The use of potassium permanganate, ozone and associated coupled processes for odor removal in drinking water: bench and pilot scale tests

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ABSTRACT

Bench and pilot scale experiments were conducted to investigate and compare the preoxidation effects of potassium permanganate ($KMnO_4$) and ozone (O_3) for odor removal in drinking water. The effects of dosage, contact time, pH, as well as couple treatment with a granular activated carbon (GAC) filter were examined using bench experiments, while the effects of $KMnO_4$ dosing points and a preozonation coupled process were investigated in pilot scale tests. Results revealed that both preoxidants at appropriate dosage worked well for odor removal because of the strong oxidizing ability and the intermediates generated in the process. The preozonation rate of O_3 was much faster than that of $KMnO_4$. Preoxidation by $KMnO_4$ was largely affected by pH because of the amount of hydrated manganese dioxide generated, which contributed to the adsorption of odorants. Pilot scale tests were highly synchronous with results of bench scale tests.

Key words | coagulation, GAC filter, $KMnO_4$, O_3, odor removal

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INTRODUCTION

Quality aspects become the primary concern for drinking water treatment when water quantity problems have been solved (Bruchet & Duguet 2004). The key issues in drinking water treatment are not only the removal of toxic pollutants, but also the removal of odorants (Tobien *et al.* 2000). Thus, the treatment and control of odor have increased in priority because odorants have long been related to the quality and safety of drinking water (Antonopoulou *et al.* 2014). Several classes of compounds have been reported to be responsible for odor: for example, sulfides, dicyclopentadiene and analogues, and disinfection byproducts (DBPs) to name a few (Park *et al.* 2007). However, it is a challenging task to target such low levels of specific compounds in a complex mixture which contains extremely low concentrations, usually in the range of ng L^{-1} (Park *et al.* 2007; Persson *et al.* 2007; Srinivasan & Sorial 2011; Watanabe *et al.* 2014). Few approaches have been identified to be efficient in

odor removal, including the use of activated carbon (both powdered activated carbon (PAC) and granular activated carbon (GAC)) and alum coagulation/sand filtration (Cook *et al.* 2001; Jung *et al.* 2004; Sattler & Rosenberk 2006; He *et al.* 2016). However, adsorption capacity is vulnerable to the existence of natural organic matter, and additional costs must be paid for regeneration of activated carbon (Bansal *et al.* 2005).

Fortunately, the use of oxidants (chlorine, chlorine dioxide, potassium permanganate ($KMnO_4$), ozone (O_3), etc.) has been proved to be an alternate approach for odor removal, even though it is ineffective in removing geosmin and 2-methylisoborneol because of the resistance of tertiary alcohols towards oxidants (Antonopoulou *et al.* 2014; Zhang *et al.* 2015). Nevertheless, chlorinated DBPs and associated odor compounds inhibited further application of both chlorine and chlorine dioxide (Srinivasan & Sorial 2011).

Previous studies have demonstrated that both $KMnO_4$ and O_3 perform well for odor removal in drinking water treatment processes (Lalezary *et al.* 1986; Jung *et al.* 2004) as strong oxidants. The outstanding advantages of $KMnO_4$ and O_3 for odor removal in drinking water lie in their strongly oxidative ability and great compatibility with conventional treatment processes such as coagulation and flocculation, as well as the excellent adsorption and catalytic capacity of the hydrated manganese dioxide (HMD) formed in the process of preoxidation of $KMnO_4$ (Tobien *et al.* 2000; Chen *et al.* 2009). These studies have indicated that both preoxidants like $KMnO_4$ and O_3 and their derived substrates like HMD and hydroxyl (·OH) are effective in odor removal.

However, the high treatment efficiencies largely depend on the conditions of the solution including oxidant type, dosage, pH and their related coupled processes, which is of economic significance in their applications. Thus, the purpose of this work is to provide some applicable information for use of $KMnO_4$ and O_3 as preoxidants in odor removal for drinking water. Both bench and pilot scale tests were performed to reveal the optimal parameters of preoxidation by $KMnO_4$ and O_3. However, conventional treatment processes could hardly remove odorants due to their limitations in cost efficiency and removal performance; the same is true for the single chemical oxidation processes. Therefore, the coupled processes including $KMnO_4$ or O_3 followed by a filter were also investigated, aiming to add some applicable insights into odor removal in drinking water treatment.

MATERIALS AND METHODS

Raw water quality

The water targeted in the present study was from a drinking water source of a city in the south of China. Reports of raw water during experiments for both bench and pilot scale tests are shown in Table 1, which was characterized by a high odor (200 and 150 on average for bench and pilot scale tests, respectively) and chroma (25 and 22 times on average for bench and pilot scale tests, respectively), moderate turbidity and a low chemical oxygen demand (COD_{Mn}). The low nutrient level in raw water explained the low

Table 1 | Raw water quality for bench and pilot scale experiments

Parameters	Units	Bench scale experiments Average value	Pilot scale experiments Average value
Temperature	$°C$	25	25
pH	-[a]	6.89	7.19
Turbidity	NTU	31.8	18.9
TON	-[a]	200	150
Chroma	Times	25	22
COD_{Mn}	$mg\ L^{-1}$	4.30	4.90
DO	$mg\ L^{-1}$	2.55	1.76
NH_4^+-N	$mg\ L^{-1}$	2.33	2.03
NO_3^--N	$mg\ L^{-1}$	0.90	1.36
NO_2^--N	$mg\ L^{-1}$	0.28	0.17
Volatile phenol	$mg\ L^{-1}$	<0.002	<0.002
Algae counts	$10^4\ cells\ L^{-1}$	234	245

[a]No unit.

concentration of algae counts (Chen *et al.* 2009). The data collected over the study period without preoxidation illustrated that the change pattern of water turbidity after settling was inconsistent with that of the raw water threshold odor number (TON) and chroma.

Bench scale experiment

Batch experiments were conducted for both preozonation and $KMnO_4$ preoxidation. Certain amounts of preoxidants and/or coagulants were dosed into jars with a working volume of 1 L. After contacting under agitation using procedures described in Table 2, a 70 cm height quartz sand filter cylinder (sand diameter of 0.7 to 1.1 mm, cylinder made of plastic with a diameter of 35 mm) was applied at a constant speed of $8\ m\ h^{-1}$. Samples were collected after those procedures for further measurements and analysis.

When coupling with PAC post-treatment, $1\ mg\ L^{-1}$ of $KMnO_4$ was added to 1 L raw water, immediately followed by various PAC dosage and adsorption for 30 min to investigate the effect of PAC dosage. Samples were taken after $40\ mg\ L^{-1}$ polyaluminium chloride (PC) coagulation, settling, and filtration (procedures were given in Table 2) for TON measurement and analysis. To investigate the effect of coagulation time, $1\ mg\ L^{-1}$ of $KMnO_4$ was used

Table 2 | Agitation procedures for bench scale experiments

Steps	KMnO$_4$ preoxidation			O$_3$ preoxidation		
	Time (min)	Speed (r min^{-1})	Dosage	Time (min)	Speed (r min^{-1})	Dosage
1	30	60	KMnO$_4$	6 s	300	Coagulants
2	6 s	300	Coagulants	2	200	_[a]
3	2	200	_[a]	2	100	_[a]
4	2	100	_[a]	3	60	_[a]
5	3	60	_[a]	20	0	_[a]
6	20	0	_[a]			

[a]No chemicals added.

for preoxidation for 30 min, then dosing 40 mg L^{-1} PC at various agitation times (1, 2, 3, 6 and 7 min), followed by 20 mg L^{-1} PAC. TON and turbidity were measured after the pretreatment stated above.

Pilot scale experiment

Based on results of the laboratory scale experiments, pilot scale tests were conducted to verify the odor removal performance and parameters for both KMnO$_4$ and O$_3$ preoxidation. The pilot scale experiment for KMnO$_4$ was carried out by dosing KMnO$_4$ to either a biological pretreatment tank or a mixing pool with a flow rate of 60 m^3 h^{-1}. The technological process for pilot experiments is given in Figure S1. The scales for treatment tanks or pools and experimental parameters are described in Table S1. (Figure S1 and Table S1 are available with the online version of this paper.)

For O$_3$, the preozonation followed by conventional treatment and GAC filter processes were applied. The quality of charcoal activated carbon used in this study can be seen in Table S2 (available with the online version of this paper). Contact time was set as 8 min because of the adverse effect on GAC adsorption capacity (Fawzy *et al.* 2014). Coagulation time was 12 min, and superficial loading rate for settling was 7.5 m^3·(m^2 h). The filtration speed for sand and GAC was 9 m h^{-1}.

Analytical methods

Analysis of water quality parameters present in our study was carried out according to Standard Methods (2005). The measurements of TON, turbidity, chroma, etc. were

carried out at room temperature of 25 °C. All experiments were conducted in triplicate and the deviation was controlled within 5%. The mean values were used for analysis.

RESULTS AND DISCUSSION

Bench scale experiment

Effect of dosage

Odor removal performance by varying the preoxidant dosage in the bench scale experiment is presented in Table 3. It can be seen that both KMnO$_4$ and O$_3$ oxidation achieved better odor removal rates at a higher dosage, which were in the range of 0.5 to 2, and 1 to 4 mg L^{-1}, respectively. A removal rate of 74.9% was gained by pure settling without preoxidant dosage. For KMnO$_4$, an ideal odor removal rate of 83.2% was achieved at a dosage of 1 mg L^{-1}, though a slight increase of 3.4% in removal rate could be achieved by doubling

Table 3 | Effect of the preoxidant dosage on odor removal in bench scale experiments

Preoxidant	Dosage (mg L^{-1})	TON	Removal rate (%)
Without	0	50.3	74.9
KMnO$_4$	0.5	40.4	79.8
	1	33.6	83.2
	1.5	28.6	85.7
	2	26.8	86.6
O$_3$[a]	1	44.4	77.8
	2	36.4	81.8
	3	30.8	84.6
	4	26.6	86.7

[a]Contact time of 2 min.

the dosage. Thus, the optimal dosage could be chosen as 1 mg L^{-1}, in view of the odor removal efficiency and financial factors. For preozonation, there also existed a relatively optimal value for dosage, as 84.6–86.7% of TON was eliminated with 3–4 mg L^{-1} O$_3$. It could be concluded from Table 3 that for the same odor removal performance, O$_3$ dosage had to be twice that of KMnO$_4$.

According to Chen et al. (2009), an optimal dosage of 1.25 mg L^{-1} was found for KMnO$_4$ preoxidation process (removal rate of 98%), both higher (up to 1.75 mg L^{-1} or lower (0.5–1 mg L^{-1}) dosages led to a decrease in removal rates. Meanwhile, there were contradictory conclusions put forward by previous studies of Posselt & Reidies (1965) and Sukenik et al. (1987), which did not report any disruption in preoxidation processes even with dosage up to 8.1 mg L^{-1}. As for preozonation, 3 mg L^{-1} was reported to be an appropriate concentration when a removal rate of 93% could be obtained (Chen et al. 2009). The release of extra- and intra-cellular organic matter at high dosage of oxidants could be responsible for the failure in odorants removal (Tobien et al. 2000). The discrepancy between our study and previous ones could be due to the raw water quality differences, such as initial TON and other odor-producing materials (algae, nutrients and so on).

Effect of contact time

Figure 1 shows the effect of contact time on odor removal by both KMnO$_4$ (Figure 1(a)) and O$_3$ (Figure 1(b)). Although both preoxidants exhibited excellent capacity for odorants removal, there still were distinct differences between them. Odorants were removed quickly in the first 10 min with KMnO$_4$ preoxidation, and were stable at 1 h. The removal rates at 10 and 30 min were 77.8 and 83.3%, respectively. Though a higher dosage was required for O$_3$ (3–4 mg L^{-1}) in order to get the same performance as KMnO$_4$ (1 mg L^{-1}), the reaction speed for preozonation was apparently faster than that of KMnO$_4$. Odor removal quickly reached its equilibrium at 8 min, as little odorant reduction occurred afterwards. The odor removal efficiency for preozonation was 88.9% at 8 min and afterwards.

The preoxidation process for KMnO$_4$ and O$_3$ could be divided into several steps. Namely, KMnO$_4$ initially removed odorants by oxidizing certain kinds of sources, which was a relatively slow and limited process (Cherry 1962; Qu et al. 2015; Haolin et al. 2016). HMD generated during this process served as an excellent adsorbent for further odor removal, which was effective though dependent on the oxidizing process by KMnO$_4$ (Qu et al. 2015). Thus, the preoxidation speed by KMnO$_4$ varied with sources of odorants. Similarly, preozonation had two particular reaction mechanisms based on initial pH: direct oxidation by O$_3$ (D reaction, pH < 8), which was slow and selective, and indirect oxidation by ·OH (R reaction, pH > 8), which was fast and adaptable (Antonopoulou et al. 2014). According to the raw water quality and oxidation process (Figure 1(b)), the preozonation process in our study was mainly dominated by the D reaction, which was still much faster than that of KMnO$_4$.
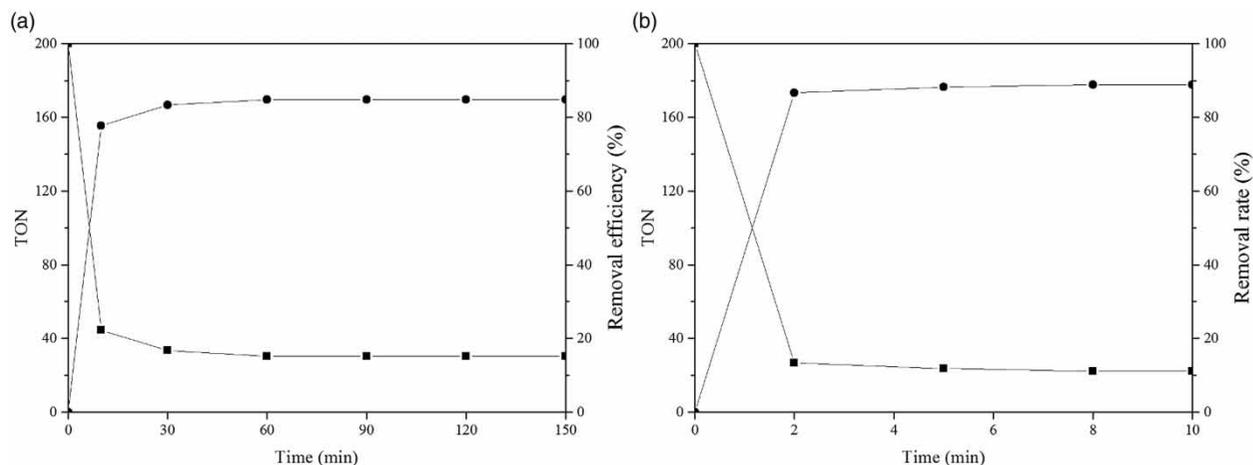

Figure 1 | Effect of contact time on preoxidation: (a) KMnO$_4$ with 1 mg L^{-1}; (b) O$_3$ with 4 mg L^{-1}.
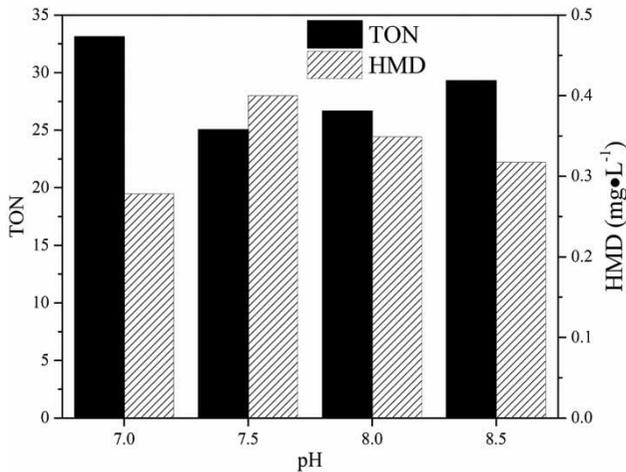
Figure 2 │ Effect of pH on preoxidation of $KMnO_4$: dosage 1 mg L^{-1}, contact time 30 min.

Effect of pH

Figure 2 illustrates the effect of various pH (7.0–8.5) on odor removal and amount of HMD generation. It is obvious that odor removal rate was positively correlated with generated HMD. HMD reached its peak (0.4 mg L^{-1}) at a pH of 7.5, when the odor removal rate was 87.5. Higher or lower pH resulted in a decrease of removal efficiency as well as the amount of HMD. It is concluded that raw water with pH around 7.5 was more favorable to preoxidation by $KMnO_4$, which contributed to HMD production and odor removal.

Intermediates generated in the process of KMnO4 oxidation varied with different pH, among which the HMD

was most effective in odor removal (Bokare & Choi 2014). The amount of HMD generated at pH about 7.5 was the largest, corresponding to the highest odor removal rate, which was in accordance with the previous study (Adcock *et al.* 2014).

Coupling with PAC filter

Preoxidation by $KMnO_4$ helped to enhance the function of PAC for the oxidation of organic compounds; however, it brought about another problem that $KMnO_4$ itself is dense purple in color, thus increasing the effluent chroma and demanding further treatment for chroma removal. Herein, we coupled $KMnO_4$ preoxidation with PAC filter, aiming to solve this problem.

It is obvious that odor removal efficiencies by adding $KMnO_4$ exceeded those without $KMnO_4$ (Figure 3(a)). Although residual TON with/without $KMnO_4$ dosage decreased with the increasing dosage of PAC (83.3–89.1% and 75.0–87.5%, respectively), the discrepancy between them tended to reduce (from 8.3 to 1.6% at dosage 1–2.5 mg L^{-1}).

Effect of coagulation time on turbidity and TON can be seen in Figure 3(b). The figure illustrates that for a coagulation time of 3 min, the odor removal rate increased to 88.3% at the same coagulant dosage; however, both longer and shorter times led to the decrease of removal efficiency. Turbidity after settling increased with time (0.89–1.43 NTU),
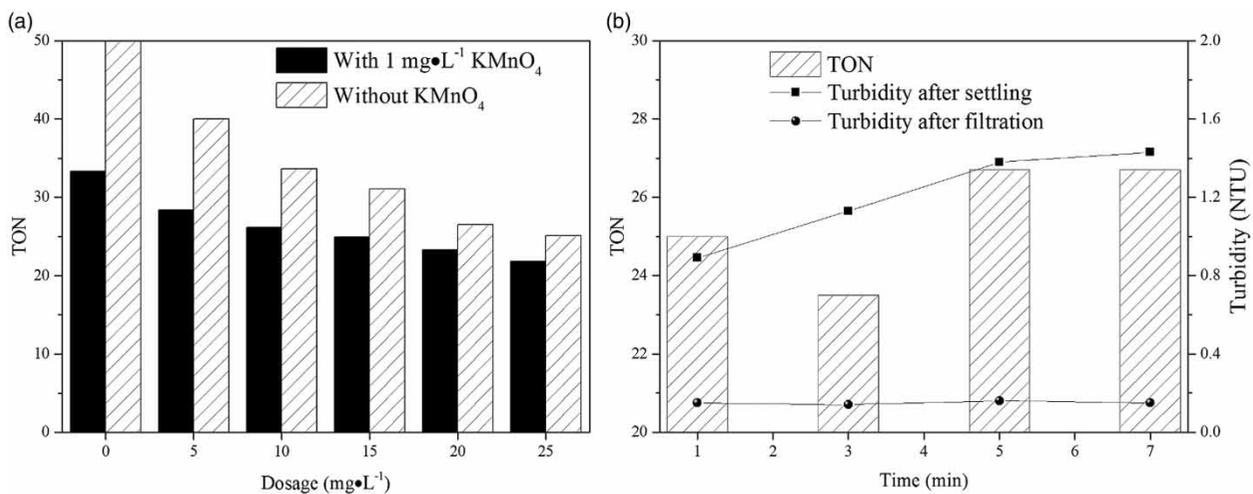

Figure 3 │ $KMnO_4$ preoxidation coupled with PAC filter: (a) effect of PAC dosage; (b) effect of coagulation time.

Table 4 | Pilot scale experiment by KMnO$_4$ preoxidation

KMnO$_4$ dosage (mg L^{-1})	Dosing point	TON[a]	Turbidity (NTU)	pH	COD$_{Mn}$ (mg L^{-1})	Total algae (10^4 cells L^{-1})	Chroma (times)	Mn (mg L^{-1})
0	Biological pretreatment tank[b]	40	0.32	7.19	3.8	28	5	0.103
0.5		29	0.28	7.21	3.1	14	5	0.082
0.8		24	0.26	7.18	2.8	8	5	0.051
1		22	0.25	7.22	2.5	6	5	0.011
1.2		22	0.26	7.17	2.4	4	5	0.045
1.5		22	0.27	7.19	2.3	4	5	0.079
0	Mixing pool	40	0.31	7.08	3.1	22	5	0.115
0.5		29	0.27	7.11	2.5	11	5	0.089
0.8		25	0.28	7.09	2.3	7	5	0.042
1		22	0.24	7.12	2.2	5	5	0.009
1.2		22	0.26	7.11	2.1	3	5	0.035
1.5		21	0.26	7.13	2	2	5	0.081

[a]No unit.
[b]Oxidation time of 5 min.

while after filtration the turbidity remained unaffected by coagulation time (0.14–0.16 NTU).
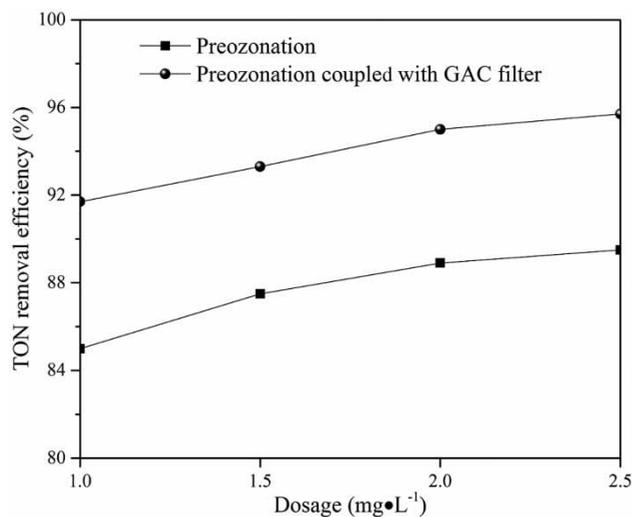
Pilot scale experiment

Pilot scale experiment results for KMnO$_4$ preoxidation with two kinds of dosing points (biological pretreatment tank and mixing pool) and various dosages (0–1.5 mg L^{-1}) are shown in Table 4. The results were in agreement with those of the bench scale tests. Preoxidation by KMnO$_4$ could achieve good odor removal efficiency at a dosage of 1 mg L^{-1}, as well as the removal of COD$_{Mn}$ and algae. In addition, the effluent chroma and Mn also reached the required standards. However, there were some differences between preoxidation at different dosing points. With the same KMnO$_4$ dosage, a slightly higher COD$_{Mn}$ removal efficiency could be obtained by dosing at the mixing pool than at the biological pretreatment tank.

This might be due to the complete mixing of preoxidants and water within the mixing pool, which contributed to complete contact and reaction. While in the biological pretreatment tank, the unevenness of KMnO$_4$ and water resulted in an incomplete oxidation reaction. Only parts of large molar organics were oxidized into smaller sized ones, thus increasing the concentration of effluent organic compounds. The similar removal efficiencies of TON (80%) and algae (over 90%) were synchronous with the results of bench scale tests. The high removal rate of algae also contributed to the odor removal process, as odorants within algae cells and released by cell lysis were eliminated to a large degree in our study.

Figure 4 represents the odor removal by preozonation only and coupled with the GAC filter in the pilot scale study. Efficient odor removal rates (over 85%) could be

Figure 4 | Pilot scale experiment by preozonation: contact time 8 min.

gained by varying O_3 dosage (1–2.5 mg/L). Consistent with the trend in the bench scale tests, removal efficiencies increased with O_3 dosage by both preozonation only (85–89.5%) and preozonation coupled with GAC filter (91.7–95.7%). It is apparent from Figure 4 that followed by a GAC filtration, the residual TON reduced further with a discrepancy of about 6% in removal rate. We could conclude that appropriate dosage of O_3 (e.g. 2 mg L^{-1}) coupled with the GAC filter could produce impressive odor removal performance.

CONCLUSIONS

Both bench and pilot scale experiments were carried out to examine the preoxidation by $KMnO_4$ and O_3 for odor removal. As for the water quality used in the present study, a dosage of 1.0 mg L^{-1} and pH ranging from 7.5 to 8.0 were favorable for odor removal by $KMnO_4$. Though a coupled process with PAC enhanced the odor removal, the generated HMD might occupy some of the adsorption sites. Besides, the excess $KMnO_4$ led to poorer behavior of PAC. Therefore, lower $KMnO_4$ dosage was recommended. Both dosage and oxidizing time mattered most for the preoxidation by O_3 and higher removal efficiencies were achieved with higher dosages and longer contact time. In addition, contact time had less effect with an increase of dosage. The coupled process of O_3 and GAC could strength the function of both components as well as saving O_3.

ACKNOWLEDGEMENTS

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