 + \alpha_5 \times Q \times \mathrm{t} + \alpha_6 \times Q \times pH + \alpha_7 \times Q \times H_2O_2 + \alpha_8 \times t \times pH + \alpha_9 \times t \times H_2O_2 + \alpha_{10} \times pH \times H_2O_2 + \alpha_{11} \times Q^2 + \alpha_{12} \times t^2 + \alpha_{13} \times pH^2 + \alpha_{14} \times H_2O_2{}^2$$

$$\% An \quad revomal = \alpha_0 + \alpha_1 \times Q + \alpha_2 \times t + \alpha_3 \times pH + \alpha_4 \times H_2O_2 + \alpha_5 \times Q \times \mathrm{t} + \alpha_6 \times Q \times pH + \alpha_7 \times Q \times H_2O_2 + \alpha_8 \times t \times pH + \alpha_9 \times t \times H_2O_2 + \alpha_{10} \times pH \times H_2O_2 + \alpha_{11} \times Q^2 + \alpha_{12} \times t^2 + \alpha_{13} \times pH^2 + \alpha_{14} \times H_2O_2{}^2$$

$$\% DBA \quad revomal = \alpha_0 + \alpha_1 \times Q + \alpha_2 \times t + \alpha_3 \times pH + \alpha_4 \times H_2O_2 + \alpha_5 \times Q \times \mathrm{t} + \alpha_6 \times Q \times pH + \alpha_7 \times Q \times H_2O_2 + \alpha_8 \times t \times pH + \alpha_9 \times t \times H_2O_2 + \alpha_{10} \times pH \times H_2O_2 + \alpha_{11} \times Q^2 + \alpha_{12} \times t^2 + \alpha_{13} \times pH^2 + \alpha_{14} \times H_2O_2{}^2$$

	α_0	α_1	α_2	α_3	α_4	α_5	α_6	α_7	α_8	α_9	α_{10}	α_{11}	α_{12}	α_{13}	α_{14}
Fl	29.61	7.39	3.02	-1.72	4.30	0.09	0.15	0.82	5.26	-1.76	5.75	5.89	1.95	8.89	9.85
Ph	13.55	8.23	6.10	-2.30	1.97	7.25	-3.27	-0.09	2.16	-3.85	4.42	5.46	3.48	10.34	8.91
An	13.54	10.08	5.38	-2.47	3.11	6.18	-3.52	0.98	3.23	-4.11	3.35	7.51	3.00	9.86	9.06
DBA	80.17	-0.72	8.72	-7.54	0.54	2.95	4.49	-13.1	0.67	-3.05	0.78	-3.61	-4.65	-9.09	-1.31

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Table 5

Parameters	Average values
pH	6.65
Moisture content (%)	97.99
Soluble total organic carbon(mg/l)	56.88
Fl initial concentration(ng mL^{-1}）	31.32
Ph initial concentration(ng mL^{-1})	107.15
An initial concentration(ng mL^{-1}）	132.35
DBA initial concentration(ng mL^{-1}）	2.64

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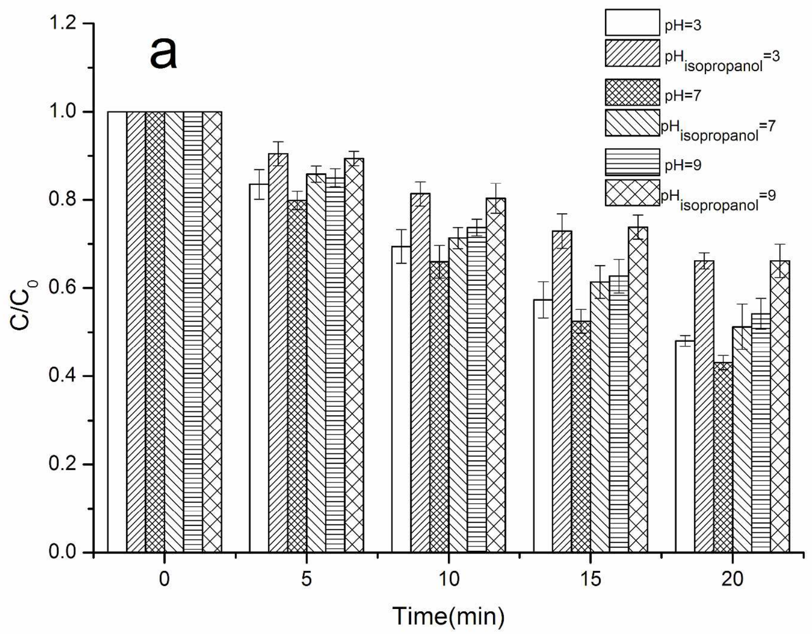

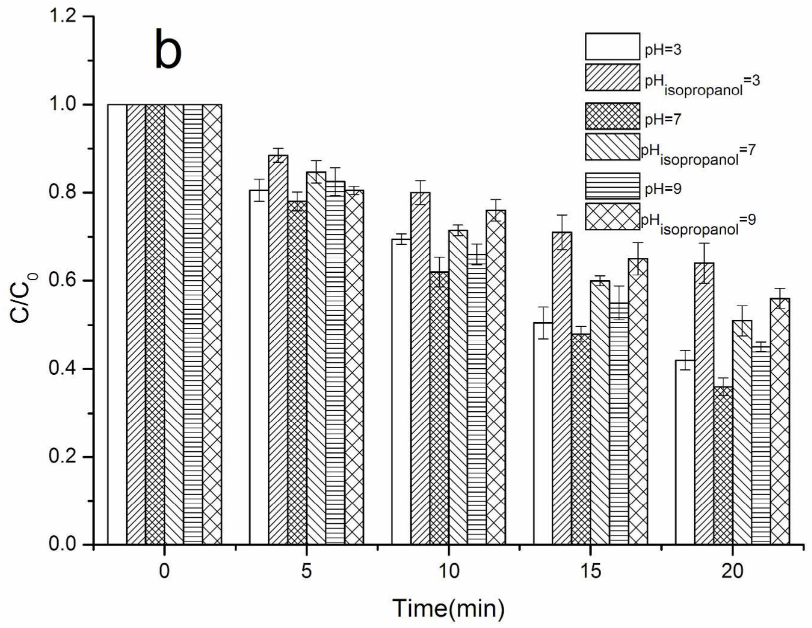

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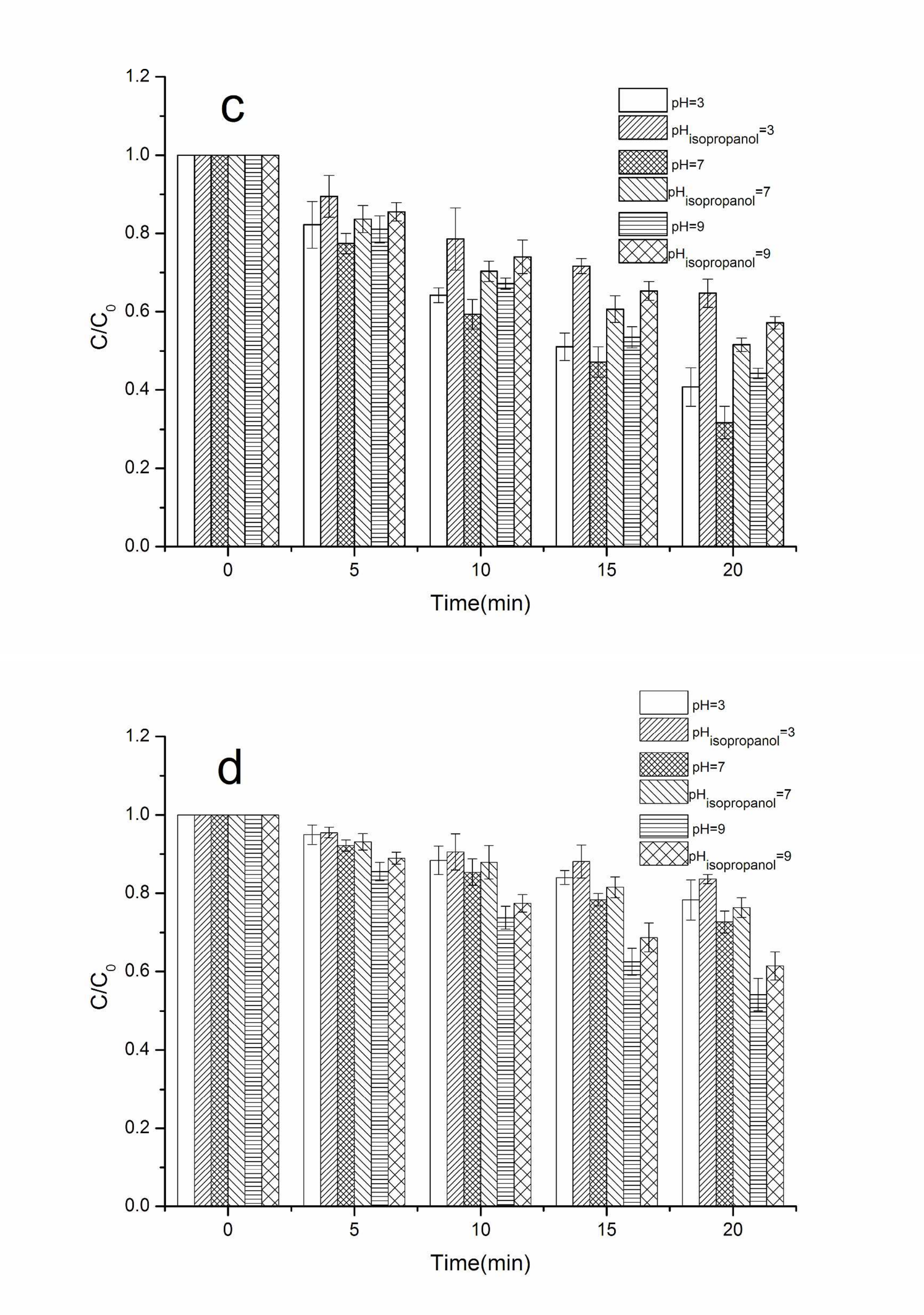

Figure 1

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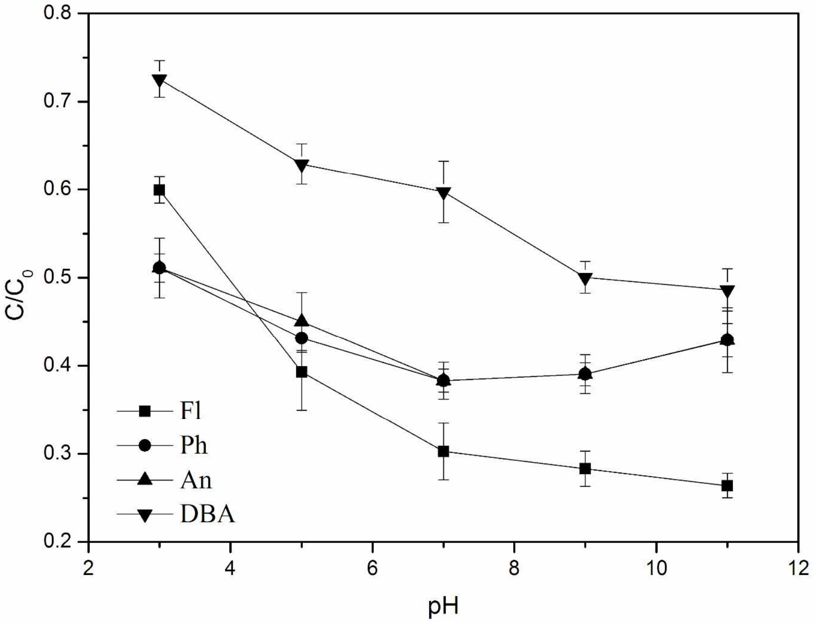

Figure 2

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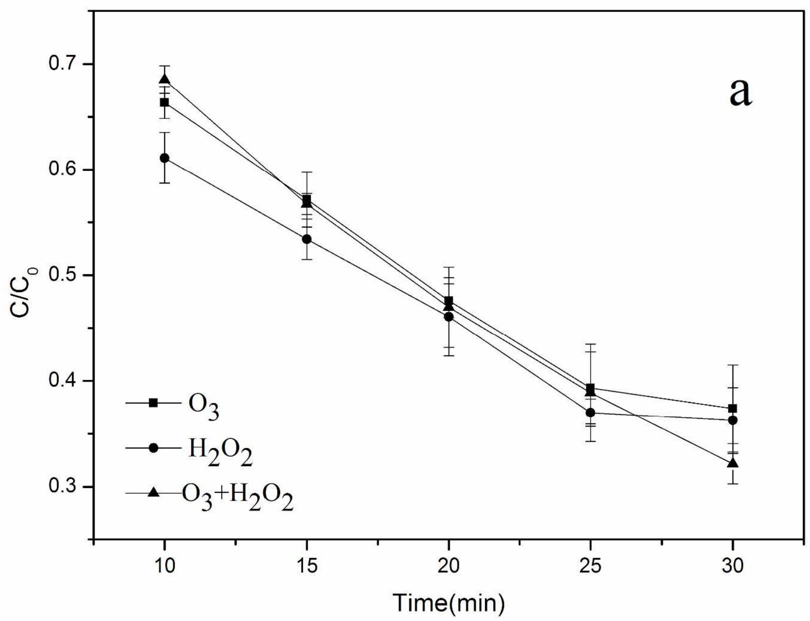

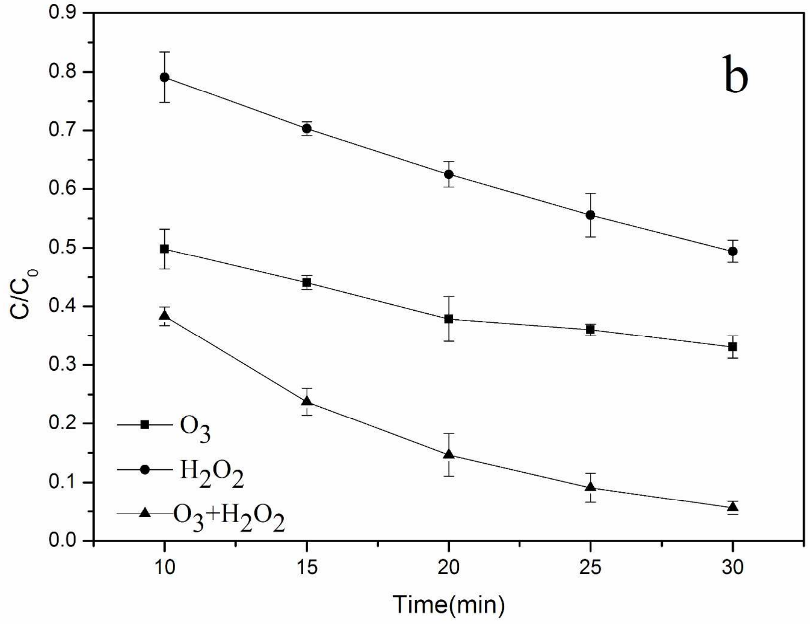

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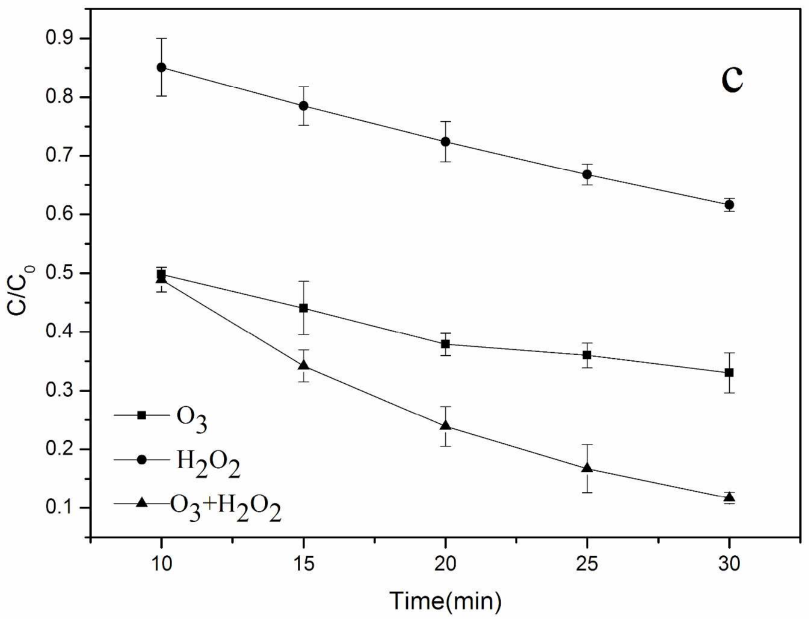

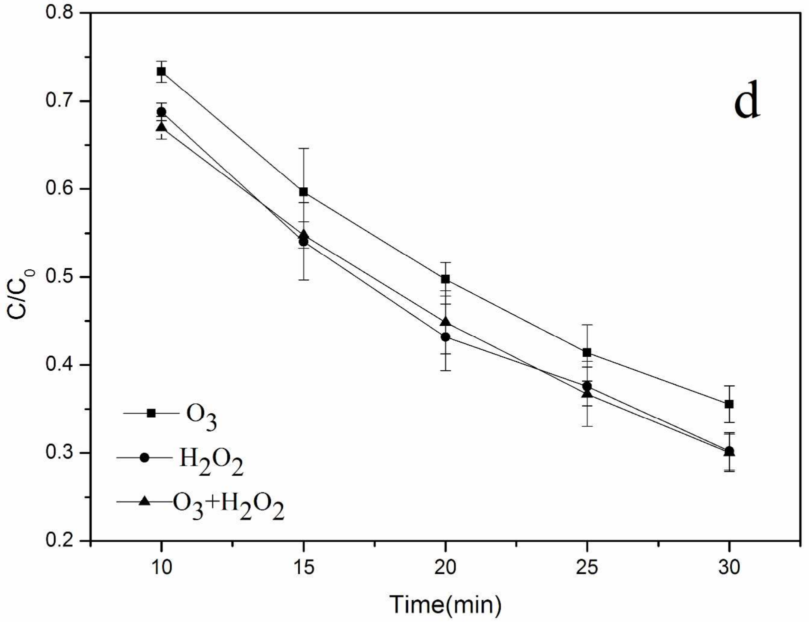

Figure 3

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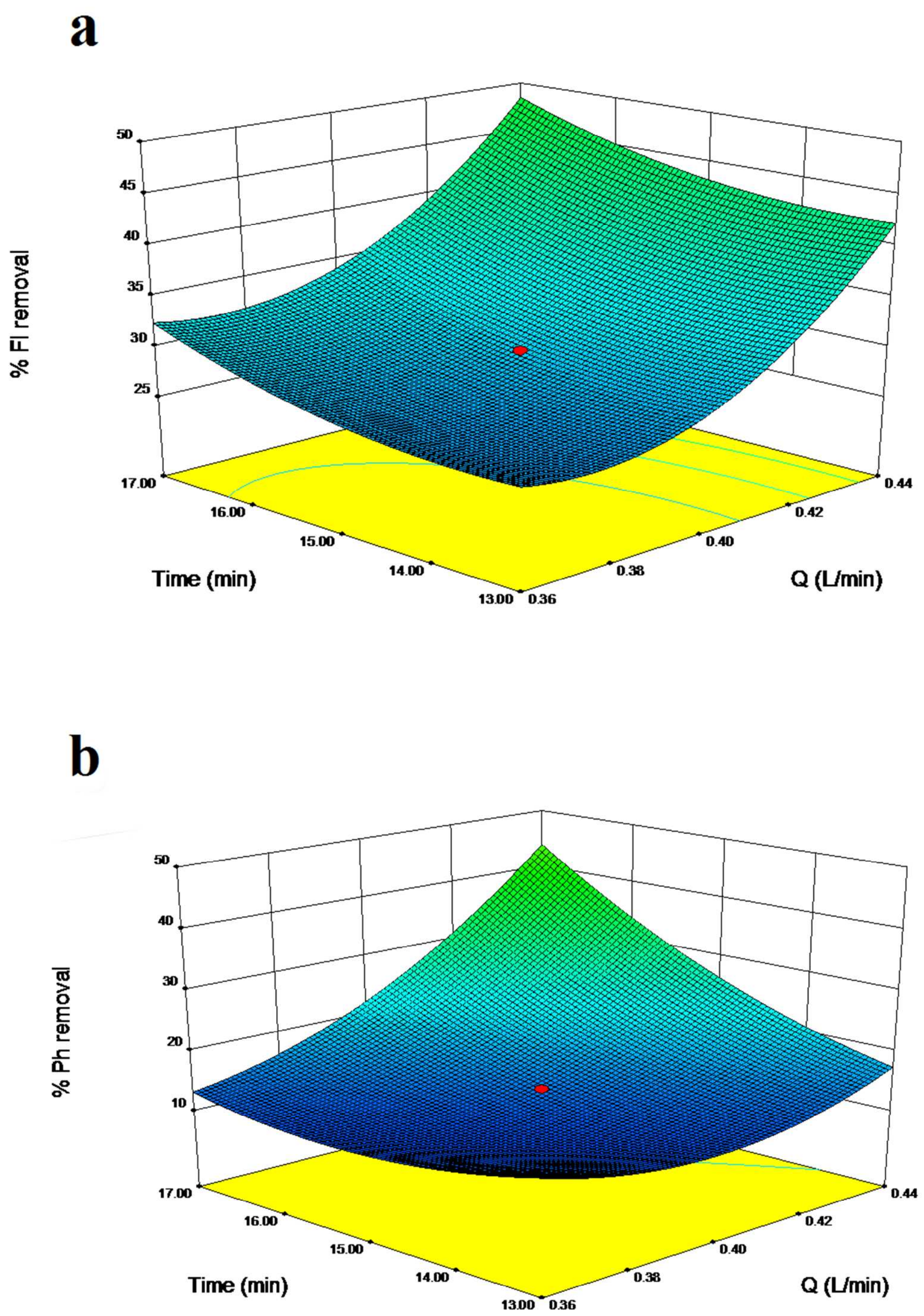

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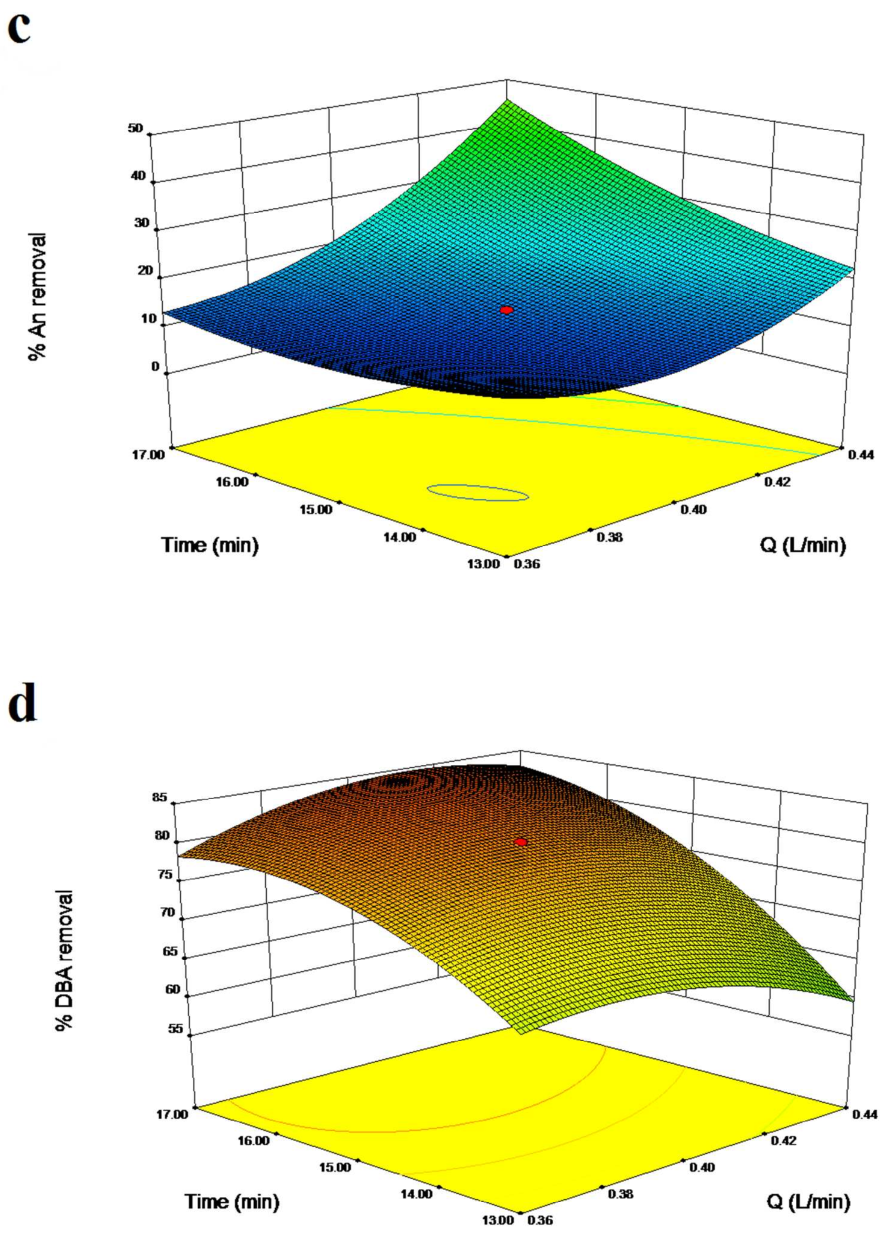

Figure 4

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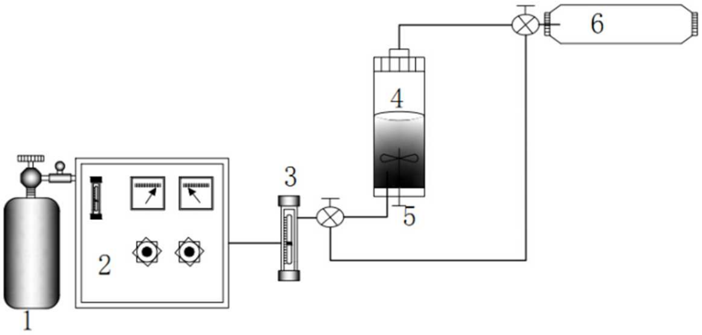

Figure 5

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