



Removal of taste and odor causing compounds by UV/H₂O₂ treatment: effect of the organic and inorganic water matrix

Hohee Bang^{a,*}, Yness M. Slokar^b, Giuliana Ferrero^b, Joop C. Kruithof^c,
Maria D. Kennedy^b

^aWater Supply Business Division, K-water, 560 Sintanjin-ro, Daedeok-gu, Daejeon 306-711, Republic of Korea, Tel. +82 10 4350 5052; Fax: +82 43 230 4229; email: bang52@kwater.or.kr

^bDepartment of Environmental Engineering and Water Technology, UNESCO-IHE Institute for Water Education, Westvest 7, 2611 AX, Delft, The Netherlands, Tel. +31 15 2151 826; Fax: +31 15 2122 921; email: y.slokar@unesco-ihe.org (Y.M. Slokar), Tel. +31 15 2151 773; Fax: +31 15 2122 921; email: g.ferrero@unesco-ihe.org (G. Ferrero), Tel. +31 15 2151 774; Fax: +31 15 2122 921; email: m.kennedy@unesco-ihe.org (M.D. Kennedy)

^cWetsus, European Center of Excellence for Sustainable Water Technology, Oostergoweg 9, 8911 MA Leeuwarden, The Netherlands, Tel./Fax: +31 348473500; email: joop.kruithof@planet.nl

Received 7 March 2016; Accepted 7 April 2016

ABSTRACT

The occurrence of taste and odor in drinking water is the most common cause of consumer complaints. In this study, the effect of water matrix constituents (i.e. TOC, alkalinity, and NO₃⁻) on the removal of geosmin/2-MIB with UV/H₂O₂ treatment was assessed. Experiments were carried out with a collimated beam apparatus equipped with a low and a medium-pressure (MP) UV lamp, with UV doses ranging from 300 to 1,200 mJ/cm² with and without the addition of 4 mg/L H₂O₂. Results showed that the removal efficiency of geosmin/2-MIB with low pressure UV/H₂O₂ was inversely proportional to both the concentration of TOC and alkalinity in the synthetic water, as both parameters acted as scavengers of ·OH radicals. In the case of geosmin, the addition of 0.8 mg C/L of fulvic acid decreased the removal efficiency by 30%. The application of MPUV/H₂O₂ to water containing NO₃⁻ resulted in formation of NO₂⁻ which is also a ·OH radical scavenger. The presence of scavengers, in particular natural organic matter, causes significant increase in energy requirement due to the strong absorption properties for UV light and high reactivity with ·OH radicals.

Keywords: Geosmin; 2-MIB; UV photolysis; Advanced oxidation processes; Taste; Odor

1. Introduction

The presence of taste and odor (T&O) causing compounds in drinking water has been a major concern for water supply utilities depending for their production on surface water. Geosmin and 2-MIB have

been reported as the most commonly occurring T&O causing compounds. They cause an earthy and musty odor, respectively, with a threshold level for humans at very low concentration levels (10 ng/L). Their presence in water is closely associated with the natural growth and decay of algae. Although from neither of the compounds it has been proven that they cause a

*Corresponding author.

toxicological threat to humans, they negatively influence the public perception about the safety of tap water [1–3].

It is predicted that global climate changes may promote severe algal blooms in the future and these predictions are already starting to become true [4]. Conventional drinking water treatment has a limited removal capacity for geosmin/2-MIB, resulting in concentrations in treated water well above the odor threshold [5–7]. Therefore, the application of additional treatment steps should be pursued to remove them from water prior to distribution.

Advanced oxidation processes (AOPs) have demonstrated to be effectively degrading recalcitrant micropollutants including the two algal-driven odorants. During AOP treatment, hydroxyl radicals, highly reactive non-selective oxidants are generated, which have the ability to degrade organic pollutants, and ultimately mineralize them into carbon dioxide and water [7]. Among various AOP technologies, the combination of UV and H_2O_2 is one of the most widely studied methods to mitigate T&O problems [8–11].

The effectiveness of UV based AOPs to degrade target compounds is impacted by the organic and inorganic water matrix. Among various water quality parameters, TOC and alkalinity in particular have been associated with a reduced efficiency of the UV/ H_2O_2 process. Not only do they compete for UV light and have a high affinity for reacting with hydroxyl radicals [12–15], but they are also present in fresh water in concentrations several orders of magnitude higher than the micropollutants of concern. Therefore, prior to the implementation of UV/ H_2O_2 treatment, it is of great importance to determine the influence of the background water matrix on the removal efficiency of the two odorants. This issue has not been extensively addressed in the past, so further research is needed.

An additional concern associated with UV/ H_2O_2 treatment when employing medium pressure (MP) UV lamps is the photolysis of nitrate. Photolysis of nitrate-rich water causes the formation of nitrite [10,16,17] and the formation of genotoxic compounds [18]. Nitrite reacts with hydroxyl radicals causing a negative impact on the removal of the target material [19], while genotoxic compounds may have a negative health impact [20].

The main goal of this research was to study the impact of water quality parameters representative for the water matrix (TOC, alkalinity and nitrate) on the removal of T&O causing compounds geosmin and 2-MIB by UV/ H_2O_2 treatment.

2. Materials and methods

2.1. Materials

The synthetic water used for the experiments was representative for the water quality characteristics of the Si-Heung water treatment plant (SH WTP) in Korea, where UV/ H_2O_2 treatment is planned to be introduced. The target compounds, geosmin and 2-MIB (Supelco), were spiked into Milli-Q water obtaining concentrations of 230 ± 3 ng/L and 224 ± 10 ng/L, respectively. To investigate the impact of the characteristics and concentration of natural organic matter (NOM) on UV/ H_2O_2 treatment, four synthetic waters were prepared adding either humic acid (HA) or fulvic acid (FA) in two concentrations. The principal water quality characteristics of each model water are shown in Table 1. In addition to NOM, methanol applied as a solvent in the geosmin/2-MIB standard solution contributed to the TOC content in the order of 0.6 mg C/L. Stock solutions of HA and FA were prepared in concentrations of 500 and 220 mg C/L as TOC, respectively. By diluting with Milli-Q water the TOC concentrations of the resulting solutions were in the range of $1.3\text{--}2.5 \pm 0.1$ mg C/L.

Sodium hydrogen carbonate (stock solution of 7,000 mg/L) was used as a source of alkalinity; hydrogen peroxide stock solution was prepared at a concentration of 250 mg/L. Sodium thiosulfate (stock solution of 20,000 mg/L) was used to quench excess H_2O_2 .

2.2. Methodology

For this research two types of collimated beam apparatus, with a low pressure (LP) UV lamp or a MP UV lamp and a 100 mL petri-dish (internal diameter of 56 mm), with and without cover, placed on a circular stirrer fixed with an adjustable stand were employed. In order to minimize the influence of natural UV light from the sun, the external windows were covered with dark color sheets. Prior to each experiment, the UV lamp in the collimated beam reactor was warmed up for at least 30 min to ensure a stable output. Thereafter, the UV irradiance at the center of the light beam was measured and regulated to 0.2 kW/cm² for LPUV and 2 kW/cm² for MPUV by controlling the height of the adjustable stand. Prior to each experiment the petri factor was determined according to Bolton and Linden [21]. The volatilization loss of geosmin/2-MIB during the exposure time was investigated to determine the net degradation rate resulting from the oxidation process by hydroxyl radicals. For the AOP experiments, prior to each UV collimated beam test 4 mg/L of hydrogen peroxide

Table 1
Characteristics of model water used for investigation of TOC effect

Model water	Humics (Low conc.)	Humics (High conc.)	Fulvics (Low conc.)	Fulvics (High conc.)
TOC (mg/L)				
NOM origin	0.7	1.8	0.8	1.9
Total ^a	1.3 ± 0.1	2.4 ± 0.1	1.4 ± 0.1	2.5 ± 0.1
UV absorbance at 254 nm (cm ⁻¹)	0.086	0.194	0.027	0.065
SUVA (L/mg/m)	6.1	8.1	1.9	2.6
Alkalinity (mg/L as CaCO ₃)	<5	<5	0	0
Turbidity (NTU)	1.2	2.3	<0.1	<0.1

^a0.6 mg/L is due to methanol contained in the commercial solution of geosmin and 2-MIB.

was added to the 100 mL petri-dish containing the model water. After the experiments residual hydrogen peroxide was completely quenched by addition of an excess of sodium thiosulfate; then the sample was transferred into a 100 mL incubation bottle and stored at 4 °C until being analyzed.

2.3. Analytical methods

The two target compounds, geosmin and 2-MIB, were analyzed by solid-phase microextraction followed by gas chromatography–mass spectrometry (GC/MS). The concentration of hydrogen peroxide was determined by two methods: the iodometric method for the relatively high concentration in the stock solution and the triiodide method for the low concentrations in the synthetic water. The intensity of the UV radiation at a wavelength of 254 nm was determined using an IL 1700 radiometer equipped with a SED 240#6602 sensor (International Light, USA). The UV spectrum in the range of 200–300 nm was measured in a 1 cm path length quartz cell UV-2510 PC spectrophotometer (Shimadzu, Japan) at room temperature (20 ± 1 °C). The TOC concentration in a solution was determined as non-purgeable organic carbon by a TOC-L analyzer (Shimadzu, Japan). Alkalinity was determined by titration with 0.02 mol/L hydrochloric acid according to Standard Methods (SM 2320); and were expressed as mg/L of calcium carbonate equivalents. For the determination of nitrate and nitrite a DR 5000 UV/vis Spectrophotometer (Hach, USA) was employed with LCK339 nitrate cuvette test and LCK341 nitrite cuvette test, respectively.

3. Results and discussion

3.1. Volatilization loss of geosmin/2-MIB by UV irradiation

The volatilization rate constants of geosmin and 2-MIB were determined carrying out experiments in an

open and covered petri-dish. As expected, the volatilization loss was proportional to the exposure time. 2-MIB showed to have a slightly higher volatility than geosmin; explained by the higher Henry's constant for 2-MIB of 0.0027 atm m³/mol at 20 °C, compared to 0.0023 atm m³/mol for geosmin [22]. Applying a petri-dish cover, volatilization loss of geosmin decreased from 37 to 7% during an irradiation time of 4 h (corresponding to the maximum UV dose of 1,200 mJ/cm²). Under the same conditions the volatilization loss of 2-MIB decreased from 45 to 14%. Based on the results, the pseudo-first-order volatilization rate constants (k_v) for both odorants were calculated. Since the experiments to determine the effect of NOM on the removal of the two compounds were carried out without a petri-dish cover, k_v values of 0.1156 h⁻¹ for geosmin and 0.1480 h⁻¹ for 2-MIB were used for the interpretation of the NOM related results. For the rest of the experiments (effect of alkalinity and NO₃⁻), the k_v values for a covered petri-dish were used: 0.0157 and 0.0374 h⁻¹ for geosmin and 2-MIB, respectively. The apparent oxidation rate constants (k_o) were calculated by subtracting the determined k_v from the observed total degradation rate constant (k_t) (Eq. (1)):

$$-\frac{d[C]}{dt} = k_t[C] = (k_v + k_p + k_o) \times [C] \\ = \frac{d[V]}{dt} + \frac{d[P]}{dt} + \frac{d[O]}{dt} \quad (1)$$

where [C] is the concentration of the studied compound (mol/L), k_t is the pseudo-first-order total degradation rate constant (s⁻¹), k_v is the pseudo-first-order volatilization rate constant (s⁻¹), k_p is the pseudo-first-order photolysis rate constant (s⁻¹), k_o is the apparent oxidation rate constant (s⁻¹), [V] is the concentration of volatilized compound (mol/L), [P] is the concentration of photolyzed compound (mol/L), and [O] is the concentration of oxidized compound (mol/L).

3.2. LPUV and MPUV photolysis of geosmin/2-MIB

In order to investigate the contribution of direct photolysis to the removal of geosmin and 2-MIB, experiments were conducted without the addition of H_2O_2 with LPUV and MPUV. As shown in Fig. 1, almost no destruction by photolysis with LPUV was observed. This confirms earlier research reporting negligible removal efficiency by LPUV photolysis up to a UV dose of $1,000 \text{ mJ/cm}^2$ [9] and even $8,000 \text{ mJ/cm}^2$ [10], due to the low molar absorption coefficient of geosmin and 2-MIB at 254 nm. MPUV photolysis showed some degradation of the recalcitrant odorants due to the fact that the molar absorption coefficients of geosmin and 2-MIB gradually increase below 250 nm. Approximately 10 and 18% of geosmin and 2-MIB, respectively, were removed at a MPUV dose of $1,200 \text{ mJ/cm}^2$ (see Fig. 1).

From the MPUV experiment the pseudo-first-order photolysis constants (k_p) were determined to be 0.9527 and 1.2664 h^{-1} for geosmin and 2-MIB, respectively. Together with the determined k_v values for volatilization loss, the determined k_p values were used to calculate the apparent oxidation rate constants (k_o) by subtracting them from the observed total removal efficiency (k_t).

3.3. Degradation of geosmin/2-MIB by LPUV/ H_2O_2 treatment

3.3.1. Effect of TOC concentration on geosmin/2-MIB degradation by LPUV/ H_2O_2 treatment

In order to study the effect of the TOC concentration on the degradation of geosmin and 2-MIB by LPUV/ H_2O_2 treatment, synthetic water was prepared with two types of NOM, i.e. HA and FA at two concentrations.

Regardless of the synthetic water composition the degradation efficiency of micropollutants was

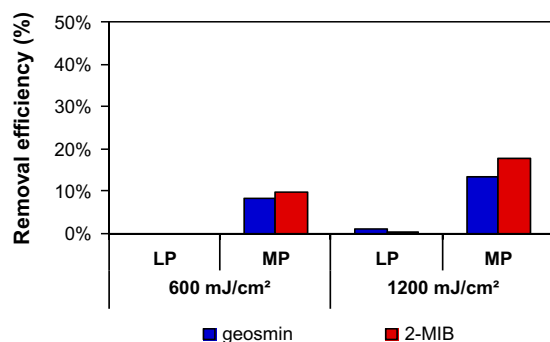


Fig. 1. Removal of geosmin/2-MIB by direct photolysis with LPUV and MPUV.

proportional to the UV dose. Increasing the NOM concentration caused a decreasing degradation of geosmin and 2-MIB. In this study, HA and FA had the same impact on the removal efficiency. The total degradation rate as a function of the irradiation time is presented in Fig. 2.

It should be noted that total degradation observed after UV/ H_2O_2 treatment is not only due to hydroxyl radical oxidation but to photolysis and volatilization loss, as well. Therefore, the contribution of these two processes must be subtracted from the total removal in order to establish the contribution of hydroxyl radical oxidation. The UV absorbance of constituents, i.e. NOM, H_2O_2 , and geosmin/2-MIB, in the model water was measured at 254 nm.

At 254 nm the UV light was predominantly (over 97%) absorbed by the NOM, with only a marginal contribution of either H_2O_2 , odorants and/or the solvent methanol. The absorption of the two micropollutants was so low that the effect of LPUV photolysis on their degradation was negligible, so only the loss by volatilization was subtracted from the observed total degradation. Therefore, the apparent oxidation rate constant (k_o) was obtained by subtracting the volatilization rate constant (k_v) from the observed total degradation rate constant (k_t) (Table 2).

As shown in Table 2, for the same synthetic water all k_o values were much higher than the corresponding k_v values, regardless of the use of a petri-dish cover, so the main removal mechanism of the two micropollutants was $\cdot\text{OH}$ radical oxidation. The k_o value decreased with increasing TOC content, regardless of the type of NOM used. The effect of HA on the oxidation of odorants was slightly higher than of FA. In addition, geosmin was more readily oxidized by $\cdot\text{OH}$ radicals compared to 2-MIB. As expected both the concentration and the character of the NOM had a strong impact on the geosmin and 2-MIB degradation. First, the absorbance of NOM at 254 nm was considerably higher than that of the taste and odor constituents in the synthetic water. Therefore, the irradiance time to achieve the desired UV dose was strongly determined by the NOM concentration. For instance, the irradiance time for the synthetic water with a FA content of 1.9 mg C/L was 27% longer than for the synthetic water with a FA content of 0.8 mg C/L to achieve the same UV dose. The impact of the NOM concentration is also reflected in a 80% difference of k_o values between the synthetic water with 0.8 and 1.9 mg C/L , respectively.

The difference of k_o values in the FA model water and in the HA model water may be caused predominantly by the character of the two NOM types. The UV

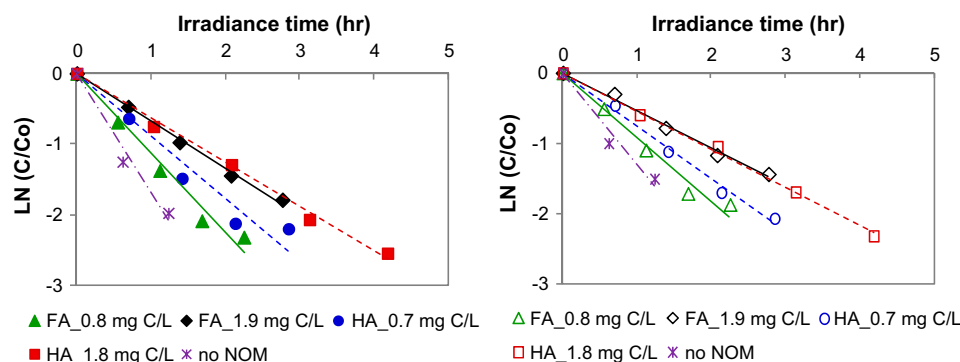


Fig. 2. Observed total degradation rate of geosmin (left) and 2-MIB (right) with and without NOM.

Table 2

Calculation of apparent oxidation rate constants of geosmin/2-MIB in presence and absence of NOM

Model water	Total degradation rate constant, k_t (h^{-1})		Volatilization rate constant, k_v (h^{-1})		Oxidation rate constant, k_o (h^{-1})	
	Geosmin	2-MIB	Geosmin	2-MIB	Geosmin	2-MIB
no NOM	1.69	1.30	0.02 ^a	0.04 ^a	1.67	1.26
FA_0.8	1.13	0.91	0.12 ^b	0.15 ^b	1.01	0.76
FA_1.9	0.67	0.54			0.55	0.39
HA_0.7	0.88	0.75			0.76	0.61
HA_1.8	0.63	0.54			0.51	0.40

^a k_v of covered petri-dish.

^b k_v of uncovered petri-dish.

absorbance at a wavelength of 254 nm and the SUVA of FA are much lower than of HA.

The total removal of the odorants was subdivided into the removal due to volatilization and oxidation, based on the data presented in Figs. 1 and 2, and Table 2 (Fig. 3).

The removal efficiency of odorants was inversely proportional to the NOM content (Fig. 3). In the absence of NOM geosmin was oxidized by $\cdot\text{OH}$ radicals for 71% at a UV dose of 300 mJ/cm and 4 mg/L H_2O_2 . However, addition of 0.8 mg C/L of FA decreased the removal efficiency by 30%, while increasing the FA content to 1.9 mg C/L caused an additional decrease of 10%. 2-MIB degradation showed the same trend.

The geosmin and 2-MIB degradation as a function of irradiance time (Fig. 2) is impacted by both the absorption of UV light and scavenging of $\cdot\text{OH}$ by the NOM. The geosmin and 2-MIB degradation as a function of the UV dose is impacted by the hydroxyl radical scavenging of the NOM only (Fig. 4).

Similarly, as for the time-based oxidation rate constant k_o , the UV dose-based oxidation rate

constant $k_{o,uv}$ decreased with increasing TOC concentration. In the absence of NOM, the $k_{o,uv}$ for geosmin was $3.4 \times 10^{-3} \text{ cm}^2/\text{mJ}$. By FA addition of 0.8 mg C/L, the $k_{o,uv}$ decreased to $1.5 \times 10^{-3} \text{ cm}^2/\text{mJ}$ which was further reduced to $1.1 \times 10^{-3} \text{ cm}^2/\text{mJ}$ by FA addition of 1.9 mg C/L. Similarly, addition of HA resulted in a decreased oxidation rate for both odorants. There was no significant difference in terms of $\cdot\text{OH}$ radical scavenging effect between the two types of NOM used in this study. A smaller $k_{o,uv}$ indicates a lower degradation of the micropollutant by reaction with $\cdot\text{OH}$ radicals formed by photolysis of H_2O_2 . One major reason is the presence and nature of TOC present in synthetic water, since TOC is a both a UV absorber and a $\cdot\text{OH}$ radical scavenger. According to Kutschera et al. [10], by addition of 1 mg C/L TOC, $k_{o,uv}$ values of geosmin and 2-MIB decreased by at least 60%. This is in agreement with the results presented in this paper.

From the two T&O causing compounds of interest, geosmin showed a higher UV dose-based oxidation rate than 2-MIB.

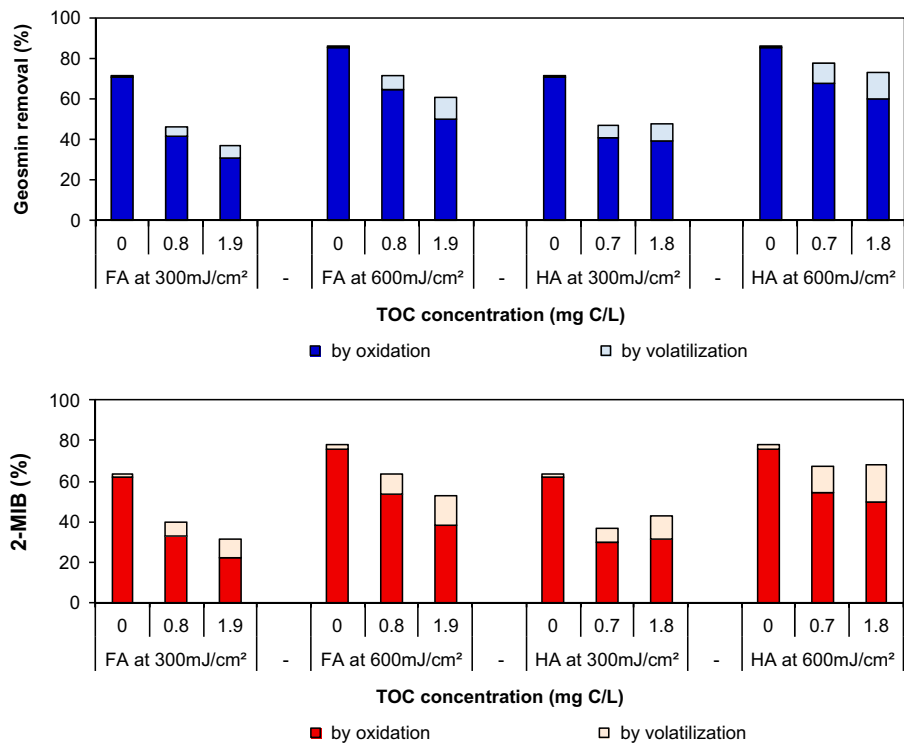


Fig. 3. Removal efficiency of geosmin (above) and 2-MIB (below) due to oxidation and volatilization with and without NOM.

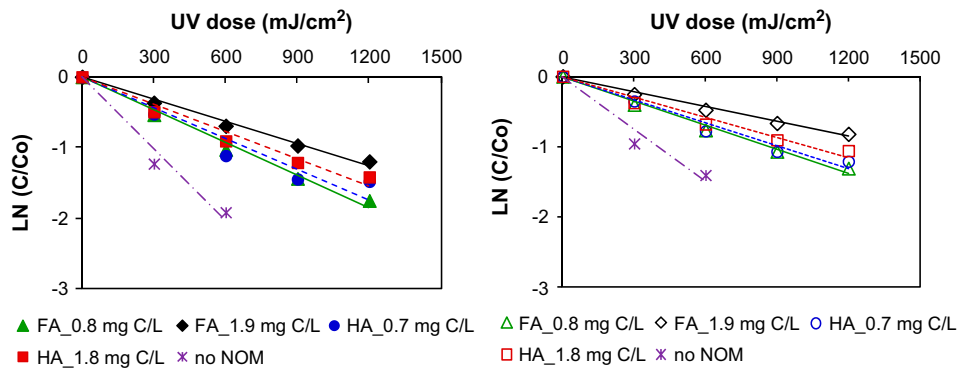


Fig. 4. UV dose-based oxidation rate of geosmin (left) and 2-MIB (right) with and without NOM.

3.3.2. Effect of alkalinity on geosmin/2-MIB degradation by LPUV/H₂O₂ treatment

In order to study the effect of alkalinity on the removal of geosmin and 2-MIB by LPUV/H₂O₂ treatment, Milli-Q water was spiked with NaHCO₃ at 109 ± 2 mg/L as CaCO₃. The pH was adjusted to 7.3 so HCO₃⁻ was the prevailing fraction causing alkalinity. Figs. 5 and 6 depict the results of these experiments (the values shown are corrected for the volatilization loss).

Increasing the alkalinity decreased the oxidation rate of T&O causing compounds by ·OH radical oxidation. Without alkalinity the UV dose-based first-order oxidation rate constant $k_{o,uv}$ of geosmin was 0.0034 cm²/mJ (Fig. 5). In the presence of 109 mg/L alkalinity, the rate constant decreased to 0.0019 cm²/mJ. As a result, at a UV dose of 300 mJ/cm² the removal efficiency of geosmin was reduced from 71 to 45% (Fig. 6). Similarly, the $k_{o,uv}$ value of 2-MIB was decreased for 48% by adding HCO₃⁻. One of the

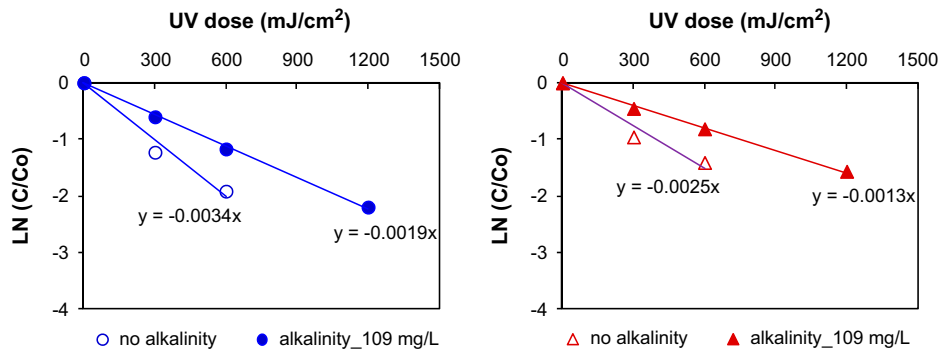


Fig. 5. UV dose-based oxidation rate constants of geosmin (left) and 2-MIB (right) with and without alkalinity. Milli-Q water with 231 ± 1 ng/L geosmin and 219 ± 10 ng/L 2-MIB; H_2O_2 dose: 4 mg/L.

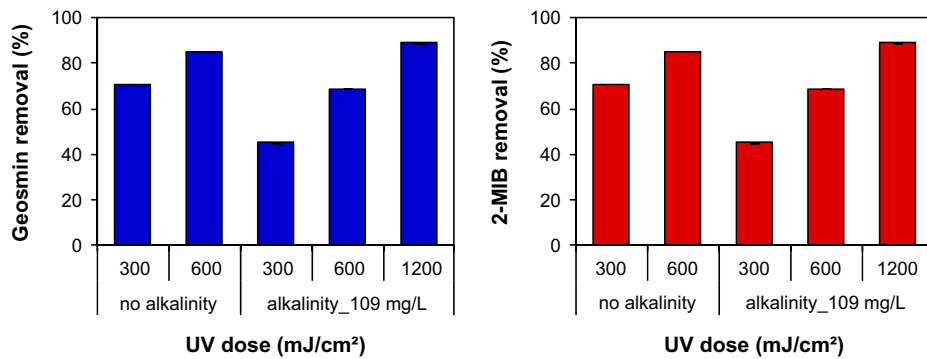


Fig. 6. Removal efficiency of geosmin (left) and 2-MIB (right) with and without alkalinity.

reasons for the reduced removal efficiency with increased alkalinity is the reactivity of HCO_3^- toward $\cdot OH$ radicals. The second-order rate constant k_{OH} of HCO_3^- oxidation by $\cdot OH$ radicals was reported to be $3.9 (10^8 \text{ L/mol s})$ by Buxton et al. [23]. Additionally, the HCO_3^- concentration was six orders of magnitude higher than the concentrations of the studied odorants, so the majority of the $\cdot OH$ radicals was consumed by bicarbonate. This result is in agreement with earlier research by Kutschera et al. [10]. In their study addition of 2 mM HCO_3^- caused a decrease of $k_{o,uv}$ by approximately 50% for both, geosmin and 2-MIB. He et al. [14] selected microcystin-LR, another type of algal-driven intermediate, as a target material to investigate the impact of background water matrix and found that the addition of 50 mg/L of HCO_3^- as $CaCO_3$ decreased the removal efficiency by 35%.

3.4. Effect of nitrate on geosmin/2-MIB degradation by MPUV/ H_2O_2 treatment

In order to study the effect of NO_3^- on the removal of geosmin and 2-MIB, MPUV collimated

beam experiments were carried out. Fig. 7 depicts results of these experiments; the values shown are corrected for volatilization loss.

The presence of NO_3^- decreased the oxidation rate of T&O causing compounds with $\cdot OH$ radicals (Fig. 8). In the presence of 18 mg/L NO_3^- , the UV dose-based oxidation rate constant $k_{o,uv}$ decreased by 33 and 25% for geosmin and 2-MIB, respectively.

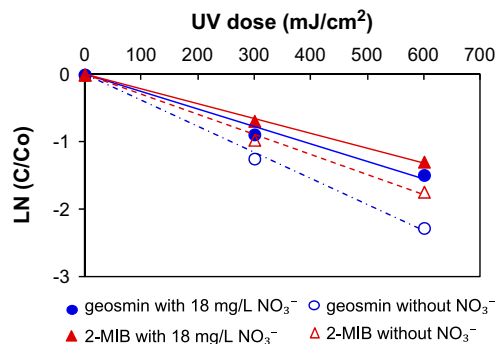


Fig. 7. UV dose-based oxidation rate constant with and without NO_3^- .

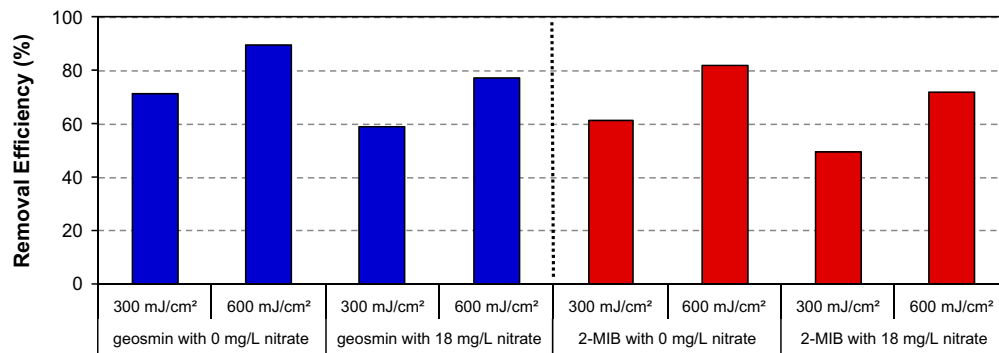
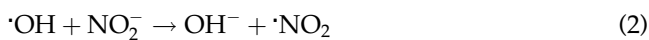


Fig. 8. Removal efficiency of geosmin (left) and 2-MIB (right) with and without NO₃⁻.

The decreased oxidation rate reduced the removal efficiency of geosmin from 71 to 59% at a UV dose of 300 mJ/cm² (Fig. 8). Similarly, the removal efficiency of 2-MIB was decreased by 10% at the same UV dose. At a higher UV dose of 600 mJ/cm², the removal efficiency decreased by an additional 13% for both, geosmin and 2-MIB. MPUV photolysis of NO₃⁻ producing NO₂⁻ might be one of the reasons of the reduced geosmin and 2-MIB removal efficiency with MPUV/H₂O₂ treatment. According to Coddington et al. [19], NO₂⁻ reacts with ·OH radical following Eq. (2); with a rate constant of 1 × 10¹⁰ L/mol s:



The photolysis of NO₃⁻ by MPUV treatment was described by Mack and Bolton [16]: as an intermediate, peroxyxynitrite anion (ONOO⁻), is formed (Eq. (3)), which reacts with ·OH. The rate constant of the reaction of ONOO⁻ with ·OH is 5 × 10⁹ L/mol s (Eq. (4)):



According to Mack and Bolton [16], the scavenging effect of the formed NO₂⁻ during the MPUV/H₂O₂ treatment becomes increasingly important in treatment of NO₃⁻ rich water, but is insignificant in the presence of organic scavengers.

Treatment of NO₃⁻ containing water with MPUV resulted in the formation of the undesired by-product, nitrite (NO₂⁻). The concentration of the NO₂⁻ formed is shown in Fig. 9; the NO₂⁻ formation was linearly proportional to the UV dose. The NO₂⁻ formation was considerably less than the US EPA guideline, but surpassed the Dutch standard for drinking water of 100 µg/L even at a relatively low UV dose of 300 mJ/cm². This result is in line with literature reporting that the application of MPUV for NO₃⁻ rich water was

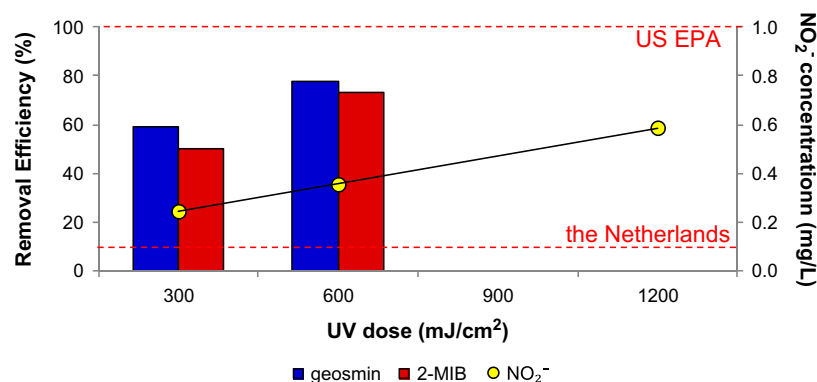


Fig. 9. NO₂⁻ formation during MPUV/H₂O₂ treatment. Milli-Q water with geosmin of 221 ± 16 ng/L and 2-MIB of 217 ± 6 ng/L; H₂O₂ dose: 4 mg/L.

susceptible to exceed the stringent regulatory limit for NO_2^- (Zoschke et al. [11]).

In conclusion, the formation of NO_2^- should be carefully monitored when MPUV-based AOP is implemented for NO_3^- -rich source waters. The installation of post-treatment to remove formed inorganic and organic by-products should be considered.

4. Conclusion

In this collimated beam study, UV/ H_2O_2 oxidation was investigated for the removal of two odorants, geosmin/2-MIB. Volatilization caused a significant contribution to the removal, especially in uncovered petri-dishes. The odorants were hardly degraded by LPUV photolysis even at a UV dose of $1,200 \text{ mJ}/\text{cm}^2$. At the same UV dose, by MPUV photolysis, 10 and 18% of geosmin and 2-MIB, respectively, were removed by photolysis. The presence of NOM had a negative effect on the removal of geosmin/2-MIB by LPUV/ H_2O_2 and the removal efficiency was inversely proportional to the concentration of TOC present in the synthetic water. The same effect was caused by alkalinity (in the form of HCO_3^-). The application of MPUV/ H_2O_2 treatment on the model water containing NO_3^- resulted in formation of NO_2^- , another scavenger. The presence of scavengers, in particular NOM, caused a significant increase in energy consumption due to the strong absorption properties and their high reactivity with $\cdot\text{OH}$ radicals.

Acknowledgments

This project was financed by K-water. The authors would like to thank Mr Bram Martijn from PWN Technologies and Mr Paul Buijs from Berson Milieutechniek BV for their kind support during this study.

References

- [1] I.H. Suffet, D. Khiari, A. Bruchet, The drinking water taste and odor wheel for the millennium: Beyond geosmin and 2-methylisoborneol, *Water Sci. Technol.* 40 (1999) 1–13.
- [2] F. Juttner, S.B. Watson, Biochemical and ecological control of geosmin and 2-methylisoborneol in source waters, *Appl. Environ. Microbiol.* 73 (2007) 4395–4406.
- [3] J.L. Graham, K.A. Loftin, M.T. Meyer, A.C. Ziegler, Cyanotoxin mixtures and taste-and-odor compounds in cyanobacterial blooms from the midwestern United States, *Environ. Sci. Technol.* 44 (2010) 7361–7368.
- [4] H.W. Paerl, J. Huisman, Climate: Blooms like it hot, *Science* 320 (2008) 57–58.
- [5] D. Cook, G. Newcombe, P. Sztajn bok, The application of powdered activated carbon for mib and geosmin removal: Predicting pac doses in four raw waters, *Water Res.* 35 (2001) 1325–1333.
- [6] D. Bruce, P. Westerhoff, A. Brawley-Chesworth, Removal of 2-methylisoborneol and geosmin in surface water treatment plants in Arizona, *J. Water Supply* 51 (2002) 183–197.
- [7] R. Srinivasan, G.A. Sorial, Treatment of taste and odor causing compounds 2-methyl isoborneol and geosmin in drinking water: A critical review, *J. Environ. Sci.* 23 (2011) 1–13.
- [8] K.G. Linden, C.M. Sharpless, S.A. Andrews, K.Z. Atasi, V. Korategere, M. Stefan, I.H.M. Suffet, Innovative UV Technologies to Oxidize Organic and Organoleptic Chemicals, AWWaRF and US EPA, Denver, CO and Washington DC, 2004.
- [9] E.J. Rosenfeldt, K.G. Linden, B. Melcher, UV and UV/ H_2O_2 treatment of methylisoborneol (MIB) and geosmin in water, *J. Water Supply Res. Technol. AQUA* 54 (2005) 423–434.
- [10] K. Kutschera, H. Börnick, E. Worch, Photoinitiated oxidation of geosmin and 2-methylisoborneol by irradiation with 254 nm and 185 nm UV light, *Water Res.* 43 (2009) 2224–2232.
- [11] K. Zoschke, N. Dietrich, H. Börnick, E. Worch, UV-based advanced oxidation processes for the treatment of odour compounds: Efficiency and by-product formation, *Water Res.* 46 (2012) 5365–5373.
- [12] G. Melin, Treatment Technologies for Removal of Methyl Tertiary Butyl Ether (MTBE) from Drinking Water, second ed., NWRI, Fountain Valley, CA, 2000.
- [13] S. Parsons, Advanced Oxidation Process for Water and Wastewater Treatment, IWA Publishing, London, 2004.
- [14] X. He, M. Pelaez, J.A. Westrick, K.E. O'Shea, A. Hiskia, T. Triantis, T. Kaloudis, M.I. Stefan, A.A. de la Cruz, D.D. Dionysiou, Efficient removal of microcystin-LR by UV-C/ H_2O_2 in synthetic and natural water samples, *Water Res.* 46 (2012) 1501–1510.
- [15] B.J. Martijn, A.L. Fuller, J.P. Malley, J.C. Kruithof, Impact of IX-UF pretreatment on the feasibility of UV/ H_2O_2 treatment for degradation of NDMA and 1,4-dioxane, *Ozone: Sci. Eng.* 32 (2010) 383–390.
- [16] J. Mack, J.R. Bolton, Photochemistry of nitrite and nitrate in aqueous solution: A review, *J. Photochem. Photobiol., A* 128 (1999) 1–13.
- [17] C.M. Sharpless, K.G. Linden, UV photolysis of nitrate: Effects of natural organic matter and dissolved inorganic carbon and implications for UV water disinfection, *Environ. Sci. Technol.* 35 (2001) 2949–2955.
- [18] A.J. Martijn, J.C. Kruithof, UV and UV/ H_2O_2 treatment: The silver bullet for by-product and genotoxicity formation in water production, *Ozone Sci. Eng.* 34 (2012) 92–100.
- [19] J.W. Coddington, J.K. Hurst, S.V. Lyman, Hydroxyl radical formation during peroxyxynitrous acid decomposition, *J. Am. Chem. Soc.* 121 (1999) 2438–2443.
- [20] B.J. Martijn, J.C. Kruithof, R.M. Hughes, R.A. Mastan, A.R. Van Rompay, J.P. Malley, Induced genotoxicity in nitrate-rich water treated with medium-pressure

- ultraviolet processes, J.—Am. Water Works Assoc. 107 (2015) E301–E312.
- [21] J.R. Bolton, K. Linden, Standardization of methods for fluence (UV dose) determination in bench-scale UV experiments, *J. Environ. Eng.* 129 (2003) 209–215.
- [22] P. Ömür-Özbek, A.M. Dietrich, Determination of temperature-dependent Henry's Law constants of odorous contaminants and their application to human perception, *Environ. Sci. Technol.* 39 (2005) 3957–3963.
- [23] G.V. Buxton, C.L. Greenstock, W.P. Helman, A.B. Ross, Critical review of rate constants for reactions of hydrated electrons chemical kinetic data base for combustion chemistry. Part 3: Propane, *J. Phys. Chem. Ref. Data* 17 (1988) 513–886.