

Removal and transformation of odorous aldehydes by UV/H₂O₂

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ABSTRACT

Removal of odorous aldehydes by UV/H₂O₂ was compared to removal of geosmin and 2-MIB by the same process. Odour transformation was investigated by sensory test and by-products were monitored by a carbonyl derivatization method. Heptadienal, decadienal and nonadienal were removed faster than geosmin and 2-MIB. The primary mechanism was the direct UV photolysis in the UV/H₂O₂ process. In sensory tests, new odours such as chalky or sweet odours were produced while the initial odour intensity of fishy/grassy-smelling aldehydes was reduced with increasing exposure time to UV/H₂O₂. New carbonyl compounds were detected from the UV photolysis of nonadienal and were not removed by further UV irradiation, which was thought to be related to production of new odours. Results indicate that new types of odour were produced from the oxidation of odorous aldehydes, and consequently, sensory tests coupled with chemical analysis should be considered in designing an oxidation process to control recalcitrant odorants.

Key words | aldehyde, AOP, odour, UV/H₂O₂, UV photolysis

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INTRODUCTION

Recently, more interest has been focused on drinking water aesthetic issues. This trend indicates that consumers demand 'more pleasant' or 'more tasty' drinking water as well as safe water (Devesa *et al.* 2004; Khiari 2004; Burlingame & Mackey 2007; Liang *et al.* 2007). Consumer comparison of tap water to bottled water may intensify this trend. Various efforts have been made to remove recalcitrant odorants in drinking water to prevent complaints and meet consumer standards about drinking water quality. Many researchers reported that advanced oxidation processes (AOPs), which involve hydroxyl radicals, efficiently reduce earthy/musty odorants (geosmin and 2-MIB) in drinking water (Rosenfeldt *et al.* 2005; Paradis & Hoffman 2006; Westerhoff *et al.* 2006; Jo 2008). Odorous aldehydes such as nonadienal and heptadienal are mostly produced from algae and can cause off-flavour in drinking water, especially in the case of insufficient chlorination (Burlingame *et al.* 1992; Andersson *et al.* 2005). Nonadienal had a greater reaction rate constant with hydroxyl radical

than geosmin and 2-MIB (Peter & Von Gunten 2007). However, it was reported that some algal metabolites were transformed into new types of odour by oxidation (Dietrich *et al.* 1995), and fruity smelling aldehydes were produced from the ozonation of drinking water (Anselme *et al.* 1988; Suffet *et al.* 1995; Bruchet & Duguet 2004). Low molecular weight aldehydes, which are possible products of oxidation of unsaturated aldehydes, were considered to be related to off-flavour events (Fabrellas *et al.* 2004).

In this research, removal of odorous aldehydes by UV/H₂O₂ was compared with that of geosmin and 2-MIB, and odour transformation was investigated by sensory test and pentafluorobenzyl-hydroxylamine hydrochloride (PFBHA) derivatization method to detect carbonyls. The UV/H₂O₂ process performs by direct UV photolysis and hydroxyl radical reaction (Cotton & Collins 2006). Hydroxyl radical produced from the UV photolysis of hydrogen peroxide plays a key role for many reactions. However, for the compounds that readily absorb UV, direct

UV photolysis may be the main mechanism in the removal of the compounds by the UV/H₂O₂ process (Nicole *et al.* 1999; Qiao *et al.* 2005; Jo 2008). The objectives of the research were: 1) to compare removal rates of fishy/grassy smelling aldehydes with geosmin/2-MIB in the UV/H₂O₂ process; 2) to elucidate the main mechanism of odorous aldehyde removal in the UV/H₂O₂ process; 3) to investigate how odour intensities and descriptors change during the reaction with UV/H₂O₂; and 4) to detect intermediates and final products.

MATERIALS AND METHODS

Four types of aldehyde were selected from the typical algae-related fishy/grassy odorants as well as geosmin and 2-MIB. Compounds used in this research were: *trans*-2,*cis*-6-nonadienal (Aldrich, 92%, CAS no. 552-48-2), hexanal

(Aldrich, 98%, CAS no. 66-25-1), *trans*-2,*trans*-4-decadienal (TCI, 98%, CAS no. 25152-84-5), *trans*-2,*trans*-4-heptadienal (TCI, 90%, CAS no. 4313-03-5), geosmin (Sigma, 98%, CAS no. 16423-19-1), 2-MIB (Supelco, 99.9%, CAS no. 2371-42-8). Structures and odour properties of these compounds are shown in Table 1. Experiments were performed with a 253.7 nm wavelength UV lamp of 7.2 mW cm⁻² intensity (Rayonet RPR-100) with quartz reactors. H₂O₂ concentration of 6 mg l⁻¹ was used on the basis of the optimal range of H₂O₂ dosage in previous research (Cotton & Collins 2006; Paradis & Hoffman 2006). Samples were prepared in de-ionized water (Nanopure) and completely mixed and headspace free while being irradiated with UV. Odorants were dosed at μg l⁻¹ concentrations and measured by solid-phase microextraction (SPME, Supelco) with scan mode of GC/MS (Agilent 5973) (Watson *et al.* 1999, 2000). UV absorbances were measured at a wavelength of 253.7 nm by UV/Vis spectrophotometer

Table 1 | Odorants selected for this research

Compounds	Structure	Odour	Odour threshold (ng l ⁻¹)	Guideline in drinking water
Trans-2, <i>cis</i> -6-nonadienal		Cucumber/fishy	80*	–
Trans-2, <i>trans</i> -4-decadienal		Fishy/oily/cucumber	300†	–
Trans-2, <i>trans</i> -4-heptadienal		Grassy/oily/fishy	25,000‡	–
Hexanal		Grassy/sweet	4,500‡	–
Geosmin		Earthy	6–10§	10 ng l ⁻¹
2-MIB		Musty	2–20§	10 ng l ⁻¹

*Young *et al.* (1996).

†Watson *et al.* (2001).

‡Rychlik *et al.* (1998).

§Rashash *et al.* (1997) and Oestman *et al.* (2004).

||Guideline in Korea and secondary standard in Japan (KNIER 2000; KMOE 2006).

(Beckman DU640). H₂O₂ concentration was determined by the iodide (I₃⁻) method (Klassen *et al.* 1994; Rosenfeldt *et al.* 2005). UV dose was verified with the iodide/iodate actinometer (Rahn 2004; Rahn *et al.* 2006). Flavour profile analysis (FPA) was performed by four trained panellists according to the Standard Method 2170 to assess the odour intensity and investigate the change of odour descriptor (Standard Methods 2005). PFBHA derivatization method was used with SPME and GC/MS to detect low molecular weight carbonyl groups (aldehydes and ketones) produced from the oxidation of nonadienal (Weinberg & Glaze 1997; Bao *et al.* 1998), where higher concentrations (10 mg l⁻¹) of nonadienal were reacted with UV/H₂O₂ and subsequently derivatized with PFBHA.

RESULTS

UV absorbance

In order to assess the contribution of direct UV photolysis, molar extinction coefficients, which indicate the UV absorbance of a compound, were measured as shown in Figure 1. Three unsaturated aldehyde compounds absorbed a greater amount of UV compared with geosmin and 2-MIB. The order of molar extinction coefficient from greatest to least was heptadienal, decadienal and nonadienal. Based on the measured molar extinction coefficients, it was expected that the three unsaturated aldehyde compounds would be reduced much faster than geosmin and 2-MIB by UV photolysis. In contrast, UV absorbance of hexanal and decanal was almost zero, which indicates that removal of these compounds, if any, would be by hydroxyl radical reaction in the UV/H₂O₂ process.

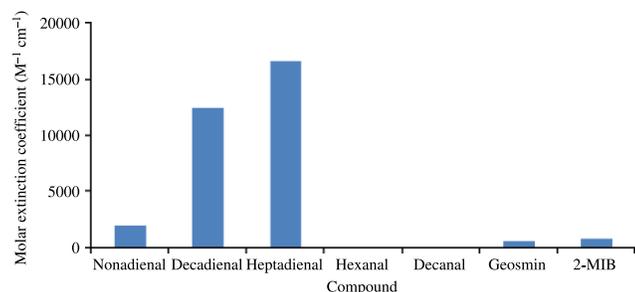


Figure 1 | Molar extinction coefficient measured at 253.7 nm (M⁻¹ cm⁻¹).

Removal rate by UV/H₂O₂

Compared with geosmin and 2-MIB, the three 'dial' compounds were removed more rapidly (Figure 2). Heptadienal was reduced faster than either nonadienal or decadienal, which is thought to be related to its higher UV absorbance. Nonadienal and decadienal had similar removal rates to each other. Hexanal was not removed more effectively than geosmin.

Sensory test

Sensory tests revealed that the initial odour intensity of odorous aldehydes was reduced with increasing exposure time to UV/H₂O₂. However, new types of odour were detected when the initial fishy/grassy odours were mostly or completely removed. The fishy/cucumber odour of nonadienal changed into a sweet/chalky odour (Figure 3) as the concentration of nonadienal was reduced by UV/H₂O₂. This sweet/chalky odour was thought to be produced from the oxidation of nonadienal. The oily/fishy/cucumber odour of decadienal changed into a sweet/stale odour (Figure 4). The grassy/oily/fishy odour of heptadienal changed into a sweet/concrete/wet cardboard odour (Figure 5). The grassy/sweet/pumpkin odour of hexanal changed into a cement/waxy/metallic/oily odour (Figure 6). Consequently, in the oxidation of odorous 'dial' compounds by UV/H₂O₂, new types of odour were produced as the concentration of the original compounds and initial odours were reduced. These results indicate that the oxidation of odorous aldehydes by UV/H₂O₂ produces by-products that have different types of odour.

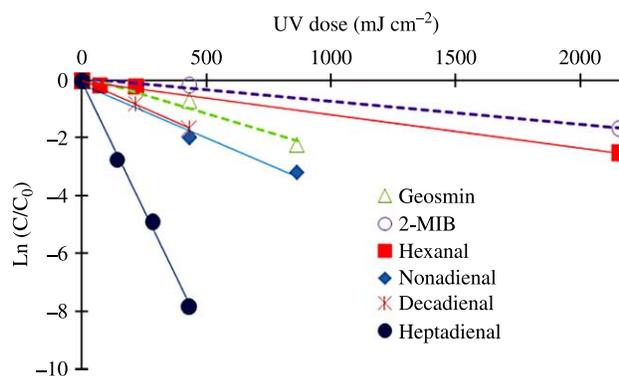


Figure 2 | Log removal of odorants with UV dose (6 mg l⁻¹ H₂O₂).

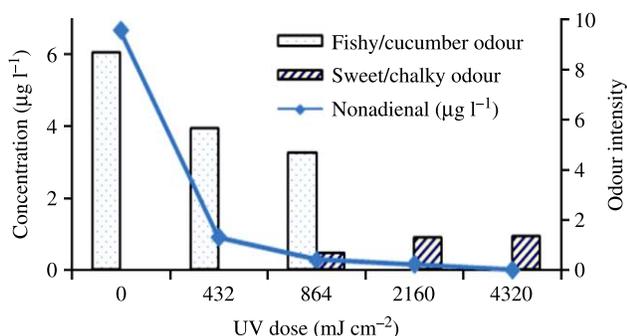


Figure 3 | Nonadienal concentration and odours as a function of UV dose (6 mg l⁻¹ H₂O₂).

Result for PFBHA derivatization of nonadienal

In order to investigate the reaction mechanism and detect the intermediates or final products, a higher concentration (10 mg l⁻¹) of nonadienal was reacted by UV/H₂O₂ and then derivatized with PFBHA. Based on the derivatized chromatograms, there was no difference between UV photolysis and the UV/H₂O₂ process (Figure 7). This result indicates that nonadienal was removed mainly by UV photolysis in the UV/H₂O₂ process because UV photolysis is faster than the radical reaction and the addition of hydrogen peroxide did not alter the reaction that produced carbonyls.

Figure 8 shows that carbonyl groups derivatized by PFBHA (oximes) were produced from the UV irradiation of nonadienal. This result indicates that nonadienal was degraded into smaller ketone or aldehyde molecules by UV photolysis. Most of these new carbonyl groups produced from the reaction were not removed by further UV irradiation, indicating that these ketone or aldehyde

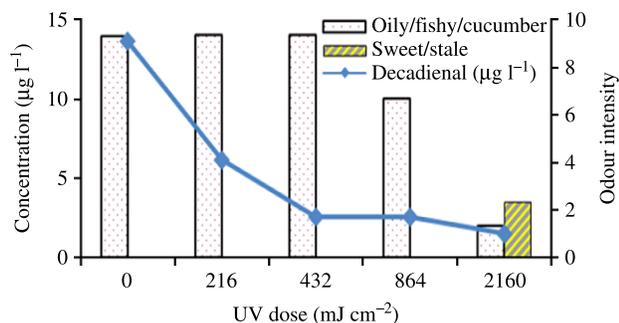


Figure 4 | Decadienal concentration and odours as a function of UV dose (6 mg l⁻¹ H₂O₂).

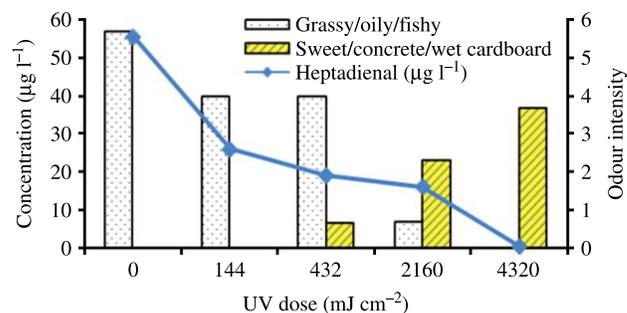


Figure 5 | Heptadienal concentration and odours as a function of UV dose (6 mg l⁻¹ H₂O₂).

compounds are highly stable to UV irradiation. However, these ketones or aldehydes were not identified in this research. Further study is required to identify these carbonyl products and to detect other alcoholic or carboxyl products that may be produced.

DISCUSSION

According to the measured molar extinction coefficients and derivatization results, nonadienal was removed by direct UV photolysis, and a similar mechanism would be expected for decadienal and heptadienal. While UV photolysis removed fishy/grassy smelling 'dienal' compounds, new types of odour were produced after the oxidation of original compounds. These transformed odours may be related to carbonyl groups produced from the UV photolysis of nonadienal, based on the result that these carbonyl groups were not removed by further UV photolysis. These results are comparable to the results of other research that reported fruity-smelling aldehydes

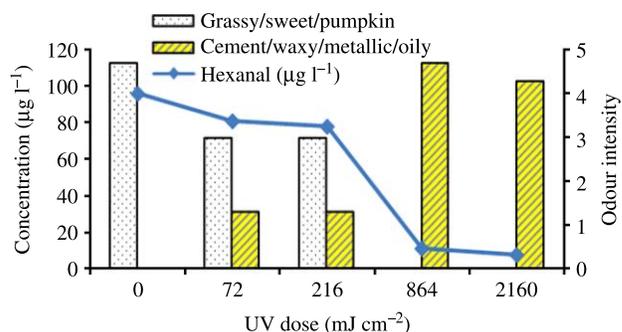


Figure 6 | Hexanal concentration and odours as a function of UV dose (6 mg l⁻¹ H₂O₂).

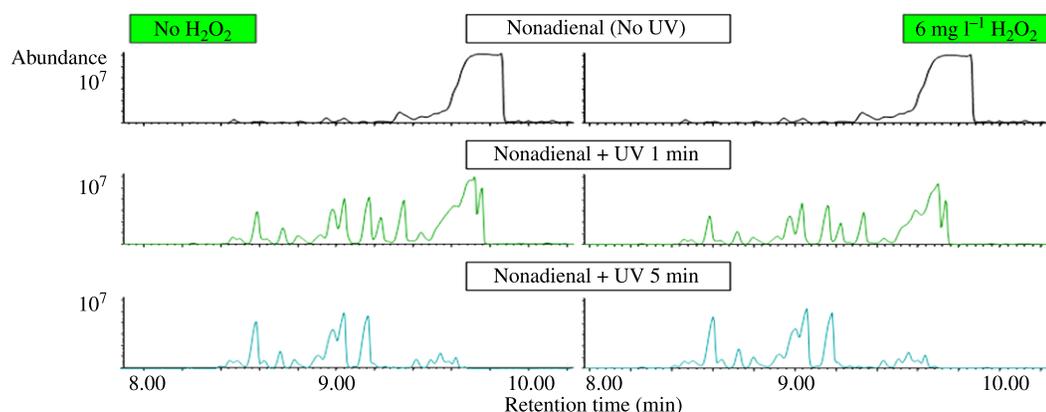


Figure 7 | Comparison of PFBHA derivatized chromatograms for UV photolysis and UV/H₂O₂ treatment of nonadienal.

production from ozonation (Anselme *et al.* 1988; Suffet *et al.* 1995; Bruchet & Duguet 2004). The C₄–C₁₂ normal aldehydes typically have odour threshold concentrations of < 1 µg l⁻¹, and are known to be problematic in drinking water (Fabrellas *et al.* 2004). Consequently, carbonyls produced from the reaction can be one of the causes of the new odours. However, these carbonyl groups produced

by UV photolysis could not be identified and no conclusive evidence was found on the relationship between carbonyl groups produced and new types of odour detected in the sensory test in this research. Further investigation is required to identify the reaction products, which may include functional groups other than carbonyls, such as carboxyl or alcohol groups.

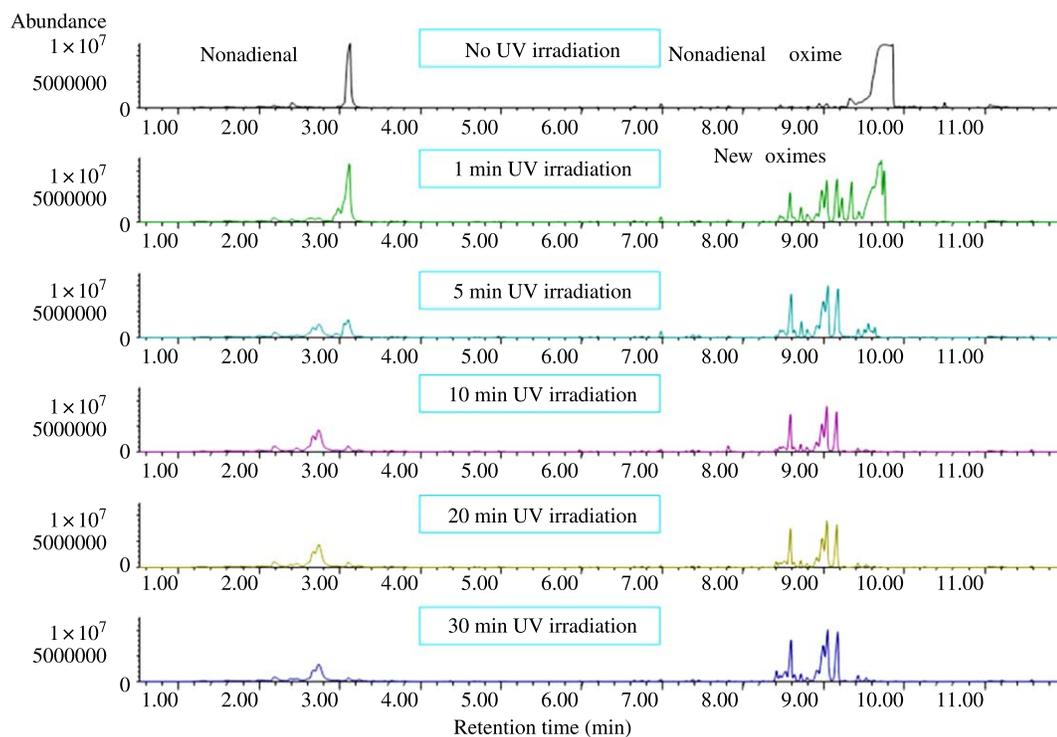


Figure 8 | GC/MS chromatograms of PFBHA derivatized nonadienal demonstrating production of stable carbonyls during exposure to UV.

CONCLUSION

The UV/H₂O₂ process was able to effectively reduce odorous aldehyde concentrations compared with removal of geosmin and 2-MIB. The result indicates that direct UV photolysis is the main mechanism involved in this removal. Although the concentration of odorous aldehydes was reduced by UV/H₂O₂, new types of odour were produced from these reactions, which was confirmed by sensory test. Carbonyl compounds were detected from the UV photolysis of nonadienal and were not removed by further UV irradiation. These carbonyl compounds were thought to be related to production of new types of odour such as chalky or sweet odour. Results indicate that new types of odour can be produced from the oxidation of odorants, and consequently sensory and chemical analysis should be considered in designing an oxidation process to control recalcitrant odorants.

ACKNOWLEDGEMENTS

This research was financially supported by Kwater (Korea Water Resources Corporation), and by the US National Science Foundation (NSF, Award DMII # 0329474). The views expressed in this report are those of authors and not those of US NSF.

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First received 13 January 2009; accepted in revised form 25 August 2009