Determination of optimum operational conditions for the removal of 2-MIB from drinking water by peroxone process: a pilot-scale study

M. Fakioglu, H. Gulhan, H. Ozgun, M. E. Ersahin and I. Ozturk

ABSTRACT

Taste and odor in drinking water are one of the main problems of the water supply and treatment sector. Peroxone is an effective advanced oxidation process, which combines ozone with hydrogen peroxide to create hydroxyl radicals that decompose organic compounds. 2-Methylisoborneol (2-MIB) is one of the significant taste and odor causing compounds, which can be removed with the peroxone process. In this study, removal of a 2-MIB compound by peroxone process was investigated in a pilot-scale treatment plant and optimum operational conditions were determined. For safety reasons, it is important that residual O_3 and H_2O_2 concentrations in the water leaving the reactor should not exceed 0.1 and 0.5 mg/L, respectively. Results indicate that while dissolved ozone concentration was below the indicated limit for all experiments, concentrations over 0.5 mg/L residual H_2O_2 were observed during the experiments with an H_2O_2:O_3 ratio of 0.5. This limit exceedance affected the decision on the ideal peroxone ratio along with the 2-MIB removal results. Therefore; optimum H_2O_2:O_3 ratio was determined as 0.3. 2-MIB removal efficiency of 81% was achieved at the optimum H_2O_2:O_3 ratio with a contact time of 15 min. According to the results, 2-MIB removal rate had a linear correlation with the contact time.

Key words | 2-MIB, drinking water treatment, geosmin, pilot plant, taste and odor

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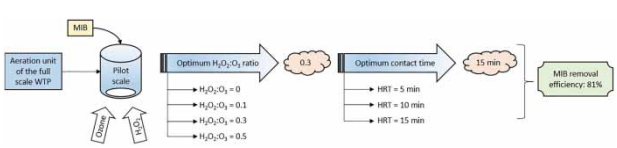
HIGHLIGHTS

- 2-MIB and geosmin are two major taste and odor causing compounds.
- Peroxone is an effective advanced oxidation process for micropollutant removal.
- Optimizing operational parameters plays a key role in water treatment.
- Results obtained from pilot plant provide major guidance for full-scale applications.

GRAPHICAL ABSTRACT



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INTRODUCTION

Taste and odor in drinking water affect the perception of customers in terms of both safety and aesthetics. Two of the most common taste and odor compounds, 2-methylisoborneol (2-MIB) and geosmin, are detectable even at concentrations below 10 ng/L (Fakioglu 2017). Water authorities not only search for the cause of taste and odor problems, but also try to find an effective process that can be integrated into existing water treatment plants.

Previous studies have shown that conventional water treatment processes such as coagulation, flocculation, sedimentation and chlorination are ineffective for removal of extracellular taste and odor compounds (Lalezary *et al.* 1986; Glaze *et al.* 1990; Bruce *et al.* 2002; Srinivasan & Sorial 2010). However, processes including powdered activated carbon, ozonation, and biofiltration have been found to be successful for the removal of these compounds where they are present dissolved in the water (Cook *et al.* 2001; Ho 2009; Hsieh *et al.* 2010; Srinivasan & Sorial 2010; Wang 2014).

Removal of taste and odor compounds by the peroxone process; that is, a combination of ozone (O_3) and hydrogen peroxide (H_2O_2), was proven to be effective by several studies (Srinivasan & Sorial 2010; Fakioglu 2017). These studies have shown that removal of 2-MIB and geosmin compounds was quite higher with the peroxone process in comparison to sole O_3 application at the same O_3 dosage. The findings of Koch *et al.* (1992) showed that 80–90% removal of 2-MIB and geosmin could be achieved with only 2 mg/L ozone dosage and 0.2 ratio of H_2O_2/O_3, which is the rate of removal that can only be achieved with a high sole ozone dosage of 4 mg/L. Determining an ideal peroxone ratio (H_2O_2:O_3 by mole) was the main objective of these studies. According to several studies, addition of H_2O_2 to O_3 has decreased the formation of potentially carcinogenic bromate, which is a byproduct of ozonation (Mizuno *et al.* 2011; Wang 2014). The operating temperature was set to a certain value in most of the studies, since the solubility of ozone is highly affected by the temperature (von Sonntag & von Gunten 2012).

In this study, optimum operational conditions such as peroxone ratio and contact time were determined for removal of 2-MIB in a pilot-scale peroxone system. Water samples used in all experiments were taken from one of the main drinking water sources of a mega city, Istanbul (Turkey). Other important parameters such as geosmin, total organic carbon and bromate were also determined along with the 2-MIB. During the experimental study, residual (dissolved) O_3 and residual H_2O_2 were monitored in order to investigate whether the applied chemical dosages were reasonable or not.

MATERIAL AND METHODS

Characteristics of raw water and reagents

Raw water was obtained from the outlet of an aeration unit in a full-scale drinking water treatment plant that was having taste and odor problems during the summer seasons. Characterization of the raw water, which was originally received from a surface water (a lake in Istanbul, Turkey), is provided in Table 1. All analyses in Table 1 were conducted in accordance with Standard Methods (APHA

Table 1 | Raw water quality

Parameter	Unit	Value
Chloride	(mg/L)	20.4
Color	(Pt-Co)	8.0
Conductivity (25 °C)	(μS/cm)	320
pH	–	7.71
Iron	(mg/L)	0.213
Manganese	(mg/L)	0.058
Sulfate	(mg/L)	19.9
Sodium	(mg/L)	16.87
Potassium	(mg/L)	3.11
Total organic carbon (TOC)	(mg/L)	2.7
Turbidity	(NTU)	3.6
UV_{254}	(cm^{-1})	0.07
2-MIB	(ng/L)	<0.5
Geosmin	(ng/L)	0.28
Bromide	(mg/L)	0.01
Total dissolved solids (TDS)	(mg/L)	192
Total Hardness	(mg $CaCO_3$/L)	144
Total Alkalinity	(mg $CaCO_3$/L)	116.4

2005). During some of the summer seasons in the previous years, the lake had experienced high 2-MIB concentrations of on average 90 ng/L. However, 2-MIB and geosmin concentrations were lower than 10 ng/L during the sampling period, which is known as the limit concentrations to be perceived. Therefore, 2-MIB was spiked into the water samples to obtain a concentration of 90 ng/L, which also simulated the average 2-MIB concentration of the investigated water source during the peak season when taste and odor problem was experienced. Chromatographic grade 2-MIB standard (Supelco, USA) (10 mg/ml) was used for maintaining the required concentration of 2-MIB in the water samples. Since 2-MIB is more difficult to be removed with O_3 in comparison to geosmin (WQTS 2009; Fakioglu 2017), operational conditions for 2-MIB removal were investigated to set the process design requirements. All reagents and solvents for H_2O_2 analysis were at least of analytical grade. All solutions were prepared with deionized water.

Pilot plant set-up

Pilot plant consisted of a raw water storage tank, reactor column (ozone contact column, of 2.4 m diameter and 5 m height), hydrogen peroxide (H_2O_2) dosing system and ozone generator along with the required pipes and measuring equipment (Figure 1). Raw water storage tank, which was fed with water from the aeration unit outlet of a full-scale water treatment plant, was made of polyethylene (PE) (of 2.8 m diameter, 2.4 m height and 15 m^3 total volume) and contained a low speed mixer (1.5 kW, 6–8 rev/min) along with an ultrasonic water level sensor (Sick AG, Germany). The ozone contact reactor was made of plexiglass (with 0.24 m diameter, 5 m height and 0.226 m^3 volume). Raw water was fed with a centrifuge feed pump (Ebara, Japan) to the reactor. The ozonation reactor contained an ultrasonic water level measuring device (Keller, Switzerland), a gas phase ozone measuring device (2B Technologies Model 106-M, USA), a dissolved ozone measuring device (Chemitec 42 Series, China), a thermometer (Chemitec 42 Series, China) and a pH meter (Chemitec 42 Series, China). Ozone was produced by the ozone generator (BNP, China), which was fed with an air compressor. Ozone was then transferred to the reactor by a ceramic diffuser (with 0.185 m diameter). H_2O_2 solution was dosed by a solenoid dosage pump (Sisdoz, Turkey) to a pipe equipped with a static mixer (Polyvinylchloride, PVC), which delivered water to the reactor.

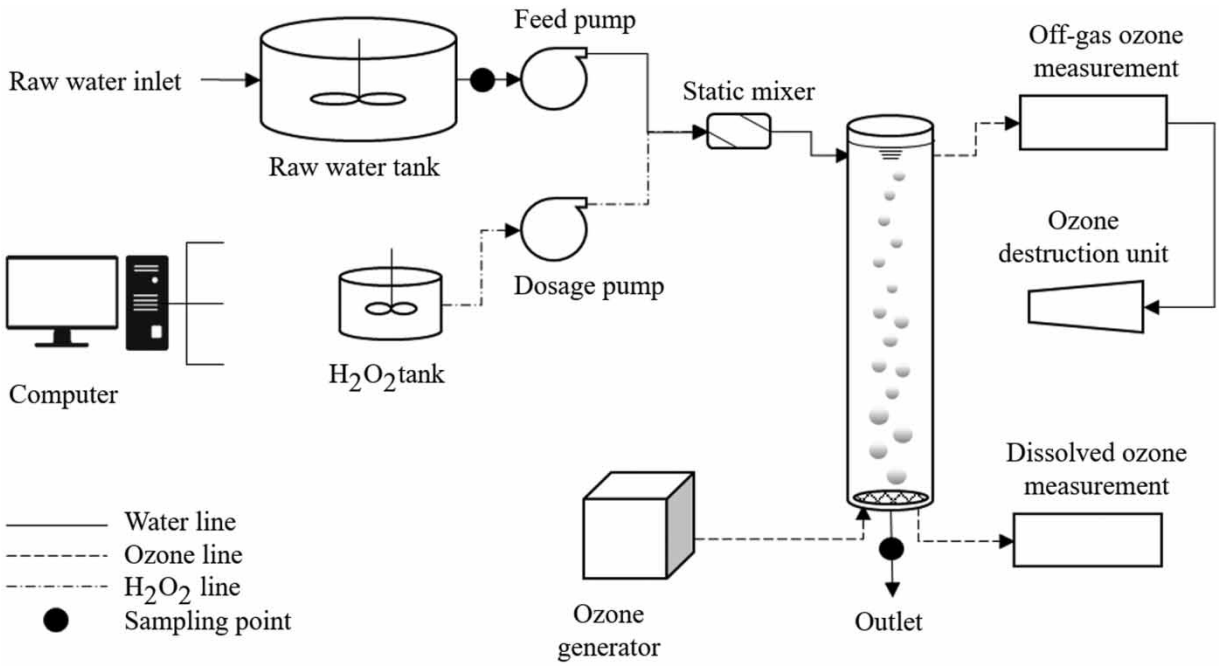

Figure 1 | Layout of the pilot-scale set-up.

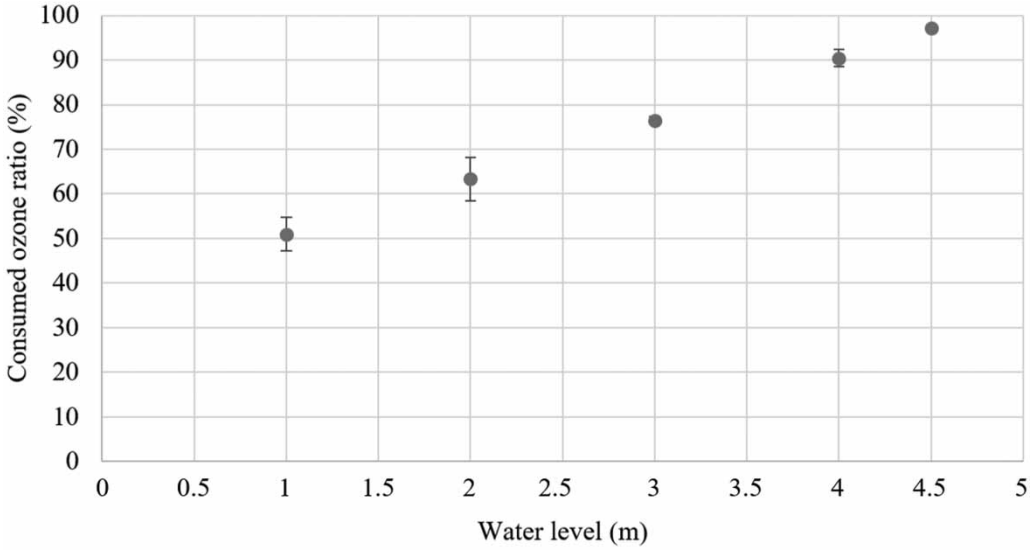

Figure 2 | Consumed ozone ratio depending on reactor height.

Gas phase ozone at the inlet and at the outlet of the reactor was measured with ozone measurement devices (2B Technologies, USA). Surplus (off-gas) ozone was destroyed by an ozone destruction unit (BNP, China) before reaching to the atmosphere.

Experimental plan

Relation between ozone consumption and reactor height

Before starting the experiments to determine the ideal peroxone ratio and contact time experiments, ozone consumption versus reactor height was investigated through running the system in batch mode. Experiments were performed with different reactor heights (1 m, 2 m, 3 m, 4 m and 4.5 m), while initial ozone concentration and contact time were set to 4 mg O_3/L and 10 minutes, respectively. Ozone consumption was calculated by using the inlet and the off-gas ozone concentrations. All experiments were conducted in duplicate and average values were used when presenting the results. Results obtained from the experiments conducted in the pilot treatment plant are given in Table 3 and Figure 2.

Determination of ideal peroxone ratio and contact time

Different H_2O_2:O_3 ratios were tested in order to find the ideal ratio for the removal of 2-MIB (Table 2). Inlet O_3 dose was set to 4 mg/L and the reactor was continuously fed with 2-MIB spiked water. Average water temperature in the pilot plant was recorded as around 16 °C. After the determination of the optimum H_2O_2:O_3 ratio, the reactor was operated at different contact times including 5, 10 and 15 min (Table 2). TOC and geosmin removal efficiencies

Table 2 | Experimental plan applied to determine the optimum H_2O_2:O_3 ratio and contact time

(a) Determination of optimum H_2O_2:O_3 ratio			(b) Determination of optimum contact time		
H_2O_2:O_3	Inlet O_3 concentration	Contact time	Contact time	Inlet O_3 concentration	H_2O_2:O_3
0	4 mg/L	10 min	5 min	4 mg/L	Selected H_2O_2:O_3 ratio
0.1			10 min		
0.3			15 min		
0.5					

were also determined throughout the experimental study. Additionally, variations in residual H_2O_2 concentration were measured during each experiment.

Analytical and instrumental procedures

Residual H_2O_2 concentration in the liquid phase was analysed following the iodide/molybdate method (HP-02) (Klassen *et al.* 1994). Concentrations of 2-MIB and geosmin were measured by gas chromatography mass spectrometry (GC/MS) (Agilent Technologies 7890B, USA) using Method 8270D (USEPA 1998). The solid phase micro extraction (SPME) method was used for preparing the samples for GC/MS. TOC analysis was conducted by a TOC analyzer (Shimadzu TOC-L Series, Japan). Bromate analysis was conducted by following Method 300.1 (USEPA 1999).

RESULTS AND DISCUSSION

Relation between ozone consumption and reactor height

Results obtained from the experiments conducted in the pilot treatment plant are given in Table 3 and Figure 1. Ozone consumption ratio was found to be 51% at 1 m reactor height and 97% at 4.5 m reactor height by applying 4 mg/L inlet ozone concentration. In order to reach an ozone consumption ratio above 75%, at least 3 m reactor height was required.

Along with the ozone consumption ratio, TOC removal was investigated during study. As seen in Table 3, TOC removal was lower than 6% for all operating conditions. Based on the results obtained from this study, ozone cannot remove TOC effectively alone. However, ozone is proven to increase the colloidal destabilization, which dramatically increases the removal efficiencies of organic compounds by coagulation, flocculation and filtration units in water treatment plants (Yuksel *et al.* 2002).

Results indicated that consumed ozone increased with increasing reactor height. With increasing heights, ozone contact time can be extended since water will stay longer in the reactor. Therefore, ozone fed at the bottom of the reactor could have more time to react with the compounds in the water and could be consumed in higher ratios.

Table 3 | Ozone consumption and TOC removal at different reactor heights

Inlet ozone concentration (mg/m^3)	4,000				
Reactor height (m)	1	2	3	4	4.5
Inlet ozone concentration (mg/m^3)	4,031	4,072	4,057	3,968	3,984
Off-gas ozone concentration (mg/m^3)	1,976	1,492	953	378	114
Ozone consumption (mg/m^3)	2,055	2,580	3,104	3,590	3,870
Ozone consumption ratio (%)	51	63	77	90	97
TOC removal (%)	0	4	5	2	2

Determination of ideal peroxone ratio and contact time

Variations in dissolved O_3 and residual H_2O_2 concentrations

Dissolved and consumed O_3 concentrations were measured for each H_2O_2:O_3 ratio at a contact time of 10 minutes (Figures 3 and 4). It is essential that the residual O_3 concentration in the water leaving the reactor should not exceed 0.1 mg/L for safety reasons (WQTS 2009). Considering Figure 3, dissolved (residual) O_3 concentration was around 0.05 mg/L, below 0.1 mg/L for each H_2O_2:O_3 ratio, while consumed O_3 concentration was around 4 mg/L. Dissolved ozone concentrations of each ratio (0.0–0.5) at the end of the 10th minute showed that the highest dissolved ozone concentration was reached with sole ozonation, which is as expected since the ozone was consumed in the peroxone reaction (Figure 3). On the other hand, the consumed ozone concentrations at the beginning showed that the most stable and unstable consumptions of ozone were in the case of having an H_2O_2:O_3 ratio of 0.5 and sole ozonation. However, overall ozone consumptions obtained for each ratio including the H_2O_2:O_3 ratio of zero showed that the consumptions were very close to each other.

Residual H_2O_2 concentration in the peroxone process was recommended not to exceed 0.5 mg/L (Oturan & Aaron 2014), since higher concentrations might cause operational problems such as residual chlorine consumption in the water treatment plants. Figure 5 shows that limit residual H_2O_2 concentration was not exceeded during the

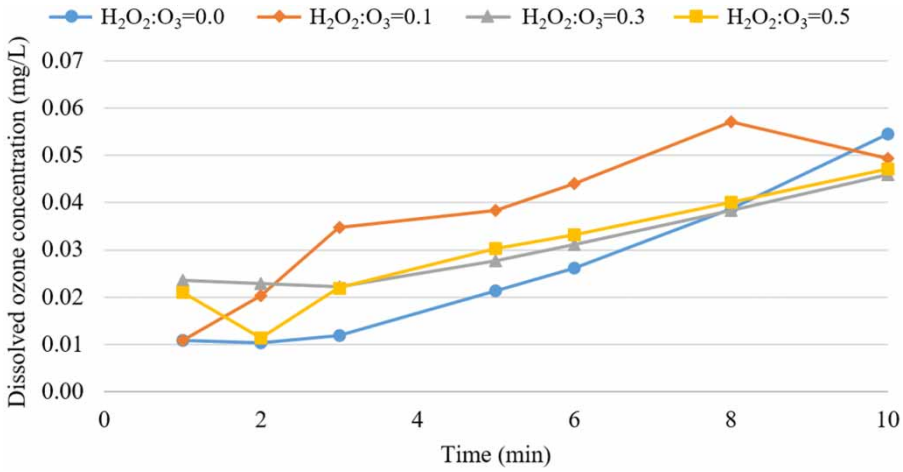

Figure 3 | Dissolved O_3 concentrations for various peroxone ratios.

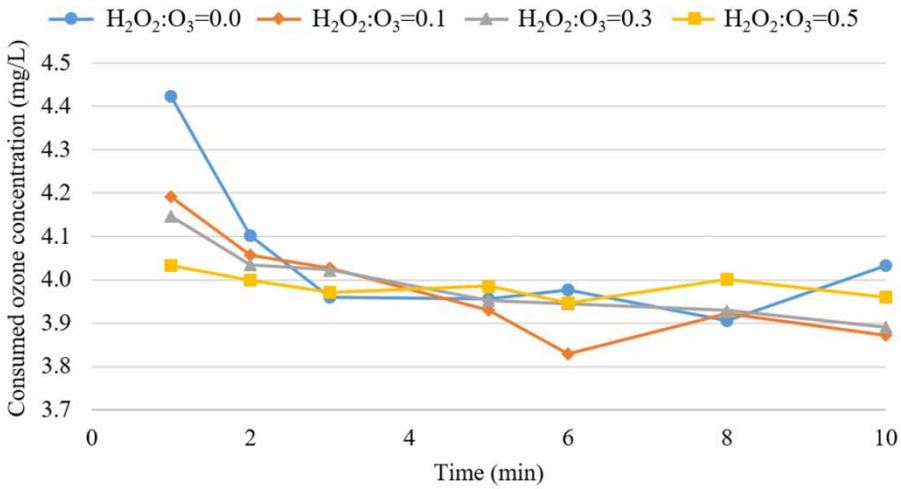

Figure 4 | Consumed O_3 concentrations at various peroxone ratios.

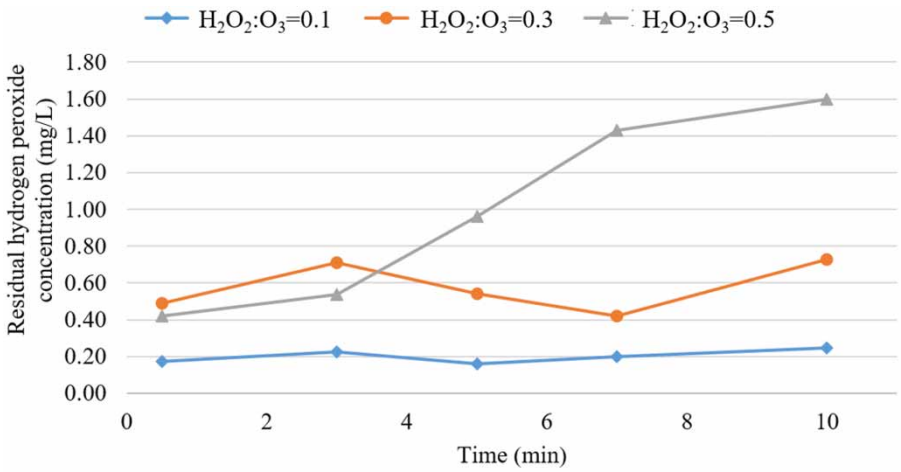

Figure 5 | Residual H_2O_2 concentrations along experiments for different peroxone ratios.

experiments at a contact time of 10 min and H_2O_2:O_3 ratio of 0.1. On the other hand, the average residual H_2O_2 concentration for H_2O_2:O_3 ratio of 0.3 peroxone ratio was around 0.5 mg/L. However, a residual H_2O_2 concentration of over 0.5 mg/L was observed even at the 4th min at a H_2O_2:O_3 ratio of 0.5.

Impact of H_2O_2:O_3 ratio on treatment performance

The experiments for determining the optimum peroxone ratio were conducted with 10 minutes contact time as depicted in Table 2. TOC removal efficiencies were below 10% during the experiments at each peroxone ratio. Geosmin removal efficiencies could not be evaluated depending on the quite low initial geosmin concentrations, which were close to the detection limit. Bromate concentrations were below detection limits for all the experiments (<2 μg/L). 2-MIB concentrations in the influent and effluent were between 75–83 and 32–52 ng/L, respectively, having a 2-MIB removal efficiency between 37.5 and 57.3% (Figure 6). High residual H_2O_2 concentration was observed in the reactor effluent during the experiments with an H_2O_2:O_3 ratio of 0.5. According to the results obtained from the pilot plant study, the ideal H_2O_2:O_3 ratio was determined as 0.3. The optimum peroxone ratio achieved 52.3% removal of 2-MIB, while sole ozonation only reached 37.5% removal of 2-MIB. The highest peroxone ratio (0.5) removed the compound by 57.3%, which shows the removal could be improved by 20% compared to sole ozonation.

Impact of contact time on treatment performance

Optimum contact time at the ideal H_2O_2:O_3 ratio was determined regarding 2-MIB removal efficiency (Figure 7). TOC removal efficiencies were below 9% during the experiments conducted at different peroxone ratios. According to the results, 2-MIB removal efficiency had a linear correlation with the contact time. Thus, the best removal efficiency (81%) was obtained at a contact time of 15 min by applying an O_3 dose of 4 mg/L. Overall results confirmed the significance of contact time on the 2-MIB removal efficiency.

CONCLUSIONS

Relation between the ozone consumption and reactor height was determined in this study. Results indicated that consumed ozone increased with increasing reactor height. In order to reach an ozone consumption ratio above 75%, at least 3 m reactor height was needed. TOC could not be removed by only ozone application.

Optimum operational conditions were investigated for the removal of 2-MIB by peroxone process. It is recommended that the residual O_3 concentration in the outlet of the reactor should not exceed 0.1 mg/L for operator safety reasons. Dissolved (residual) ozone concentration was below the limit residual O_3 concentration at all H_2O_2:O_3 ratios. Results show that addition of an ozone quenching chemical to the

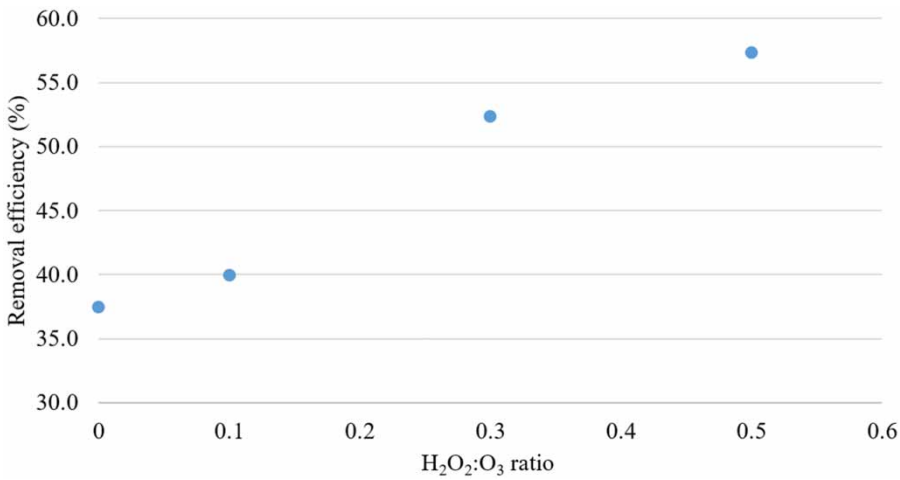

Figure 6 | 2-MIB removal efficiency at different peroxone ratios.

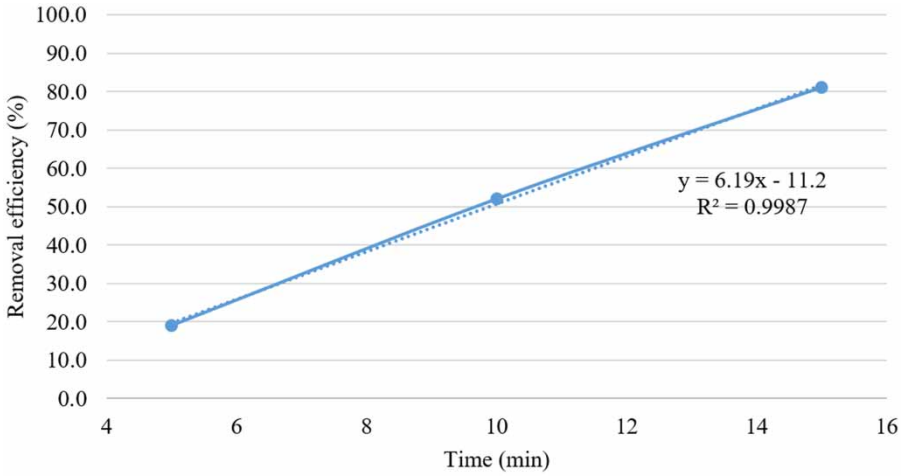

Figure 7 | 2-MIB removal efficiency at different contact times (H_2O_2:O_3 ratio: 0.3).

reactor is not necessary for any of the cases in this study. Besides, it is important not to exceed 0.5 mg/L of residual H_2O_2 concentration in the peroxone process. However, a residual H_2O_2 concentration of over 0.5 mg/L was measured at an H_2O_2:O_3 ratio of 0.5. Although the average residual H_2O_2 concentration with an H_2O_2:O_3 ratio of 0.3 was around 0.5 mg/L, the removal rate at H_2O_2:O_3 ratio of 0.3 showed a slight increase in comparison to an H_2O_2:O_3 ratio of 0.1. Therefore, the optimum H_2O_2:O_3 ratio was determined as 0.3 for the peroxone process in the tested conditions. A 2-MIB removal efficiency of 81% was achieved at the optimum H_2O_2:O_3 ratio with a contact time of 15 min. According to the results, the 2-MIB removal rate had a linear correlation with the contact time.

Authors suggest that further studies should be conducted for both ozone and peroxone processes regarding the formation of disinfection by-products. In addition to this, if the water treatment plant has a disinfection concern other than the taste and odor problem, virus and bacteria inactivation rates should be investigated with the peroxone process. Last but not least, the effect of temperature for the removal of taste and odor compounds in a full-scale water treatment should be taken into consideration.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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