

Article

A Novel Coupling of a Biological Aerated Filter with Al^{3+} Addition- $\text{O}_3/\text{H}_2\text{O}_2$ with Microbubble for the Advanced Treatment of Proprietary Chinese Medicine Secondary Effluent

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Abstract: The advanced treatment of proprietary Chinese medicine secondary effluent (PCMSE) was strongly needed with the recent implementation of a more stringent discharge standard. Based on the features of PCMSE and the reuse of Al^{3+} from wastewater from soaking of *Pinellia Ternata* with alumen (WSPTA), three new combined processes were designed for the advanced treatment of PCMSE on a larger pilot scale. A pilot scale study showed that compared with two other combined processes, the new coupling of a biological-aerated filter with Al^{3+} addition (BAFA)- $\text{O}_3/\text{H}_2\text{O}_2$ with microbubble (OHOMB) (CBAFAOHOMB) obtained the maximum pollutant removal (with removals of 91.71%, 94.64%, and 82.32% being observed for color, total phosphorus (TP), and chemical oxygen demand (COD), respectively) and acquired the lowest Al^{3+} residual in the effluent. During CBAFAOHOMB treatment of PCMSE, the vast majority of TP elimination, 35.20% of COD removal, and 49.40% of color removal were achieved by BAFA; OHOMB obtained 64.80% of COD removal and 60.60% of color removal, and biofilm activity in BAFA slightly changed under a 10 mg/L Al^{3+} dose. Furthermore, microbubble aeration was more efficient in removing organics than conventional bubble aeration during $\text{O}_3/\text{H}_2\text{O}_2$ oxidation, and suspended solid (SS) relatively significantly lowered oxidation ability in the OHOMB system. These results indicated that CBAFAOHOMB markedly integrated advantages of BAFA and OHOMB, and was a proposed process for the advanced treatment of PCMSE. Meanwhile, it was feasible that WSPTA was reused for PCMSE treatment as an Al^{3+} source.

Keywords: proprietary Chinese medicine secondary effluent; wastewater from soaking of *Pinellia Ternata* with alumen; $\text{O}_3/\text{H}_2\text{O}_2$ with microbubble; biological-aerated filter with Al^{3+} addition



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1. Introduction

In Taizhou, proprietary Chinese medicine production is one of its pillar industries, and is closely associated with large amounts of wastewater. Proprietary Chinese medicine wastewater not only contained high concentrations of phosphorus but also included plenty of organics as denoted by high concentrations of COD and SS, and a dark color [1–5]. A biological approach, such as an activated sludge system, has been always considered as a cost-competitive technology for proprietary Chinese medicine wastewater treatment. Nevertheless, phosphorus and organics in biotreated proprietary Chinese medicine wastewater (namely, proprietary Chinese medicine secondary effluent (PCMSE)) considerably surpassed the discharge limited value of the standard (GB21906-2008) in China [6]. Hence, the

efficiently advanced treatment of PCMSE was strongly needed, with the recent implementation of a more stringent discharge standard.

As was well known from the literature, organics in secondary effluent were usually removed by a combined ozone–biological-aerated filter process [7–9]. In this process, partially non-biodegradable organics were converted to biodegradable ones by ozonation, and then the organic substance was biodegraded by the subsequent biological-aerated filter at a relatively lower cost. But ozonation alone presented a higher expense and limited pollutant removal [7–9]. To enhance pollutant removal and decrease cost, catalytic ozonation is often applied [10–13]. For example, catalytic ozone oxidation with hydrogen peroxide (namely, O_3/H_2O_2 oxidation) has recently attracted more and more attention, owing to some advantages (i.e., lower operation cost, powerful oxidation ability, etc.) [14,15]. Correspondingly, a combined O_3/H_2O_2 -biological-aerated filter process was developed in eliminating organics in secondary effluent [16,17]. However, SS in water or wastewater usually presented an adverse effect during ozonation, such as decreasing ozone utilization efficiency [18,19]. That resulted in the increase in operation cost and the decline in organic removal in the O_3/H_2O_2 system. Thus, for the elimination of organics in wastewater containing a lower concentration of SS (e.g., PCMSE), a biological-aerated filter placed in the front of O_3/H_2O_2 (namely, the combined biological-aerated filter– O_3/H_2O_2 process) was possibly a more reasonable choice compared with a combined O_3/H_2O_2 -biological-aerated filter process. Unfortunately, to our knowledge, it was rarely reported that a combined biological-aerated filter– O_3/H_2O_2 process was used for removing organics in wastewater (or water). Additionally, as already known, a biological-aerated filter has a poor performance in TP removal. However, some researchers pointed out that the biological-aerated filter with Al^{3+} addition (BAFA) can improve the removal of TP from domestic sewage [20,21]. Nevertheless, now, there is no relevant report that a combined BAFA- O_3/H_2O_2 process was used for eliminating TP and organics in wastewater (or water).

Recently, it was proved that microbubble aeration can initiate highly reactive free radicals during ozonation [22]. It means that the performance of ozonation in removing organics can be improved by the microbubble aeration. Thus, OHOMB could remove organics more efficiently in comparison to O_3/H_2O_2 with a conventional bubble (OHOCB). That was to say, OHOMB should be a hopeful alternative for OHOCB in removing organics, based on the removal of organic pollutants (mainly including emerging contaminants or pure individual compounds) in water or model wastewater, and this point was confirmed by laboratory scale tests in the previous studies [23–26]. Regretfully, until now, it was scarcely reported that OHOMB as an advanced oxidation process was used to treat actual industry wastewater on a larger pilot scale; in particular, it was not unambiguous as to how organics in actual industry wastewater were eliminated during OHOMB treatment.

Thereby, based on PCMSE characteristics, the coupling of BAFA-OHOMB (CBAFAO-HOMB) was designed for the advance treatment of PCMSE. First, general quality indicators, such as COD, SS, TP, and color, were determined to assess the performance of BAFA and OHOMB. Organic removal in a relevant oxidation system was then evaluated to better understand OHOMB. Subsequently, performance comparison on three combined processes (i.e., CBAFAOHOMB, coupling of BAFA-OHOCB (CBAFAOHOCB), and coupling of OHOMB-BAFA (COHOMBBAFA)) was executed in treating PCMSE. Finally, the impact of SS on OHOMB was investigated. It was noted that Al^{3+} used in the present study was not from a commodity chemical but from WSPTA. WSPTA was closely associated with the soaking of Pinellia Ternata (a toxic Chinese medicine herb), and contained a high concentration of Al^{3+} . Based on this characteristic, WSPTA can probably be reused for PCMSE treatment as an Al^{3+} source. Now, there is no relevant report on WSPTA reuse.

2. Materials and Methods

2.1. Features of PCMSE (or WSPTA)

PCMSE was taken from an outlet in a mixing pool after a biotreatment secondary-sedimentation system in a proprietary Chinese medicine factory in Jiangsu province, China.

Table S1 presents the main features of PCMSE. Meanwhile, the value of the relevant indicator in WSPTA (collected from a Pinellia Ternata mill in Jiangsu province, China) is given in Table S2.

2.2. Pilot Device and Experiment Arrangement

2.2.1. Pilot Device

The flowsheet of the pilot device is shown in Figure 1; this mainly included a biological-aerated filter (design treatment capacity $2.4 \text{ m}^3/\text{d}$) and a oxidation reactor (design influent flow $24 \text{ m}^3/\text{d}$). The main equipment is listed in Table S3.

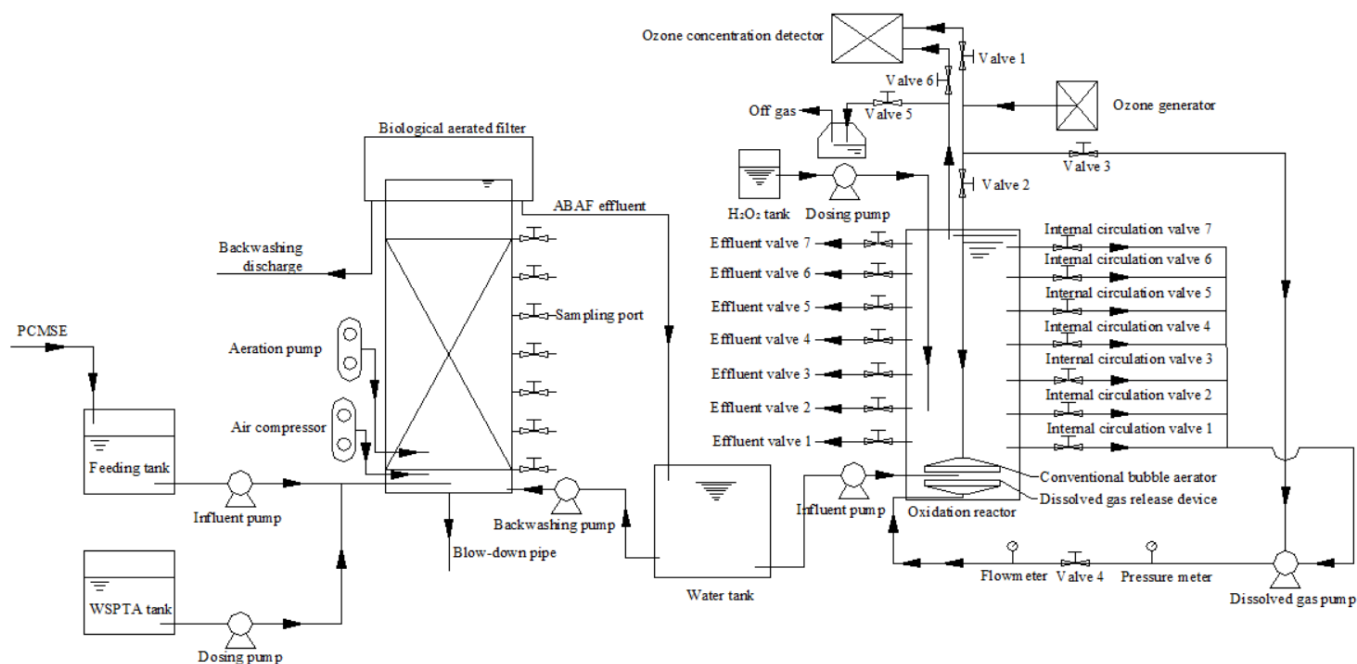


Figure 1. Flow scheme for pilot setup.

The biological-aerated filter ($\Phi 600 \text{ mm} \times 3000 \text{ mm}$, 304 L stainless steel) was packed with ceramic particles (Figure 1). The oxidation reactor was made of 304 L stainless steel, 0.45 m diameter and 4.3 m height. The microbubble aeration system consisted of an ozone generator, dissolved gas-release device (stainless steel, model TS-III, purchased from DongRun Environmental Protection Technology Co., Ltd., Yixing, China), and dissolved-gas pump (stainless steel, model 20QY-1, purchased from Nanfang Pump Industry Co., Ltd., Hangzhou, China). A dissolved-gas pump was operated at 0.4 MPa pressure to generate microbubbles with a mean diameter smaller than $50 \mu\text{m}$ [25]. A conventional bubble aeration system mainly included the ozone generator and titanium plate aerator with $60 \mu\text{m}$ microspore (the mean size of a produced bubble larger than 1 mm) [25]. The ozone–oxygen gas stream was generated from the ozone generator fed with pure oxygen (99%, industry grade) provided by Tianhong gas supply station, Taizhou, China and 30 wt% H_2O_2 (industry grade) was purchased from Wuhan Galaxy Chemical Co., Ltd., Wuhan, China.

2.2.2. Experiment Arrangement

In the whole experiment, different kinds of oxidation were realized by opening and closing the relevant valve and equipment (Figure 1). After the successful startup of the biological-aerated filter, a six-stage experiment was gradually executed (Figure S1):

- (1). The optimum operation conditions of a biological-aerated filter without Al^{3+} dose were firstly examined in the preliminary test (Figure S2), and are given in Table S4;
- (2). After this, the optimum Al^{3+} dose in BAFA was explored (Figure S2 and Table S5);

- (3). Subsequently, the optimum condition for OHOCB oxidation of BAFA effluent was determined in the preliminary test (Figure S3), and is listed in Table S6;
- (4). Apart from this, to facilitate comparisons, the performance of OHOMB and OHOCB in treating BAFA effluent was respectively investigated under the same condition (namely, the optimum oxidation condition examined in step No. 3) (Figure S4 and Table S7). The oxidation reactor in Figure S4 was operated in continuous mode with internal circulation. Correspondingly, the optimum operation condition for OHOMB was defined, and is given in the Section 3.2;
- (5). Then, the performances of these oxidation systems (i.e., ozonation alone with microbubble, ozonation alone with conventional bubble, and H_2O_2 oxidation alone) in treating BAFA effluent were investigated, respectively, under the corresponding condition (Figure S5 and Table S7), and the experiment was executed with the same operation mode as step No. 4;
- (6). Finally, the removal of organics and TP in PCMSE by these combined processes (i.e., CBAFAOHOMB, CBAFAOHOCB, COHOMBBAFA) was assessed under the corresponding conditions (Figure S6). During this period, the pilot device was operated in semi-batch mode.

2.3. Analysis Method

2.3.1. Wastewater Sample

Samples from OHOMB effluent, BAFA effluent, and BAFA influent were withdrawn from the time function and used for measurement of relevant indicator value. To ensure determination accuracy, during the analysis process, the residual oxidation reaction in the OHOMB effluent sample was rapidly terminated by adding 8.50 mM Na_2SO_3 solution at the Na_2SO_3 solution volume/wastewater sample volume ratio of 1/50 [17].

2.3.2. Analysis Method

BOD_5 , COD, color, $\text{NH}_4^{4+}\text{-N}$, TN, SS, TP, and Al^{3+} were measured, respectively, based on the Standard Methods [27]. Each sample was examined in triplicate. During the analysis period, $\text{K}_2\text{Cr}_2\text{O}_7$ was used for examining COD, and color was measured by the dilution level method. Relevant information about the mainly analytical reagent is presented in Table S8.

Furthermore, pH, turbidity, and zeta potential were determined by a pH meter (PHS-2F, Leici Co., Ltd., Shanghai, China), a turbidimeter (TU5200, HACH Co., Ltd., Loveland, CO, USA), and a zeta potential analyzer (ZS90, Malvern Panalytical Co., Ltd., Malvern, United Kingdom), respectively. Meanwhile, ultraviolet absorbance at 280 nm (UV_{280} , symbolic of ozonation of dissolved organic matter from Chinese medicine wastewater) was determined by a UV-Visible Spectrophotometer (UV-3600, Shimadzu Co., Ltd., Jingdu, Japan) [17].

Finally, an ozone monitor (HD80- O_3 , Suzhou Runqi Electronic Technology Co., Ltd., Suzhou, China) was used for measuring ozone concentration in gas.

2.4. SOUR Determination

The specific oxygen uptake rate (SOUR) was defined as the descending slope of dissolved oxygen per unit of volatile suspended solid, which can be used for evaluating biofilm activity. The volatile suspended solid was determined according to the weight-difference method, during the measurement. Meanwhile, the dissolved oxygen concentration was determined by a dissolved oxygen probe (YSI500A; YSI Inc., Yellow Springs, OH, USA) at 30 s intervals for 10 min [28]. Then, SOUR can be calculated by Equation (1).

$$\text{SOUR} = \frac{\text{Oxygen uptake rate (Dissolved oxygen(mg/L)/Time(h))}}{\text{Volatile suspended solid (mg/L)}} \quad (1)$$

2.5. Filtration Test

A filtration test in a batch mode was used for examining the change in particle size. The particle size distribution was characterized by the filter paper with pore diameter values of 0.45, 2.5, 8, and 15 μm [18], and each fraction was collected for the relevant indicator analysis.

3. Results

3.1. BAFA Performance

Based on features of PCMSE and WSPTA, the effect of the Al^{3+} dose on the pollutant removal was mainly investigated.

3.1.1. TP and SS Elimination

According to the TP discharge limit as presented in Table S1, 0.5 mg/L was defined as the control target of TP in effluent. As is known, a biological-aerated filter has a poor performance in TP removal. In the present study, TP in PCMSE decreased from 3.46 mg/L to 2.74 mg/L after the use of biological-aerated filter, giving a removal efficiency of 18.45%. TP in treated PCMSE with the biological-aerated filter was evidently higher than 0.5 mg/L.

Figure 2a shows that the biological-aerated filter with Al^{3+} addition markedly enhanced the TP removal. After the BAFA treatment, the average values of TP in the effluent were 2.11, 1.84, 0.87, 0.66, 0.18, 0.16 and 0.15 mg/L for adding 2, 4, 6, 8, 10, 12, and 14 mg/L Al^{3+} , respectively. The results shown in Figure 2a indicate that before the 10 mg/L Al^{3+} dose, the TP removal rapidly increased with the increase in Al^{3+} dose. During this process, Al^{3+} can form precipitate with P (Equation (2)) [20]; thereafter, the precipitate formed was intercepted by the filtration media in the biological-aerated filter.



At the same time, some polynuclear hydroxyl complexes with larger specific-surface area (or higher positive load) formed during the process, such as $\text{Al}(\text{OH})_4^-$, could enhance the coagulation performance [20]. Therefore, they could stimulate phosphorus elimination. But, TP removal began to slow after the 10 mg/L Al^{3+} dose (Figure 2a). When the WSPTA dose was beyond 2.5 L (namely, the Al^{3+} dose exceeded 10 mg/L, as shown in Table S5), the relatively obvious decrease in the influent pH could occur, and this decrease would probably result in the decline in the TP removal. The tendency of the TP removal was also reported in the relevant studies [20,21].

Moreover, the relevant studies reported that the optimum mass ratio of Al^{3+} /P was varied [20,21]. For example, Ma (2011) found that the best mass ratio of Al^{3+} /P was about 2.50 [20]. The optimum mass ratio of PAC/P (5.0) was chosen in treating TP with an activated sludge system [21]. The optimum mass ratio of Al^{3+} /P from the present study was approximately 3.14. Tables S9 and S10 show that when the Al^{3+} dose was under 10 mg/L, the wt% of fine particles and Zeta potential basically decreased with the increase in Al^{3+} dose [29]. The results suggested that some features of colloidal particles or fine suspended particles (i.e., size, charge, etc.) changed with the Al^{3+} dose, which was similar to that reported by [29,30]. Meanwhile, colloidal particles (or fine suspended particles) can compete with TP for Al^{3+} [20]. Therefore, the inconsistency in the features of colloidal particles or fine suspended particles in the studied wastewater perhaps resulted in the deviation in optimum mass ratio of Al^{3+} /P. The above phenomenon also existed in the Fe/P system [31,32].

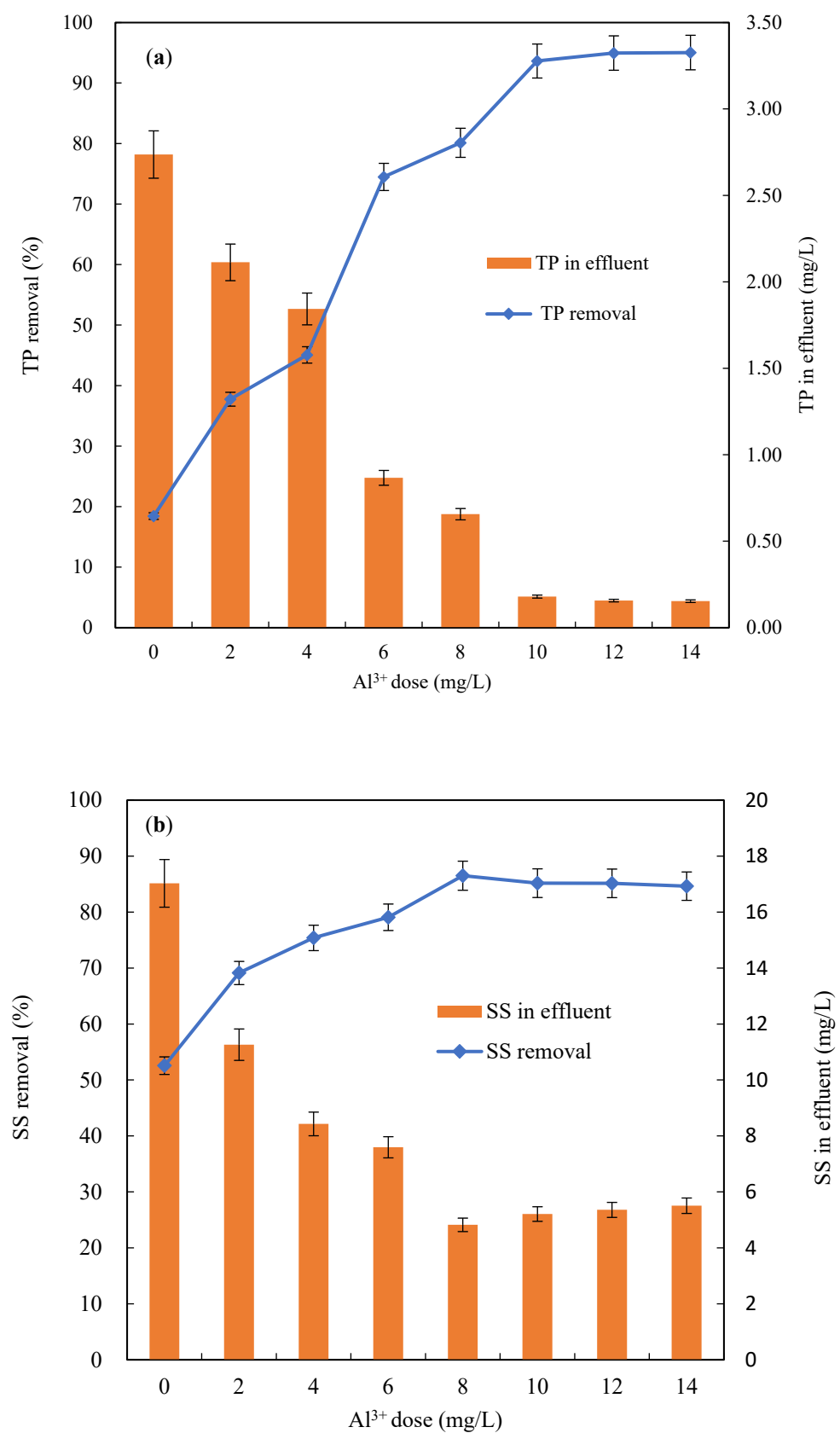


Figure 2. Effect of Al^{3+} dose on TP and SS removal ((a) TP; (b) SS) in the biological-aerated filter. (Average values of TP and SS in influent are 3.38 mg/L and 35.70 mg/L, respectively).

Figure 2b shows that when the Al^{3+} dose was less than 8 mg/L, the SS removal rapidly increased, relatively to the increase in the Al^{3+} dose. The SS removal with 8 mg/L Al^{3+} dose increased up to 86.52% (from 35.84 mg/L to 4.83 mg/L), which was higher than that without the Al^{3+} dose (52.23% removal) (Figure 2b). Meanwhile, Table S9 shows that the wt % of large-size particles increased as the Al^{3+} dose increased, but decreased when the Al^{3+} dose was higher than 10 mg/L. The results indicated that during the removal of SS, some fine particles can be transformed into large-size ones by Al^{3+} coagulation, which was consistent with the results in the literature [29,30]. Then, the large-size particles were intercepted by the filters. On the other hand, a proper Al^{3+} dose enhanced biofilm activity in the biological-aerated filter (as shown in the subsequent Section 3.1.3), and, correspondingly, more large-size particles which formed by coagulation (Al^{3+} coagulation or bio-flocculation) could be removed by bio-filtration or bio-adsorption [20]. Meanwhile, SS removals from the present study contradicted those documented in the literature [19]. In the literature, Wu et al. (2017) reported that the difference in SS removal between the biological-aerated filter with Fe^{2+} and the biological-aerated filter without Fe^{2+} was extremely slight [19]. The contradictory consequence was possibly attributed to the change in characteristics of the suspended particle (i.e., size, specific surface area, etc.) from the studied wastewater. Figure 2b, likewise, displays the fact that after a dose of 8 mg/L Al^{3+} , the SS removal decreased. A possible explanation for this was that a too-high solid load was formed under a higher Al^{3+} dose, as well as more SS penetrated the filtering media.

In engineering practice, the oxidation unit was usually placed in the front of the biological-aerated filter. But, several researchers implied that SS adversely influences ozonation [18,19]. As is known to all, the biological-aerated filter had a good performance in SS removal. Thus, the BAFA in the present study was laid in the front of the oxidation system containing ozone (i.e., OHOMB).

3.1.2. COD and Color Removal

Figure 3a shows that before the 10 mg/L Al^{3+} dose, the COD removal was increased with the increase in the Al^{3+} dose. Likely reasons for this were the following: (I) partial colloidal particles were removed by coagulant; (II) Al^{3+} formed complexes with organics containing an unsaturated coordinate bond, which facilitated organic removal [33]; and (III) biofilm activity (i.e., bio-degradation, bio-flocculation, etc.) was enhanced under the proper Al^{3+} dose (as shown in the subsequent Section 3.1.3). Correspondingly, more biodegradable organics can be biodegraded, more colloidal particles can be removed by bio-adsorption or bio-flocculation, and more large-size particles can be bio-filtered [20]. At a 10 mg/L Al^{3+} dose, COD removal was up to 29.18% (Figure 3a).

Figure 3a also displays the fact that the difference in the COD reduction between the biological-aerated filter with 10 mg/L Al^{3+} and the biological-aerated filter without Al^{3+} was 14.81%. The results indicated that the addition of Al^{3+} into the biological-aerated filter enhanced COD removal to a certain extent, which was similar to that reported by Ma and Wu et al. [19,20]. In their works, Wu et al. (2017) reported that the biological-aerated filter with proper Fe^{2+} removed more COD than that without Fe^{2+} [19]. Ma (2011) examined how COD removal by a biological-aerated filter with a proper Al^{3+} dose (92.0%) was approximately 7.0% more than that without Al^{3+} (85.0%) [20]. Furthermore, Figure 3b shows that results for the removal of color followed similar trends to that of COD. Generally speaking, the removal in COD was not obvious compared with that in SS.

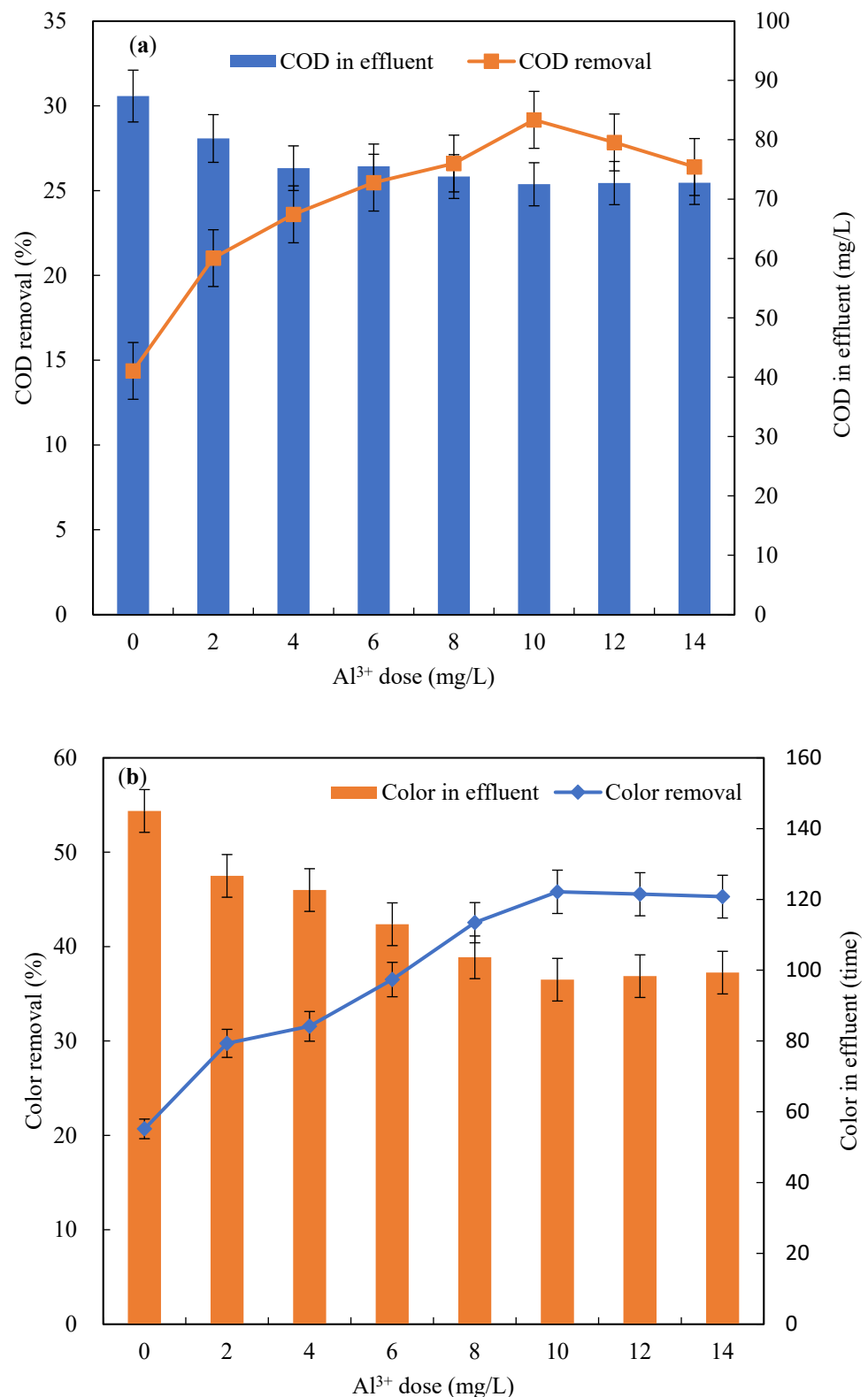


Figure 3. Effect of Al^{3+} dose on COD and color removal ((a) COD; (b) color) in the biological-aerated filter. (The average values of COD and color in the influent were 100.74 mg/L and 180 times, respectively).

3.1.3. Impact of Al^{3+} Addition on Biofilm Activity

At a lower Al^{3+} dose, the SOUR value slowly increased as the Al^{3+} dose increased, as shown in Figure 4. This result indicated that a proper Al^{3+} dose could enhance biofilm

activity to some extent, which was the same as that reported by others [34,35]. Figure 4 also illustrates that the SOUR of biofilm at the 8.0 mg/L Al^{3+} dose was up to 5.12 mg O_2/g (volatile suspended solid)•h, and biofilm activity declined after the 8.0 mg/L Al^{3+} dose. This phenomenon was documented in the Fe/P system [19]. This change may be because plenty of flocs formed under Al^{3+} flocculation were covered on the surface of the BAFA filters, and, subsequently, the overlaid flocs prevented oxygen and mass transfer, to a certain extent.

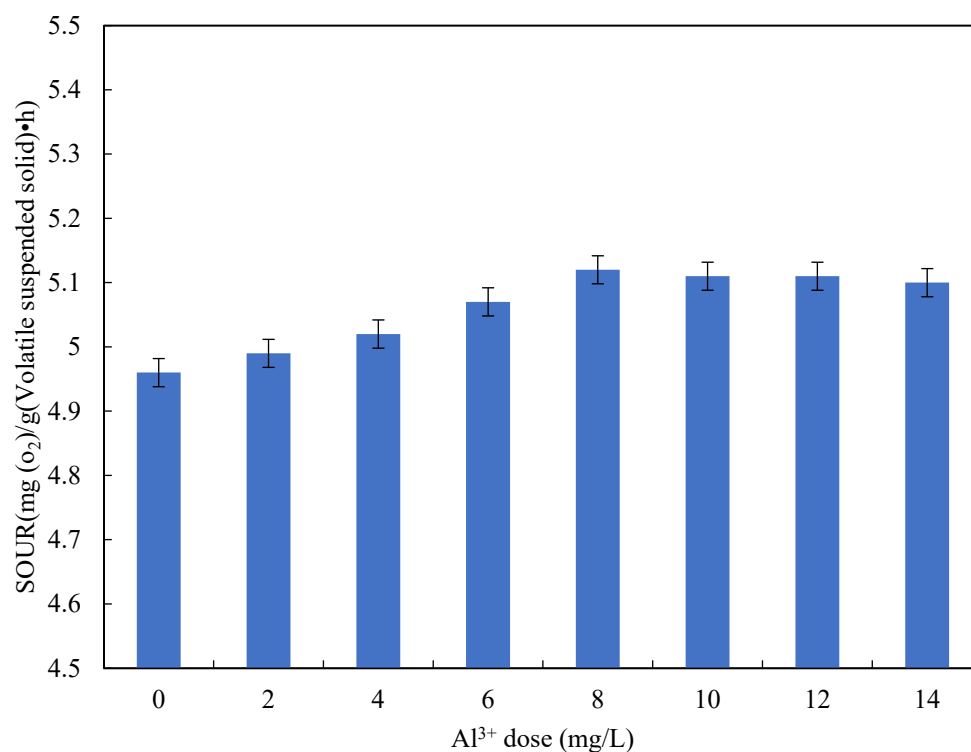


Figure 4. Effect of Al^{3+} dose on the SOUR of the biofilm in biological-aerated filter.

Moreover, based on biofilm SOUR and SS removal, the optimum Al^{3+} dose was 8.0 mg/L in the present study. Actually, instead of significantly inhibiting biofilm activity, the 10.0 mg/L Al^{3+} dose promoted more pollutant removal (as well as an extremely slight decrease in SS) (Figures 2 and 3). Thus, 10.0 mg/L was chosen as the optimum dose during subsequent experiments. Meanwhile, the biological-aerated filter with 10.0 mg/L Al^{3+} removed the organics more efficiently than that without the Al^{3+} dose, with the difference in removal efficiency of approximately 14.81%, 34.29%, and 25.11% being examined for COD, SS, and color, respectively (Figures 2 and 3). These figures demonstrated that the addition of Al^{3+} into the biological-aerated filter exalted the organic removal relatively markedly.

Finally, the concentration of residual Al^{3+} in BAFA effluent was 0.15 mg/L at the 10.0 mg/L Al^{3+} dose. The vast disparity in Al^{3+} concentration between influent and effluent implied that plenty of aluminum ions transferred into the biofilm in BAFA, which was consistent with that documented in the literature [21]. Subsequently, the majority of Al^{3+} can be removed with excess sludge by backwash of BAFA. In this case, the receiving water body was safer, and was a just target for this study.

So far, the optimum conditions for the BAFA operation are defined as the following: the initial PCMSE pH, Al^{3+} dose = 10 mg/L (namely, 2.5 L WSPTA/ m^3 PCMSE), hydraulic retention time = 3.5 h, ratio of gas/water = 4:1, backwashing period = 7 days, and temperature = 13–27 °C. Effluent after BAFA treatment under the optimum conditions was used for the following oxidation experiment.

3.2. Performance at OHOMB Stage

3.2.1. Organic Removal

To facilitate comparison, the performance of O_3/H_2O_2 oxidation with either conventional bubble aeration or microbubble aeration was investigated, respectively, under the same condition (namely, the optimum condition for OHOCB operation), and the outcome is shown in Figure 5.

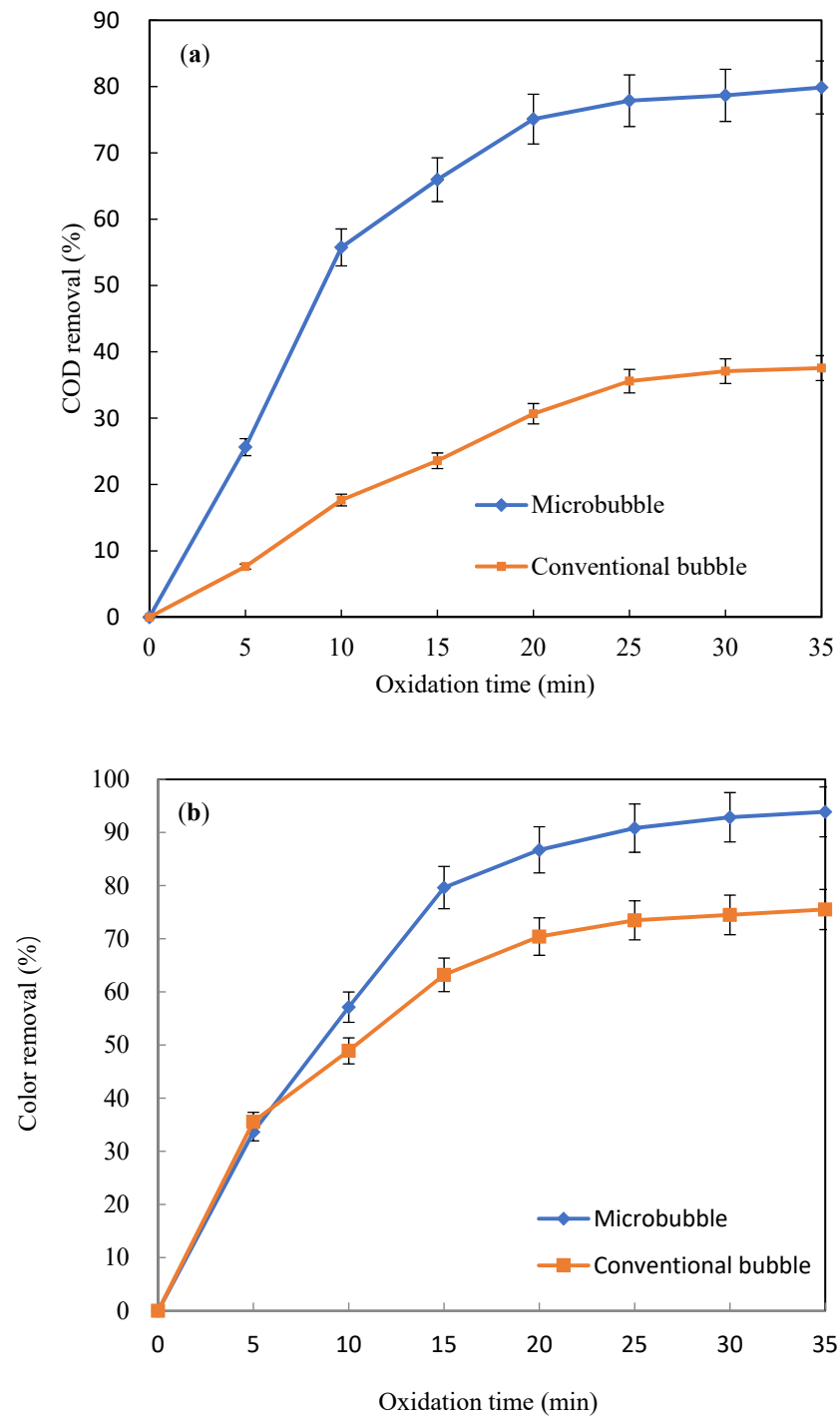


Figure 5. COD and color removal during O_3/H_2O_2 oxidation of BAFA effluent ((a) COD; (b) color).

It can be seen from Figure 5a that COD removal was up to 75.09% at 20 min for OHOMB oxidation and 35.58% at 25 min for OHOCB oxidation, respectively. COD removal increased with the extension of the oxidation process, and OHOMB oxidation obtained

77.86% COD removal at 25 min (Figure 5a). These findings suggested that organics in PCMSE were relatively successfully mineralized by OHOMB, which was also reported in these oxidation systems [36–38]. Apart from this, 81.63% color removal at 15 min for microbubble aeration and 70.41% color removal at 20 min for conventional bubble aeration were obtained, respectively, during O_3/H_2O_2 oxidation. During OHOMB oxidation, 86.73% color removal was achieved at 20 min (Figure 5b). High removal of color in the PCMSE demonstrated that the organic structure was significantly decomposed by O_3/H_2O_2 oxidation [39–41]. Relatively speaking, OHOMB displayed better de-coloration performance than OHOCB [42]. Furthermore, the decrease in color was generally higher than that in COD (Figure 5).

Figure 5a also illustrates that the optimum oxidation time for OHOMB (20 min) was approximately 80% of that for OHOCB (25 min); nevertheless, the COD removal by OHOMB at 20 min (75.09%) was about 210% of that by OHOCB at 25 min (35.58%). A relatively similar trend was also presented in color removal (Figure 5b). These results mean that COD and color during OHOMB oxidation decreased more sharply than that during OHOCB oxidation, which was observed during ozonation of pollutants [26,42]. Meanwhile, this was confirmed by the reaction rate during O_3/H_2O_2 oxidation from the present study (Table 1).

Table 1. Reaction rate during O_3/H_2O_2 oxidation.

Process	COD	Color
OHOMB	$k = 0.24$ $R^2 = 0.902$	$k = 0.42$ $R^2 = 0.963$
OHOCB	$k = 0.11$ $R^2 = 0.936$	$k = 0.21$ $R^2 = 0.903$

The reaction rate of COD during OHOMB oxidation was 0.24, which was significantly higher than that examined during OHOCB oxidation (0.11) (Table 1). The reaction rate of color followed similar trends to that of COD (Table 1). A significant divergence in reaction rate indicated that during O_3/H_2O_2 oxidation, microbubble aeration was more efficient in enhancing organic degradation compared with conventional bubble aeration, which was fundamentally in line with results observed in the oxidation system containing ozonation [37,43]. A possible explanation for this was that under microbubble aeration, the increased solubility of ozone in the liquid phase directly degraded more organics. Another important reason for this was that more hydroxyl radicals were formed in the OHOMB system. This point was proved by COD removal by indirect reaction (Table S11). During O_3/H_2O_2 oxidation, direct reaction was usually due to ozone and H_2O_2 , whereas the hydroxyl radical mainly accounted for indirect reaction [40]. Table S11 shows that COD removal by indirect reaction during OHOMB oxidation ranged from 48.20% to 75.09%, which was obviously higher than that during OHOCB oxidation (from 5.79% to 35.58%). Indirect reaction contribution in terms of color removal followed analogous trends to that of COD (Table S11). Additionally, as aforementioned, optimum oxidation time in OHOMB (20 min) was only 80% of that in OHOCB. These consequences demonstrated that, in comparison to conventional bubble aeration, microbubble aeration more efficiently enhanced the initiation of the hydroxyl radical in the O_3/H_2O_2 system. Wu et al. (2019) also found that microbubble aeration could significantly improve hydroxyl radicals' generation during ozonation of nitrobenzene [43]. This may be because, under microbubble aeration, self-decomposition of the increased solubility of ozone in the liquid phase promoted more hydroxyl radical generation, based on a series of chain reactions.

3.2.2. Cost Evaluation

The economic performance of OHOMB and OHOCB was investigated, and the calculated cost is presented in Table S12.

The ozone utilization efficiency for OHOMB was more than 99% at 20 min; however, ozone utilization efficiency for OHOCB was only 89.73% at 25 min (91.64% at 20 min) (Table S12). At the same time, OHOMB obtained a lower ozone consumption compared with OHOCB (Table S12). Based on the above results, it was summarized that microbubble aeration could enhance ozone mass transfer in the O_3/H_2O_2 system. This was mainly because, compared with the conventional bubble, the microbubble has some advantages (i.e., large interfacial area, longevity in aqueous solutions, etc.) [22].

Clearly, OHOMB attained a lower operation cost (12.84 CNY/Kg COD removed), and which cut down 52.78% of expenses in comparison with OHOCB (Table S12). In addition, the average concentration of ozone in off-gas during OHOMB was 2.11 mg/L, which was obviously smaller than that during OHOCB (22.29 mg/L). A lower concentration of ozone in off-gas was desirable to reduce operation costs. In a word, OHOMB was more cost-competitive in comparison to OHOCB. Thereby, it can be expected that in engineering practices, OHOMB would present better economics. Regretfully, the relevant cost comparison of OHOMB and OHOCB for treating the same actual industrial wastewater was extremely limited in the previous studies.

Hereto, the optimum conditions of OHOMB oxidation are the following: the BAFA effluent pH, ozone dose = 16 mg/L, 30 wt% H_2O_2 dose = 30 mg/L, oxidation time = 20 min, microbubble aeration (effluent flow of dissolved gas pump = 1.0 m³/h, outlet pressure of dissolved gas pump = 0.4 Mpa, operation pressure of 30 g/h ozone generator = 1 atm, working electricity of 30 g/h ozone generator = 1.5 A, input gas flow of 30 g/h ozone generator = 60 L/h, cooling water flow = 0.1 m³/h), and temperature = 16–28 °C.

3.3. Performance of CBAFAOHOMB

Based on the above results, the optimum operation conditions for CBAFAOHOMB were defined as the following: the initial PCMSE pH, Al^{3+} dose = 10.0 mg/L (namely, 2.5 L WSPTA/m³ PCMSE), hydraulic retention time in BAFA = 3.5 h, gas/water ratio in BAFA = 4:1, backwashing period in BAFA = 7 days, ozone dose = 16 mg/L, 30 wt% H_2O_2 dose = 30 mg/L, oxidation time = 20 min, microbubble aeration (effluent flow of dissolved gas pump = 1.0 m³/h, outlet pressure of dissolved gas pump = 0.4 Mpa, operation pressure of 30 g/h ozone generator = 1 atm, working electricity of 30 g/h ozone generator = 1.5 A, input gas flow of 30 g/h ozone generator = 60 L/h, cooling water flow = 0.1 m³/h), and temperature = 18–31 °C. Under the optimum operation conditions, treatment of PCMSE by CBAFAOHOMB was executed.

Table S13 shows that the reduction of COD in PCMSE by OHOMB (42.48%) was significantly higher than that by OHOCB (16.14%), and the removal of color in PCMSE by OHOMB (65.75%) was higher than that by OHOCB (46.67%). At the same time, BAFA obtained the removal of 94.96%, 45.05%, and 28.78%, respectively, for TP, color, and COD (Table S13). After BAFA (or OHOMB, OHOCB) treatment, COD and color in the effluent all significantly exceeded the discharge value (COD = 50 mg/L and color = 30 times) (Table S1).

However, the coupling of BAFA-OHOMB (CBAFAOHOMB) was extremely effective in eliminating organics and phosphorus from PCMSE (with removals of 94.64%, 82.32%, and 91.76% being observed for TP, COD, and color, respectively) (Figure 6 and Table S13). COD, color, and TP in the effluent after BAFA treatment were, respectively, 72.34 mg/L, 100 times, and 0.17 mg/L. Meantime, color and COD in the effluent after OHOMB treatment were 15 times and 18.27 mg/L, respectively (Figure 6 and Table S13). These results indicated that during CBAFAOHOMB treatment of PCMSE, the vast majority of TP elimination, 35.20% of COD removal, and 49.40% of color removal were achieved by BAFA, and OHOMB obtained 64.80% of COD removal and 60.60% of color removal. Overall, during CBAFAOHOMB treatment of PCMSE, organic removal depended on the OHOMB and the BAFA, while TP removal was attributed to the BAFA (Figure 6 and Table S13).

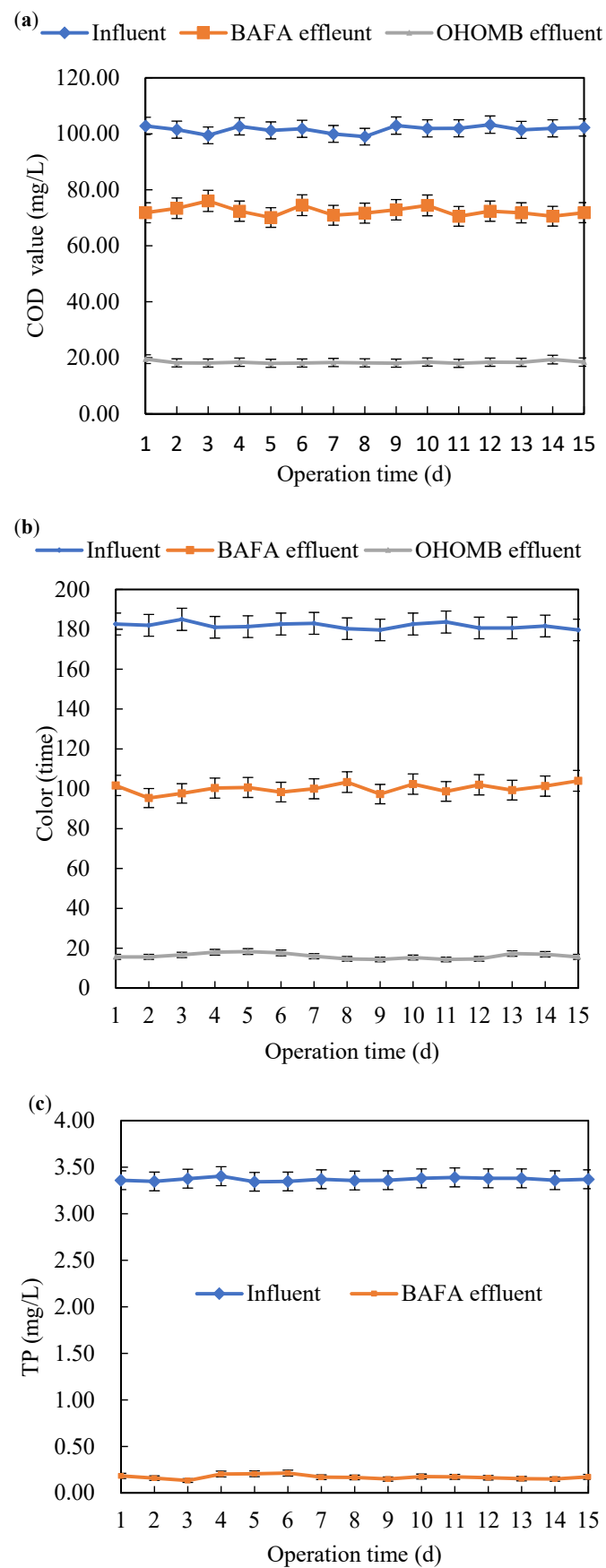


Figure 6. Performance of CBAFAOHOMB for treating PCMSE ((a) COD; (b) color; (c) TP).

Furthermore, Figure 6 and Table S13 show that CBAFAOHOMB has a better performance in organic degradation and TP removal, in contrast with CBAFAOHOCB (or COHOMBBABA), and the concentration of residual Al^{3+} in the effluent after COHOMBBABA treatment (0.26 mg/L) was markedly higher than that after CBAFAOHOMB treatment (0.15 mg/L) (Table S13). Although the value of key indicators in the effluent after three combined process treatments were all less than the discharge limit (Table S1), effluent quality after CBAFAOHOMB treatment was the best (Table S13). Meanwhile, the cost for CBAFAOHOMB was 8.77 CNY/Kg COD removed, being only 86.83% and 66.14% of that for COHOMBBABA and CBAFAOHOCB (Table S13). It is worth stressing that these cost figures should be treated with caution because of the fluctuations in energy and material prices. In conclusion, CBAFAOHOMB was more suitable for PCMSE treatment, and it was feasible that WSPTA was reused for treating PCMSE as an Al^{3+} source. Unfortunately, now, there is no cost comparison of these combined processes for treating the same wastewater.

Finally, the performance of OHOMB in treating PCMSE and filtered PCMSE with BAFA was elaborately compared. Table S14 shows that ozone utilization efficiency during OHOMB oxidation of PCMSE was slightly lower than that of filtered PCMSE with BAFA. But, by OHOMB oxidation, COD was eliminated by 42.92% and 75.16% for PCMSE and filtered PCMSE with BAFA, respectively (Table S14). That was to say, applying the filtration with BAFA decreased the amount of particles, resulting in improved organic degradation. A probable explanation for the phenomenon was that more applied ozone did not react with dissolved organic matter, but reacted with particles. In other words, the generation yield of $\text{HO}\bullet$ during the ozonation of particles was possibly lower than that of dissolved organic matter [18,44]. Correspondingly, the $\text{HO}\bullet$ and ozone exposure declined (thus, lowering the oxidation ability in OHOMB).

Employing the filtration with BAFA relatively significantly eliminated SS in the PCMSE (Figure 2), and thus, fewer particles in the filtered PCMSE with BAFA resulted in a relatively markedly decrease in ozone consumption and operation cost (in terms of CNY/Kg COD removed) (Table S14). During OHOMB oxidation of PCMSE, the oxidation ability decrease can be explained by particle reaction with applied ozone (in competition with dissolved organic matter). At the same time, higher removal in the filtered PCMSE with BAFA suggested that the removal of UV_{280} was correlated with filtration (Table S14) [18]. Therefore, with fewer particles in the filtered PCMSE with BAFA, more ozone reacted with dissolved organic matter, causing an increase in the removal of UV_{280} [18].

Although mineralization of organics in PCMSE by OHOMB was not significant (42.92%), the structure of organics was destroyed, as denoted by considerable color elimination (65.75%) and high removal of ultraviolet absorbance at 280 nm (71.47%) (Table S14). Therefore, decolorization was perhaps the first step in the OHOMB oxidation of organics in PCMSE [36], and the further OHOMB oxidation would decompose large-size organics into small-size ones (accompanied by the decrease in UV_{280}) and directly mineralize small-size organic [36] because of a lack of highly reactive oxidation species, small-size organics were fully not mineralized at the end of oxidation.

In brief, as the other factors have been excluded under the steady oxidation state, SS was primarily responsible for the fact that, for removing organics, the performance of OHOMB in COHOMBBABA was not as good as that in CBAFAOHOMB (Table S13 and Figure 6). To be exactly, SS lowered the oxidation performance relatively significantly and increased the operation cost during OHOMB oxidation of PCMSE.

4. Conclusions

A pilot experiment in the present study provided a novel coupling of a biological-aerated filter with Al^{3+} addition- $\text{O}_3/\text{H}_2\text{O}_2$ with microbubble (CBAFAOHOMB) for the advanced treatment of PCMSE. Under the optimum operation conditions, CBAFAOHOMB efficiently treated PCMSE, with the removal of 94.64%, 82.32%, and 91.71% for TP, COD, and color, respectively. The TP, color, and COD in the tread PCMSE with CBAFAOHOMB were approximately 0.15 mg/L, 15 times, and 18.27 mg/L, which fully meets the discharge-

limit value of the standard (GB21906-2008). In particular, some important conclusions were the following:

- (1) CBAFAOHOMB markedly exerted the merits of BAFA and OHOMB, and was an efficient process for advanced treatment of PCMSE.
- (2) TP elimination depended on BAFA, and organic reduction was mainly owed to BAFA and OHOMB.
- (3) The addition of Al^{3+} into the biological-aerated filter significantly enhanced TP removal and relatively markedly improved organic elimination; bio-film activity in BAFA was not affected under a 10 mg/L Al^{3+} dose.
- (4) During $\text{O}_3/\text{H}_2\text{O}_2$ oxidation, microbubble aeration more efficiently enhanced organic removal than conventional bubble aeration.
- (5) SS lowered oxidation performance relatively significantly and increased the operation cost during OHOMB oxidation of PCMSE.
- (6) Reuse of WSPTA was feasible, and this reuse not only saved PCMSE treatment costs but also recycled Al^{3+} resources.

Although this research supplied many useful data on CBAFAOHOMB, a more complicated study should be executed on the advanced treatment of varied wastewater to magnify CBAFAOHOMB application.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/w16142030/s1>, Figure S1: Experiment arrangement; Figure S2: Biological-aerated filter in the pilot device; Figure S3: The oxidation reactor used for optimizing OHOCB operation conditions; Figure S4: The reactor for investigating the performance of OHOMB and OHOCB for oxidizing BAFA effluent; Figure S5: The reactor for investigating the performance of these oxidations (i.e., ozonation alone with microbubble, ozonation alone with conventional bubble, OHOCM, OHOMB, H_2O_2 oxidation alone) in BAFA effluent treatment; Figure S6: Flow scheme of the combined processes; Table S1: Main characteristic of PCMSE; Table S2: Value of relevant indicator in WSPTA; Table S3: Relevant information about main equipment; Table S4: Operation condition optimization of biological-aerated filter without Al^{3+} dose; Table S5: Relationship between addition of WSPTA into PCMSE and dose of Al^{3+} into PCMSE; Table S6: Oxidation condition optimization of OHOCB for treating BAFA effluent; Table S7: Comparison of performance of different oxidation processes; Table S8: Relevant information about the main chemical; Table S9: Change in particle size distribution; Table S10: Relevant performance of ABAF; Table S11: Removal from indirect reaction during OHOMB oxidation; Table S12: Economy performance of two oxidation processes; Table S13: Calculated cost and average value of relevant indicators during PCMSE treatment with varied approaches; Table S14: Performance of OHOMB in treating PCMSE and filtered PCMSE with BAFA. Reference [45] is cited in the supplementary materials.

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Data Availability Statement: The datasets generated and analyzed during the current study are available from the corresponding author upon reasonable request.

Conflicts of Interest: Authors Ying Xv, Chengwei Hua were employed by the company Jiangsu Kintep Environmental Protection Co., Ltd., China. The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Abbreviations

PCMSE	Proprietary Chinese medicine secondary effluent
BAFA	Biological-aerated filter with Al ³⁺ addition
OHOMB	O ₃ /H ₂ O ₂ with microbubble
CBAFAOHOMB	Coupling of BAFA-OHOMB
TP	Total phosphorus
COD	Chemical oxygen demand
SS	Suspended solid
WSPTA	Wastewater from soaking of Pinellia Ternata with alumen
OHOCB	O ₃ /H ₂ O ₂ with conventional bubble
CBAFAOHOCB	Coupling of BAFA-OHOCB
COHOMBBAFA	Coupling of OHOMB-BAFA
UV ₂₈₀	Ultraviolet absorbance at 280 nm
SOUR	Specific oxygen uptake rate

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