

Original Research

Novel Advanced Treatment of Physically Treated Effluent from Herbal Decoction Pieces Wastewater Using a Combined Ozone/Persulfate-UBAF Process

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Abstract

Performance of ozone/persulfate-UBAF used for advanced treatment of physically treated effluent from herbal decoction pieces of wastewater was investigated in a pilot scale experiment. Under optimum conditions – i.e., an initial pH, temperature 13-27°C, 30 min of oxidation, 35 mg/L O₃ dosage, S₂O₈²⁻/COD (g/g) ratio (0.15), gas/liquid ratio in UBAF (3), hydraulic retention time in UBAF (5h) – the COD and NH₃-N removal efficiencies were 87.54-89.53% and 82.94-86.77%, respectively. Under optimum conditions, ozone/persulfate oxidation lowered pH values by about 0.1 pH units (average value), presented lower OCC (from 0.14 to 0.16 kg O₃/kg COD removed), and significantly improved the wastewater biodegradability from 0.16 to 0.55 (average value). Compared with O₃/H₂O₂ oxidation, the ozone/persulfate system achieved a better enhancement effect in wastewater treatment (i.e., decreased 24.0% OCC and saved 11.4% in operational costs). Furthermore, the COD removal rate in ozone/persulfate oxidation stage followed the first order $\ln\left(\frac{C}{C_0}\right) = -0.0167t$, and the COD concentration in UBAF effluent was expressed by the model $\frac{C}{C_0} = \exp\left(-\frac{0.2940}{L^{0.0912}} H\right)$ at various hydraulic loading rates

for maintenance and selection of UBAF. Finally, the study proved that the combined process was an efficient technology in treating physically treated effluent from herbal decoction pieces wastewater.

Keywords: physically treated effluent; herbal decoction pieces wastewater; ozone/persulfate oxidation; biodegradability; ozone consumption coefficient

Introduction

Herbal decoction pieces wastewater, a typical refractory biodegradable industry wastewater, contains plenty of refractory organic pollutants (e.g., cellulose, lignin). Recently, biological-physically treated effluent from herbal decoction pieces wastewater was often discharged into natural water environments beyond standard without appropriate treatment [1, 2]. Meanwhile, with the implementation of more stringent discharge standards, the efficient and reliable operation of a wastewater treatment system had also become a severe problem in herbal decoction pieces factories. Therefore, aiming at the strictest discharge standards, it was imperative for herbal decoction pieces factories to seek an advanced treatment technology possessing a series of advantages (e.g., good operational stability, high-quality effluent). Unfortunately, until now, relevant research has not been reported publicly.

Compared with other advanced treatment technologies, the coupling process of advanced oxidation-advanced aerobic treatment has recently caused more and more attention [3-5]. upflow biological aerated filter (UBAF), as a typical representative of advanced aerobic treatment, presented an excellent performance in advanced treatment of industry wastewater containing low concentrations of SS and COD. Among the numerous oxidation reagents, the usual oxidant mainly included Fenton reagent and ozone in engineering practice. However, in the use of these oxidants, there were some troublesome problems such as voluminous sludge production, low removal efficiency, and worse ability of wastewater biodegradability enhancement. Compared with the above oxidant, persulfate ($E^0 = 2.01V$), as the newest advanced oxidant, has recently raised more and more attention. What's more, sulfite-free radical initiated from persulfate possess a strong oxidation ability ($E^0 = 2.7V$) [6-13]. The previous study reported that hydroxyl-free radicals could be generated under the O_3 effect [14, 15]. Compared with the hydroxyl-free radical, sulfate-free radical was more effective in

degradating some organic compounds in wastewater because it was more selective to oxidation. However, up till now, a rare study has been published regarding ozone/persulfate as the advanced oxidation process used to treat real industry wastewater. Thus, a new combined process (ozone/persulfate-UBAF) was designed in the advanced treatment of physically treated effluents from herbal decoction pieces wastewater.

The main objectives of the study included: (1) determining optimum operational conditions; (2) examining the treatment performance on the combined process and ozone/persulfate oxidation under optimum operational conditions; (3) identifying COD removal behaviors in ozone/persulfate oxidation and UBAF; (4) evaluating the effect of ozone/persulfate oxidation on ozone consumption coefficient, wastewater biodegradability, and wastewater pH; and (5) comparing between O_3/H_2O_2 and $O_3/S_2O_8^{2-}$.

Experimental

Experimental Influent

The physically treated effluent in the sampled factory flowed into the influent tank in the experiment. The influent quality was shown in Table 1.

Experimental Setup

Setup I

The optimization experiment on ozone/persulfate oxidation time and the COD removal behavior experiment on ozone/persulfate oxidation were carried out with a 500 mL-capacity glass in setup I (Fig. 1a).

To rapidly terminate oxidation reaction, the 0.2 mL Na_2SO_3 solution (85.0mM) was immediately added into the wastewater sample (10 mL) and withdrawn at regular time interval. Subsequently, the sample was used to the following indicator analysis.

Table 1. Experiment influent quality.

Indicator	COD (mg/L)	NH_3-N (mg/L)	BOD_5 (mg/L)	pH	SS (mg/L)
Value	350-360	28-35	52-62	7.2-8.9	80-95

Note: The key indicators assigned by the local environmental protection bureau included COD and NH_3-N .

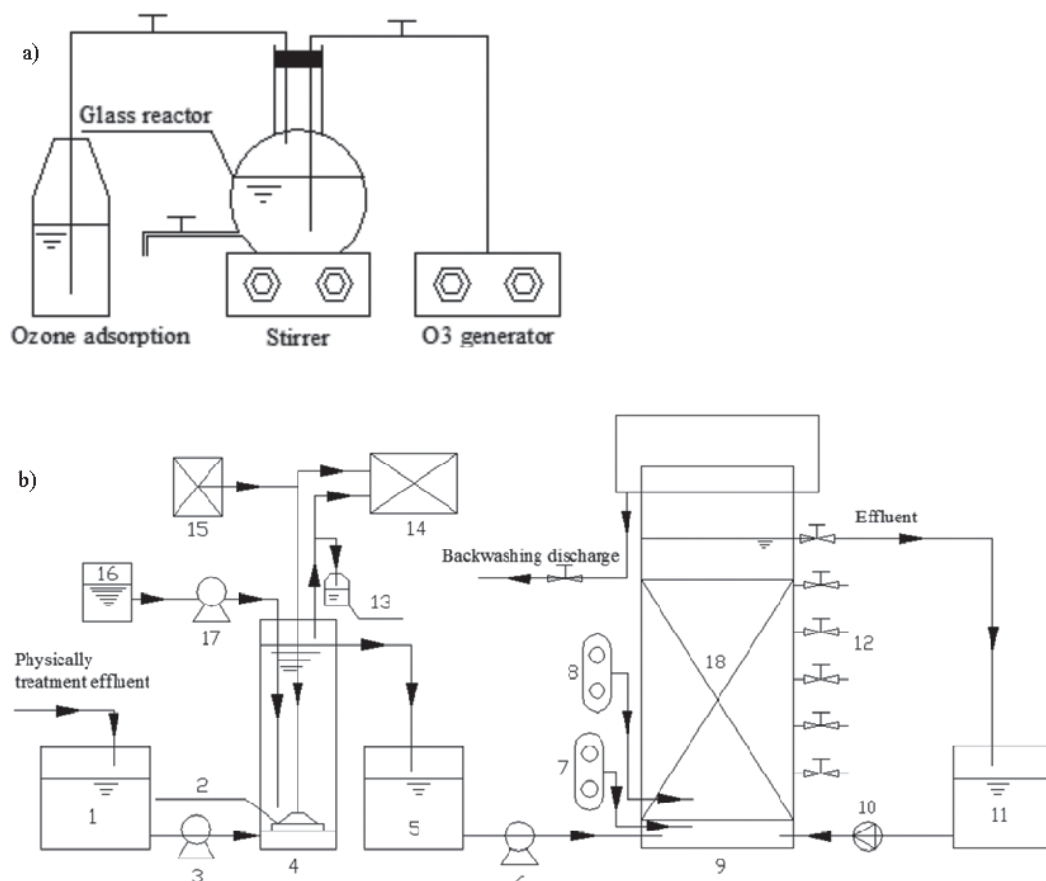


Fig. 1. Experiment setup: a) setup I, b) setup II. (1) influent tank (1100 × 1100 × 1000 mm); (2) microspore aerator (Φ100 mm); (3) influent pump (JGX-170/0.3); (4) oxidation reactor (Φ200 × 2000 mm); (5) intermediate water tank (350 × 350 × 400 mm); (6) influent pump (JGX-170/0.3); (7) backwashing air blower (ACO500); (8) aeration blower (MPQ-904); (9) BAF (Φ600 × 3000 mm); (10) backwashing pump (DBZ-45); (11) effluent tank (1100 × 1100 × 1000 mm); (12) sampling port; (13) excessive ozone absorbed system; (14) ozone monitor (HD80-O3); (15) ozone generator (CF-G-2); (16) persulfate solution tank; (17) wringgle pump; (18) ceramic particle.

Setup II

The other experiments were carried out in setup II (an ozone/persulfate-UBAF reactor) (Fig. 1b).

In the experiment, $S_2O_8^{2-}$ as sodium persulfate ($Na_2S_2O_8$, industrial grade) was provided by Wuhan Galaxy Chemical Co. Ltd and diluted into liquor with 15% mass concentrations to facilitate dosing. The O_3 was produced by a CF-G-2 generator (Guolin and Baifeng, China) fed with pure oxygen (industry grade), following a gas flow rate of 10 L/min, and pressure of 1 atm. The ozone concentration in input gas was adjusted by working electricity.

The UBAF was packed with ceramic particles (diameter (3-5 mm), packed density (0.95 g/cm³)), HRT at UBAF was 5 h, gas/water ratio at UBAF was 3, and backwash period was one week. All experiments were carried out at 13-27°C.

Analytical Methods

Standard methods of P.R. China were used for determining COD, pH, NH_3-N , BOD_5 , and SS in wastewater [16]. Among these indicators, COD and pH

were determined respectively by dichromate method and glass electrode method, salicylic acid spectrophotometry and gravimetric method were used for determining NH_3-N and SS, respectively, and BOD_5 was measured with dilution and seeding method. Finally, an ozone analyzer (Model HD80- O_3) was used to determine the concentration of the ozone in gas.

COD Removal Behavior in BAF

With the assumption of plug flow and pseudo first-order kinetics in UBAF, COD removal rate may be described as follows [17]:

$$\frac{dC}{dt} = -k_1XC \quad (1)$$

...where C was COD concentration value (mg/L), dC/dt was COD removal rate (mg/L·h), k_1 was a rate constant (L/mg·h), and X is the volatile suspended solids concentration (VSS, mg/L).

Generally, X was expressed as follows:

$$X = f(A) \quad (2)$$

...where A was specific surface area of the medium (m^2/m^3). Substituting Eq. (2) into

Eq. (1), leads to Eq. (3):

$$\frac{dC}{dt} = -k_1 f(A)C = -K_1 C \quad (3)$$

...where K_1 was the reaction rate constant.

Integrating Eq. (3) yields:

$$\frac{C}{C_0} = \exp(-K_1 t) \quad (4)$$

...where t was hydraulic retention time (HRT), which could be described as:

$$t = \frac{DH}{L^n} \quad (5)$$

...where n and D were constants related to specific surface and the medium and, respectively, L was the hydraulic loading rate and H was the medium height.

Substitution Eq. (5) into Eq. (4), leads to

$$\frac{C}{C_0} = \exp\left(-\frac{KH}{L^n}\right) \quad (6)$$

...where $K = K_1 D$.

Integrating Eq. (6) yields:

$$\ln \frac{C_0}{C} = \frac{K}{L^n} H \quad (7)$$

By plotting $\ln(C_0/C)$ against H , the value of $\left(\frac{K}{L^n}\right)$ could be determined.

Integrating $\left(\frac{K}{L^n}\right)$ yields:

$$\ln\left(\frac{K}{L^n}\right) = \ln K - n \ln L \quad (8)$$

By plotting $\left(\frac{K}{L^n}\right)$ against $\ln L$, the constant n and the constant K could be determined.

Results and Discussion

The Overall Performance of the Combined Process

The startup of the UBAF seed with activated sludge from the sampled factory took about two months. Then the combined process turned to continuous operation.

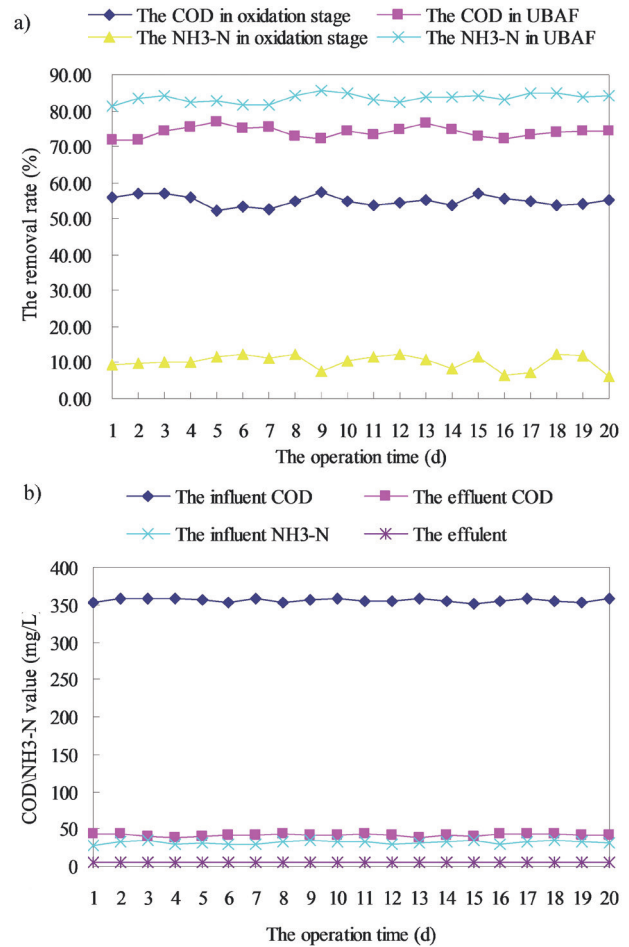


Fig. 2. Operational performance: a) oxidation stage and UBAF, b) the combined process. Under optimum conditions (30 min oxidation, O_3 dosage (35 mg/L), $\text{S}_2\text{O}_8^{2-}/\text{COD}$ (g/g) ratio (0.15), initial pH, a gas to liquid ratio (3), hydraulic retention time of UBAF (5h), temperature (13-27°C).

A subsequent period of a month was allowed for the steady operation. The overall performance of the combined process was examined (Fig. 2).

The ozone/persulfate oxidation respectively achieved 52.37-57.15% COD removal and 6.17-12.36% NH₃-N removal, the COD and NH₃-N in the effluent after ozone/persulfate oxidation were 152.3-170.2 mg/L and 25.53-31.51 mg/L, respectively (Fig. 2a).

Furthermore, it can be also seen from Fig. 2a) that a 71.83-76.63% COD removal and 81.16-85.69% NH₃-N removal were attributed to the UBAF, the COD and NH₃-N in the effluent after the UBAF were 38.56-44.0 mg/L and 4.51-4.86 mg/L, respectively.

Overall, the removal efficiencies for COD and NH₃-N were, respectively, 87.54-89.53% and 82.94-86.77% in the combined process, and the effluent COD and NH₃-N were always below 45 mg/L and 5.0 mg/L. COD removal depended on ozone/persulfate oxidation and UBAF, and the NH₃-N removal was mainly attributed to the UBAF (Fig. 2b).

Evolution of Removal Efficiency as Afunction of Operation Parameter in Oxidation Stage

Reaction Time

The effect of reaction time on removal efficiency is shown in Fig. 3a), which showed that removal efficiency was rapidly increased before 30 min, and that COD removal rate was 25.6% at 30 min, but the rising tendency began to slow after 30 min. This was perhaps because the oxidant (e.g., O₃, persulfate, HO[•], SO₄^{-•}) in the wastewater was less and less after 30 min, which resulted in the decrease of rising tendency on removal efficiency. An optimum reaction time (120 min) was reported during the S₂O₈²⁻/H₂O₂ oxidation of the stabilized landfill leachate [18]. Abu Amr et al. [15] obtained an optimum reaction time (210 min) during the ozone/persulfate oxidation of the stabilized leachate. Lu et al. [19] achieved a 95.9% Rhodamine B (RhB) degradation within 30 minutes with the Fe³⁺/persulfate system. The deviation on the optimal reaction time maybe was mainly due to the variations on the oxidation system (e.g., structure of experimental setup and oxidants such as H₂O₂ and Fe³⁺).

O₃ Dosage

Fig. 3b) shows the evolution of removal efficiency as a function of O₃ dosage. The removal efficiency was

also increased rapidly before 35 mg/L of O₃ dosage, and COD removal efficiency was up to 40.1% at 35 mg/L of O₃ dosage, and the rising tendency on removal efficiency was not obvious after 35 mg/L of O₃ dosage (Fig. 3b). At a lower O₃ dosage, the O₃ increase has led to a rapid increase of HO[•] concentration in wastewater (Eqs. (9-11)) [14]. Accordingly, the SO₄^{-•} concentration in the solution would be significantly improved under the HO[•] effect (Eq. 12) [15]. Meanwhile, HO[•] generated under SO₄^{-•} effect (Eqs. 13-14) [20, 21] would initiate more sulfate-free radicals (Eq. 12). At the moment, the wastewater contained large amount of HO[•] and SO₄^{-•}, which resulted in the formation of the oxidation system possessing stronger oxidation ability.

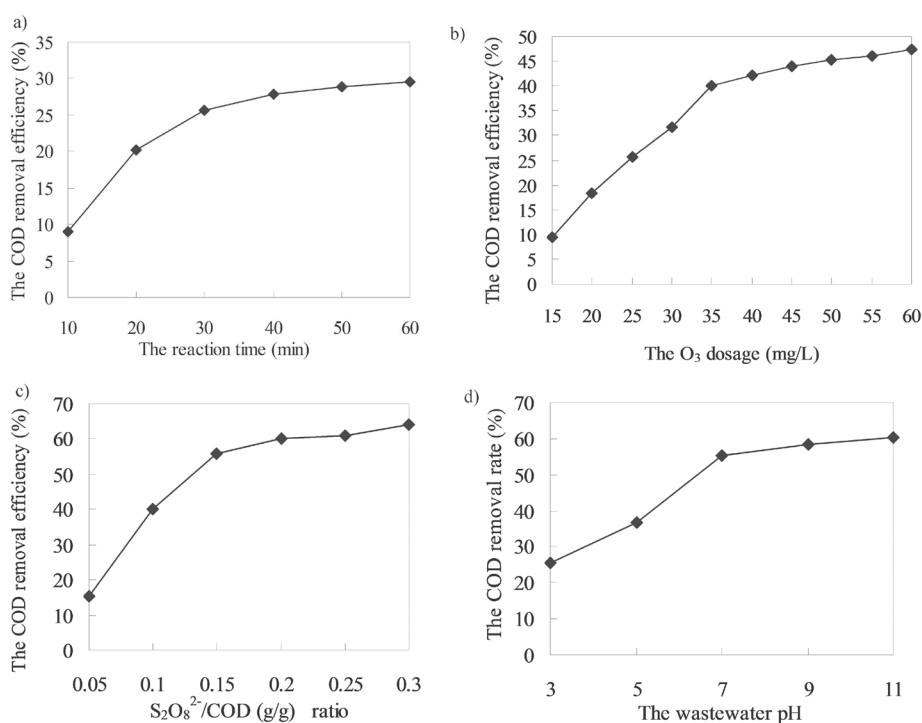
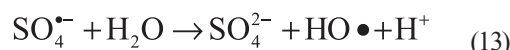
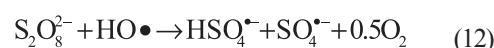
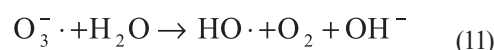
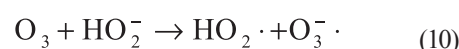
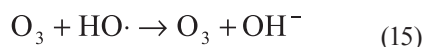


Fig. 3. Evolution of removal efficiency as function of operation parameter: a) reaction time, b) O₃ dosage, c) S₂O₈²⁻/COD (g/g) ratio, d) wastewater pH) in oxidation stage under operation conditions. a) O₃ dosage (25 mg/L), S₂O₈²⁻/COD (g/g) ratio (0.10), initial pH, temperature (13-27°C); b) 30 min oxidation, S₂O₈²⁻/COD (g/g) ratio (0.10), initial pH, temperature (13-27°C); c) 30 min oxidation, 35 mg/L of O₃ dosage, initial pH, temperature (13-27°C); d) 30 min oxidation, 35 mg/L of O₃ dosage, S₂O₈²⁻/COD (g/g) ratio (0.15), temperature (13-27°C).

But at a high dosage, the excessive O_3 would perhaps consume $HO\cdot$ in the wastewater (Eq. 15) [22], and $SO_4^{\cdot-}$ would subsequently decrease under this effect (Eq. 12), which resulted in the decrease of oxidation ability in the ozone/persulfate system.



The phenomenon was also observed in other advanced oxidation processes. Abu Amr et al. [15] reported the optimum O_3 dosage was $80\text{g}/\text{m}^3$ during the ozone/persulfate oxidation of the stabilized leachate. Yang et al. [23] observed a 62.43% BPA removal at a $1.0\text{ mg}/\text{L}$ O_3 dosage. Qi et al. [24] obtained an optimal ozone dosage ($20\text{-}30\text{ mg}/\text{L}$) while treating textile wastewater with O3-BAF-membrane filtration process.

$S_2O_8^{2-}$ Dosage

As Fig. 3c) illustrated, the increasing tendency on removal efficiency began to decrease after a $S_2O_8^{2-}/\text{COD}$ (g/g) ratio of 0.15. At the $S_2O_8^{2-}/\text{COD}$ (g/g) ratio of 0.15, the COD removal efficiency was up to 55.9%. At a lower $S_2O_8^{2-}$ dosage, enough sulfate-free radicals could not be generated in the wastewater, thus the removal efficiency on COD was limited. With the increase of the $S_2O_8^{2-}$ dosage, more and more sulfate-free radicals and hydroxyl-free radicals would be generated in the wastewater (Eqs. 9-14), which led to the rapid increase of removal efficiency. But at a high $S_2O_8^{2-}$ dosage, perhaps the excessive $S_2O_8^{2-}$ would not generate more $SO_4^{\cdot-}$ (namely the effective content of sulfate-free radical in wastewater was not improved) because of the exhausting of the $HO\cdot$ (Eq. 12), which resulted in the decrease of rising tendency on removal efficiency. It was reported that the optimum ratio of $S_2O_8^{2-}/\text{COD}$ (g/g) was 7 during the $O_3/S_2O_8^{2-}$ oxidation of the stabilized leachate [15]. Shabimam and Anil Kumar [25] obtained an optimum ratio of $S_2O_8^{2-}/\text{COD}$ (g/g) (2.14) during the $S_2O_8^{2-}$ alone oxidation of the municipal landfill leachate. An optimum ratio of $S_2O_8^{2-}/\text{COD}$ (g/g) (9.0) was reported during the treatment of reverse osmosis concentrate from the textile and dyeing industry [26]. The deviation on the optimal ratio of $S_2O_8^{2-}/\text{COD}$ (g/g) may have resulted from the variations on influent quality and experimental conditions.

At present, it was reported that persulfate could be activated by these methods mentioned in literature (i.e., thermolysis, iron catalysis) [27-29]. Nevertheless, the above results suggest that ozone has good performance on activating persulfate to initiate sulfate-free radical. Compared with ozone oxidation alone and persulfate oxidation alone, the ozone/persulfate oxidation could achieve more excellent performance on pollutant removal.

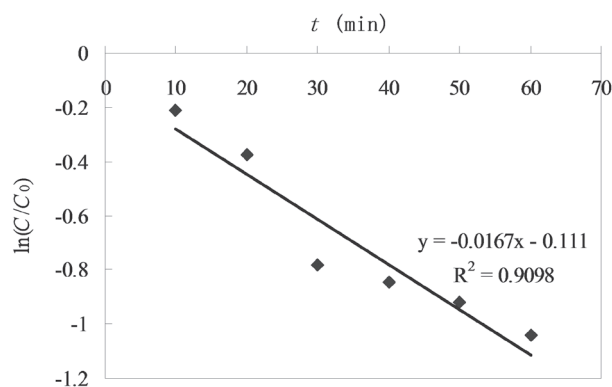


Fig. 4. Relationship between $\ln(C/C_0)$ and t .

pH

Fig. 3d) shows that removal efficiency was improved by increasing the pH, and the ozone/persulfate system could also achieve satisfactory removal performance even at initial pH. As pH further increases, the removal efficiency also increased. This was perhaps because the hydroxide ion was helpful for the generation of the hydroxyl free radical, and consequently more sulfate-free radical was formed under the hydroxyl free radical effect, which resulted in the increase in removal efficiency. Abu Amr et al. [15] reported that the ozone/persulfate system achieved a preferred removal rate at $\text{pH} = 10$. Zheng et al. [26] obtained a satisfactory treatment effect at $\text{pH} 5.0$. Furthermore, it was also reported that the optimal removal efficiency was achieved at low pH (2-4.5) [25].

COD Removal Behavior in the Oxidation Stage

With the assumption of pseudo-first-order kinetics, the following Eq. (16) could be used to describe COD removal rate in the oxidation stage.

$$\ln\left(\frac{C}{C_0}\right) = -Kt \quad (16)$$

...where t was the ozone/persulfate oxidation time, C was COD value at different t , C_0 were the COD in influent, and K was the rate constant. Under optimum operational conditions, the relationship between $\ln(C/C_0)$ and t is shown in Fig. 4.

The linear fitting of $\ln(C/C_0)$ as a function of t leads to $K = 0.0167$, as shown in Fig. 4. Therefore, in the ozone/persulfate oxidation system, the COD removal rate followed the first order (Eq. 17).

$$\ln\left(\frac{C}{C_0}\right) = -0.0167t \quad (17)$$

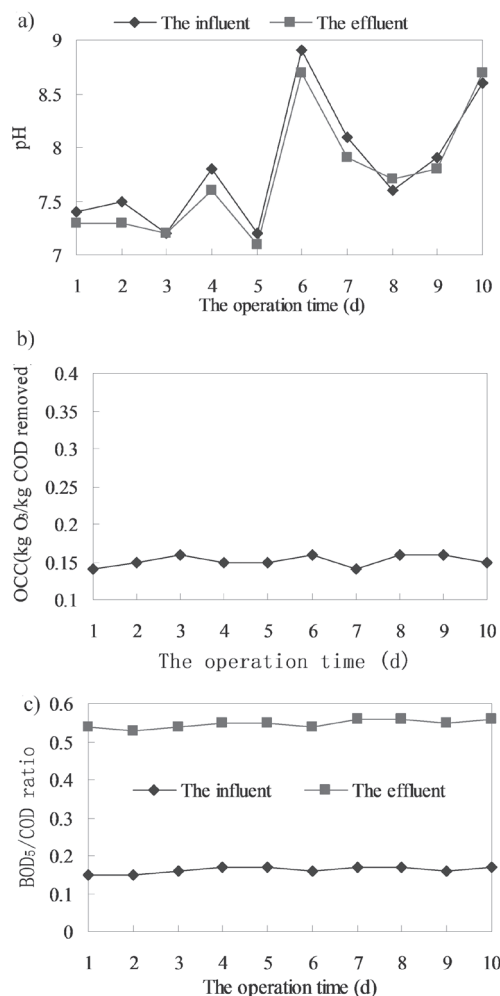


Fig. 5. Effect of ozone/persulfate oxidation: a) pH, b) OCC, c) wastewater biodegradability.

The effect of ozone/persulfate oxidation on wastewater pH, OCC and wastewater biodegradability.

Wastewater pH

Because the subsequent nitrification in UBAF consumes alkalinity, the pH change of the effluent after ozone/persulfate oxidation was measured (Fig. 5a).

It was obvious that the effluent pH after oxidation ranged from 7.1 to 8.7 under an initial pH (7.2-8.9) (Fig. 5a), which means the alkalinity in the effluent could reach the requirement of the subsequent nitrification in UBAF. Furthermore, Fig. 5a) showed the ozone/persulfate oxidation lower pH values by about 0.1 pH units (average value). This was perhaps because organic acids (e.g., carboxylic acids) were formed during oxidation.

Ozone Consumption Eoefficient (OCC)

For a continuous operation system, ozone consumption coefficient (OCC) could be calculated as follows:

$$OCC = \frac{Q_G \times C_{AG0} \times \int_0^t (1 - \frac{C_{AG}}{C_{AG0}}) dt}{V \times (COD_0 - COD)} \quad (18)$$

...where *OCC* was ozone consumption coefficient (kg O₃/kgCOD removed), *Q_G* was the gas flow (L/min), *C_{AG0}* was the concentration of ozone in the input gas (mg/L), *C_{AG}* was the concentration of ozone in the off-gas (mg/L), *V* was wastewater volume (L), *t* was the aerated time in the oxidation stage (min), and *COD₀* and *COD* were respectively COD concentration in influent and effluent (mg/L).

As Fig. 5b) illustrated, *OCC* value during ozone/persulfate oxidation ranged from 0.14 to 0.16 kg O₃/kgCOD removed and remained constant at about 0.152 kg O₃/kgCOD removed on average. A wide variation on *OCC* value (from less than 1 kg O₃/kgCOD removed to up to 16 kg O₃/kgCOD removed) was reported in the previous studies [30]. The deviation on *OCC* value maybe due to the differences in wastewater characteristics and experimental conditions (e.g., influent quality, structure of oxidation setup).

Wastewater Biodegradability

To investigate the effect of ozone/persulfate oxidation on the biodegradability of wastewater (described in terms of BOD₅/COD ratio), the BOD₅/COD ratio of the wastewater were determined before and after ozone/persulfate oxidation. As Fig. 5c) shows, the influent presented poor biodegradability (BOD₅/COD ratio ranged from 0.15 to 0.17, average value (0.16), but the biodegradability of the effluent after ozone/persulfate oxidation was significantly enhanced (BOD₅/COD ratio ranged from 0.53 to 0.56, average value 0.55). The result indicated that the ozone/persulfate oxidation has good performance on the enhancement of the wastewater biodegradability. The phenomenon was also observed in other studies. Abu Amr et al. [15] reported that the biodegradability of the stabilized leachate after ozone/persulfate oxidation increased from 0.043 to 0.29. Cortez et al. [30] observed an enhancement of biodegradability from 0.01 to 0.17 during O₃/H₂O₂ oxidation.

Comparison between Ozone/Persulfate and O₃/H₂O₂

Tang et al. [31] used O₃/H₂O₂ oxidation to treat traditional Chinese medicine wastewater, and relevant experiment data are detailed in Table 2.

As Table 2 shows, the ozone/persulfate system obtained a lower operational cost (1.0625 \$/Kg COD removed), and saved 11.4% on operational costs compared with O₃/H₂O₂ oxidation. Furthermore, the ozone/persulfate system achieved a lower *OCC* value (0.152 kg O₃/kgCOD removed), and decreased 24.0% *OCC* compared with O₃/H₂O₂ oxidation. Finally, the difference on BOD₅/COD ratio between the two

Table 2. Comparison between $O_3/S_2O_8^{2-}$ and O_3/H_2O_2 .

Performance	O_3/H_2O_2	$O_3/S_2O_8^{2-}$
Operational cost (\$/kg COD removed)	1.1994	1.0625
BOD ₅ /COD after oxidation	0.56	0.55
OCC	0.20	0.152

Note:

1. The exchange rate on RMB to USD (6.3) was used in this report.
2. Power consumption was 20 kWh/kgO₃ during the generating O₃.
3. The price on H₂O₂ (27.5%) was 1000 RMB/t.
4. The price on a power unit was 1.2 RMB/kWh.
5. The price on sodium persulfate (99%) was 7000 RMB/t.
6. The optimum conditions on O_3/H_2O_2 were described in the literature [31].

oxidation systems was negligible. These results indicated that compared with O_3/H_2O_2 oxidation, the ozone/persulfate system achieved a better enhancement effect in wastewater treatment.

COD Removal Behavior in UBAF

COD concentrations at various hydraulic loading rates (L) are listed in Table 3.

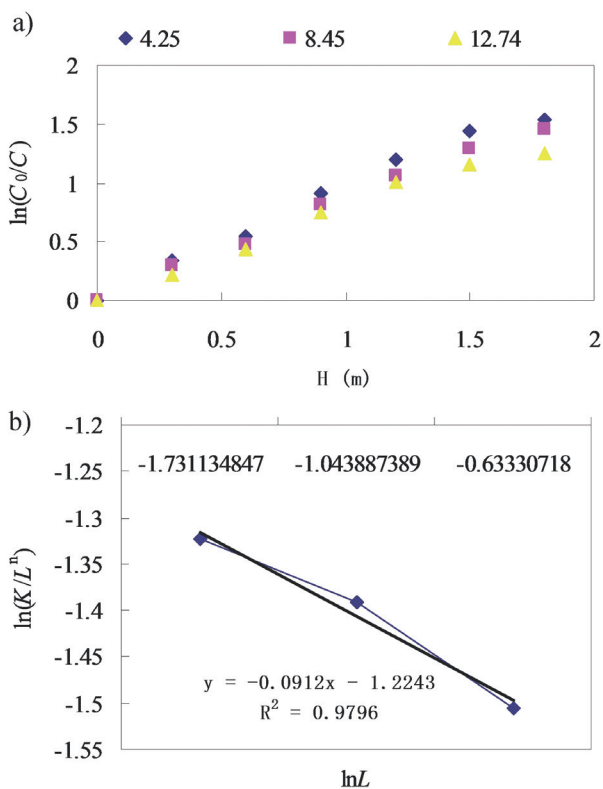


Fig. 6. Relationship between two parameters: a) $\ln(C_0/C)$ with H , b) $\ln(K/L^n)$ with $\ln L$.

Table 3. COD concentrations at various hydraulic loading rates (L).

H (m)	COD value (mg/L)		
	$L = 4.25$ $m^3/m^2 \cdot d$	$L = 8.45$ $m^3/m^2 \cdot d$	$L = 12.74$ $m^3/m^2 \cdot d$
0	170.0	170.0	170.0
0.3	120.3	126.53	136.75
0.6	98.26	105.42	110.38
0.9	68.24	74.86	80.67
1.2	51.43	58.74	62.14
1.5	40.26	46.53	53.46
1.8	36.45	39.52	48.56

Table 4. Values of K/L^n and L .

L ($m^3/m^2 \cdot d$)	K/L^n
4.25	0.2663
8.45	0.2487
12.74	0.2219

According to Eq. (7), the linear regression of $\ln(C_0/C)$ with H yields the value of n at different hydraulic loading rates (L), as shown in Fig. 6(a) and Table 4. The linear fitting of with $\ln L$, leads to $n = 0.0912$ and $K = 0.2940$, as shown in Fig. 6(b).

Substituting n and K values into Eq. (8) leads to the COD removal kinetics equation as follows:

$$\frac{C}{C_0} = \exp\left(-\frac{0.2940}{L^{0.0912}} H\right) \quad (19)$$

The COD concentration at different hydraulic loading rates was predicted by Eq. (19) in the UBAF.

Conclusions

The study investigated performance of the combined ozone/persulfate-UBAF process used to advanced treatment of physically treated effluents from herbal decoction pieces wastewater. Under optimum operational conditions (i.e., initial pH, temperature (13-27°C), 30 min of oxidation, 35 mg/L O₃ dosage, S₂O₈²⁻/COD (g/g) ratio (0.15), gas/liquid ratio in UBAF (3), hydraulic retention time in UBAF (5h)), the COD and NH₃-N removal efficiencies were 87.54-89.53% and 82.94-86.77% in the combined process respectively, and the ozone/persulfate oxidation achieved an about 55% COD removal. The results indicated that the combined process could efficiently treat physically treated effluents from herbal decoction pieces wastewater, and that COD

removal depends on ozone/persulfate oxidation and UBAF, and $\text{NH}_3\text{-N}$ removal was mainly attributed to the UBAF. Under optimal conditions, the ozone/persulfate oxidation lowered pH values by about 0.1 pH units (average value), presented a lower OCC (from 0.14 to 0.16 kg O_3/kg COD removed), and significantly improved wastewater biodegradability from 0.16 to 0.55 (average value). Compared with $\text{O}_3/\text{H}_2\text{O}_2$ oxidation, the ozone/persulfate system achieved a better enhancement effect in wastewater treatment (decreased 24.0% OCC and saved 11.4% operational costs). This study revealed that the combined process was an efficient technology in treating physically treated effluents from herbal decoction pieces wastewater. Furthermore, under optimum conditions the COD removal rate in the ozone/persulfate oxidation system followed the first order $\ln\left(\frac{C}{C_0}\right) = -0.0167t$, and

the COD concentration at different hydraulic loading rates in the BAF was predicted by the model $\frac{C}{C_0} = \exp\left(-\frac{0.2940}{L^{0.0912}}H\right)$, which was helpful for applying feasibility improvement of the combined process for other herbal decoction pieces factories.

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Conflict of Interest

The authors declare no conflict of interest.

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