Photocatalytic removal of taste and odour compounds for drinking water treatment
H. Tran, G. M. Evans, Y. Yan and A. V. Nguyen

ABSTRACT
Photocatalytic degradation of geosmin and 2-methylisoborneol (MIB), which are two taste and odour compounds commonly found in drinking water supply sources, was investigated using an immobilised TiO₂ photoreactor. It was found that the degradation of geosmin and MIB followed similar pseudo-first-order kinetics with reaction rate constants being approximately 0.025 min⁻¹ for typical geosmin and MIB concentrations of 250 and 500 ng/L. The normalised formal quantum efficiency was calculated to be in the range of 162–182 L/mol. Influence of additives (i.e. sodium bicarbonate and alcohols) on the degradation process was also investigated. It was found that there was a small reduction in the degradation rate constants of geosmin and MIB with increasing sodium bicarbonate concentration. At 50 mg/L sodium bicarbonate the degradation rate constants decreased by approximately 5%. Similarly, for methanol and ethanol concentrations up to 35 and 50 mg/L, respectively, these constants were found to also decrease. While addition of sodium bicarbonate and alcohols was seen to have relatively small negative effects on the photocatalytic degradation performance, the magnitude of their influence was consistent with the hypothesis that the degradation mechanism of geosmin and MIB was predominately that of attack involving HO₂ radicals.

Key words | advanced oxidation, geosmin, MIB, photocatalysis, TiO₂, water treatment

INTRODUCTION
Geosmin and 2-methylisoborneol (MIB) are secondary metabolites commonly produced by blue-green algae under eutrophic conditions in many lakes and reservoirs used for drinking water supply. These compounds are responsible for the majority of taste and odour events in municipal water supplies (Mallevalle & Suffet 1987). Hence, removal of these compounds from water supplies to below human taste and odour thresholds (as low as 4 ng/L) is essential (Young et al. 1996). Unfortunately, conventional water treatment methods are ineffective in removing extracellular (i.e. dissolved) geosmin and MIB, and more advanced processes such as activated carbon adsorption, ozonation and ozone/biological activated carbon are often required. More recently, the use of advanced oxidation processes (AOPs) such as UV/H₂O₂ has also been investigated.

AOPs, which are believed to utilise highly reactive hydroxyl radicals to accelerate the reaction rate, provide attractive alternatives to other water treatment methods for removing low concentrations of refractory organic pollutants such as geosmin and MIB. In fact, AOPs such as UV/H₂O₂, ozone/UV, ozone/H₂O₂ and ultrasonic irradiation have been studied for applications in removing geosmin and MIB from drinking water (Romain et al. 2003; Rosenfeldt et al. 2005; Song & O'Shea 2007).

UV/TiO₂ photocatalysis is another AOP known for its effectiveness in destroying a range of recalcitrant organics. TiO₂ photocatalysts are inexpensive, chemically-inert,
non-toxic and reusable. In the UV/TiO$_2$ process the photocatalyst becomes energetically excited under UV illumination that possesses photons of energy equal to or greater than its band gap energy (i.e. wavelengths below 380 nm). Electrons are excited from the valence band to the conduction band, generating electrons and holes. Positively charged holes are very strong oxidising agents and can directly oxidise organic pollutants, or they can react with water molecules to form hydroxyl radicals. Hydroxyl radicals can then oxidise organic pollutants into carbon dioxide and water (Carp et al. 2004). However, to date there have been very few studies on the effectiveness of UV/TiO$_2$ in removing geosmin and MIB for drinking water treatment applications (Lawton et al. 2003; Bellu et al. 2008; Tran et al. 2008a, b). Also, whether the degradation of geosmin and MIB involves positively charged holes or hydroxyl radicals has not been reported.

In real applications drinking water supply sources contain a range of dissolved components. Since the concentration of geosmin or MIB is typically at nanogram-per-litre level, which is far below the levels of other common dissolved organic and inorganic components (milligram-per-litre level), the photocatalytic degradation efficiency of geosmin and MIB could be significantly influenced by these other dissolved species, in a manner similar to that for powdered activated carbon (Ho & Newcombe 2005) and ozonation (Morioka et al. 1993; Ho et al. 2002).

The aim of this study was to investigate the photocatalytic degradation of geosmin and MIB in an immobilised TiO$_2$ photoreactor. Degradation reaction rates and normalised formal quantum efficiencies for two initial concentrations (often encountered in potable water supply) of geosmin and MIB were determined. The effect of sodium bicarbonate and alcohols (methanol and ethanol) was then investigated. Finally, a mechanism involving hydroxyl radicals was proposed.

**METHODS**

**Materials**

Standard solutions of geosmin and MIB (100 µg/mL in methanol) were purchased from Supelco (Bellefonte, PA, USA). Their molecular structure and physical property are given in Table 1. Two stock solutions of geosmin and MIB of 250 ng/L each (1.37 nM for geosmin and 1.49 nM for MIB) and 500 ng/L each (2.74 nM for geosmin and 2.97 nM for MIB) were prepared using Milli-Q water. An internal analysis standard, biphenyl-d$_{10}$, sourced from Isotec (Miamisburg, Ohio, USA), was used for geosmin and MIB quantification. Methanol, ethanol and sodium bicarbonate, all from Sigma–Aldrich, were spiked to the geosmin and MIB working solutions to make up concentrations of (0, 0.4, 3.5, 7 and 35 mg/L), (0, 0.5, 5, 10 and 50 mg/L) and (0, 4, 8, 20, 50 mg/L), respectively.

Degussa P25 TiO$_2$ particles (Degussa AG) with a nominal BET specific surface area of 50 ± 15 m$^2$/g and an

<table>
<thead>
<tr>
<th>Property</th>
<th>Geosmin</th>
<th>MIB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular formula</td>
<td>C$<em>{12}$H$</em>{22}$O</td>
<td>C$<em>{11}$H$</em>{20}$O</td>
</tr>
<tr>
<td>Molecular structure</td>
<td><img src="image" alt="Geosmin Structure" /></td>
<td><img src="image" alt="MIB Structure" /></td>
</tr>
<tr>
<td>Aqueous solubility at 20°C (mg/L)</td>
<td>150.2</td>
<td>194.5</td>
</tr>
<tr>
<td>Vapour pressure (atm)</td>
<td>5.49 × 10$^{-5}$</td>
<td>6.68 × 10$^{-5}$</td>
</tr>
<tr>
<td>Henry’s Law constant (atm m$^3$/mol)</td>
<td>6.66 × 10$^{-5}$</td>
<td>5.76 × 10$^{-5}$</td>
</tr>
</tbody>
</table>
average crystalline size of 30 nm were used. These particles were deposited onto a Petri dish by filling the dish with 60 mL of the 1 g/L TiO2 suspension and allowing it to stand for 30 minutes. The dish was then drained and dried in an oven at 80°C for 1 hour. This process was repeated four times. The mass of TiO2 film deposited on the inside of the Petri dish was measured, after rinsing, to be 0.039 grams. The coating density was calculated to be 0.5 mg/cm².

Reactor

Photocatalytic degradation of geosmin and MIB in an immobilised TiO2 system was conducted in a closed reactor under ambient conditions and at pH = 6.6 (unless stated otherwise). A 60 mL sample, containing both geosmin and MIB, was transferred to the TiO2 coated Petri dish (see 1 in Figure 1) and quickly sealed with a dish cover to form a closed photoreactor system (Figure 1). Mixing in the system was achieved by means of a magnetic stirrer (2) and a stirrer bar (3). A mixing speed of 600 rpm, at which the degradation kinetics was found to be reaction rate limited, was chosen. The Petri dish was placed in a UV block chamber (4) and two UV lamps with a main emission wavelength of 365 nm were used. The total incident light intensity of these UV lamps was determined to be $14.82 \times 10^{-5}$ E/min using ferrioxalate actinometry (Hatchard & Parker 1956).

Detection method

The degradation of geosmin and MIB at two initial concentrations of 250 and 500 ng/L each was quantified by measuring geosmin and MIB concentrations remaining in the sample as a function of reaction time by gas chromatography/mass spectrometry (GC/MS) analysis. For each reaction time the entire sample (i.e. 60 mL) was used for analysis. Therefore, a new sample, from the same stock solution, was used in the next reaction time investigation. This avoids complications associated with changes in sample thickness, if successive samplings are made from the same sample.

Dual layer 50/30 μm DVB/CAR/PDMS fibre assemblies and manual holders for solid-phase micro-extraction (SPME) were obtained from Supelco (Sigma–Aldrich). A Varian CP-3800 gas chromatograph coupled to a Varian 1200 Quadrupole mass spectrometer was used to detect geosmin and MIB. Geosmin and MIB remaining in the sample were pre-concentrated using the SPME technique before analysing by GC/MS.

The following conditions were used in the SPME process: dual layer fibre of 50/30-μm DVB/CAR/PDMS, 6 grams of sodium chloride (24 wt%), extraction temperature of 65°C, extraction time of 30 minutes, 25 mL sample in 40 mL capacity vials and biphenyl-d10 as an internal standard. The extraction procedure was similar to that reported by Watson et al. (2000).

For GC/MS analysis selected ion monitoring mode was used and three ions were monitored (m/z 112 for geosmin, 95 for MIB and 164 for biphenyl-d10). The dwell time of 0.5 ms for each ion and the higher multiplier voltage of 1,500 volts were selected. The oven temperature programme involved: Hold at 50°C for 2.5 minutes; raise to 120°C (20°C/min) and hold for 4 minutes; raise to 150°C (20°C/min) and hold for 4 minutes; finally raise to 250°C (50°C/min) and hold for 2.5 minutes. The carrier gas was helium at a flow rate of 1 mL/min. Splitless mode was used and the split line was opened after 2.5 minutes. The 1,177 glass injector was fitted with a 0.75 mm id glass liner. The transfer line temperature was 250°C and the ion-trap temperature was 180°C. The fibre was held in the injector for 3 minutes at 270°C for complete desorption of biphenyl-d10, geosmin and MIB.

Control experiments confirmed that in the absence of either UV illumination or TiO2 photocatalysts the concentrations of geosmin and MIB remained constant throughout the experimental duration.
The pH of the geosmin and MIB samples was 6.6. It increased slightly to 7.5 with the addition of the highest concentration of sodium bicarbonate (50 mg/L), or remained constant with the addition of different concentrations of methanol and ethanol.

**RESULTS AND DISCUSSION**

**Geosmin and MIB degradation kinetics**

The percentage remaining of geosmin and MIB, as a function of oxidation time and initial concentrations of 250 and 500 ng/L, is shown in **Figure 2**. It can be seen that for all four curves the percentage remaining decreased in an approximately steady rate with time. Only 19% of the geosmin and MIB remained after 60 minutes exposure time for an initial concentration of 250 ng/L. Similarly, 22% was remaining for an initial concentration of 500 ng/L.

**Figure 2** (inset) shows that ln($C/C_0$) vs time produced a straight line with $R^2 > 0.93$ (see **Table 2**), indicating that the photocatalytic degradation of geosmin and MIB could be described by a pseudo-first-order kinetics process in accordance with Equation (1):

$$-\ln \frac{C}{C_0} = kt,$$

where $C_0$ and $C$ are the remaining concentrations of geosmin or MIB at reaction time zero and $t$, respectively, and $k$ is the reaction rate constant (min$^{-1}$).

<table>
<thead>
<tr>
<th>Compound</th>
<th>$C_0$ (ng/L)</th>
<th>$k$ (min$^{-1}$)</th>
<th>$R^2$</th>
<th>$r_0$ (nM/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Geosmin 250</td>
<td>1.371</td>
<td>0.027</td>
<td>0.980</td>
<td>0.0370</td>
</tr>
<tr>
<td>Geosmin 500</td>
<td>2.742</td>
<td>0.026</td>
<td>0.936</td>
<td>0.0713</td>
</tr>
<tr>
<td>MIB 250</td>
<td>1.486</td>
<td>0.027</td>
<td>0.982</td>
<td>0.0401</td>
</tr>
<tr>
<td>MIB 500</td>
<td>2.972</td>
<td>0.024</td>
<td>0.975</td>
<td>0.0713</td>
</tr>
</tbody>
</table>

The rate constants and the initial reaction rates of geosmin and MIB degradation are listed in **Table 2**. It can be seen that for an initial concentration of 250 ng/L the rate constants for geosmin and MIB degradation were both 0.027 min$^{-1}$. The rate constants decreased very slightly when the initial concentrations of geosmin and MIB were increased to 500 ng/L. **Table 2** also shows that the initial reaction rates, $r_0$, for both geosmin and MIB were about 0.037–0.040 nM/min for the initial concentration of 250 ng/L and approximately doubled (0.071 nM/min) when the initial concentration was increased to 500 ng/L.

The effectiveness of the degradation process can also be quantified in terms of photonic quantum efficiency. For polychromatic light sources (blacklight bulbs), as used in this study, it is appropriate (Mills & Le Hunte 1997) to use the formal quantum efficiency, FQE, defined as:

$$FQE = \frac{\text{Initial reaction rate}}{\text{Incident light intensity}}$$

Generally, FQE is dependent on the initial concentrations of organic compounds since the initial rate of reaction decreases with decreasing initial concentrations of the organic compounds for photocatalytic processes. Hence, the normalised formal quantum efficiency, NFQE, is used, i.e.:

$$NFQE = \frac{FQE}{\text{Initial concentration}}$$

The FQE and NFQE values are reported in **Table 3**. It can be seen that the NFQE was in the range of 162–182 L/mol. The values can be compared with: (1) Immobilised system: 1,000 + L/mol for 17-$\beta$-oestradiol (Coleman et al. 2000); and (2) Suspended system: 59.1–83.8 L/mol for 4-chloropenol (Al-Sayyed et al. 1991), 11 L/mol for 4-chloropenol (Mills & Morris 1993),
bicarbonate concentrations ($M$ greater than 50) $K$ decreased to 0.9. Since bicarbonate concentration in natural surface waters is typically less than 50 mg/L NaHCO$_3$, its presence is therefore expected to have only a small negative influence on the photocatalytic removal of geosmin or MIB.

**Effect of alcohols on degradation rate constant**

Similarly to the case of adding sodium bicarbonate, the rate constant of the geosmin and MIB degradation reactions in the presence of methanol or ethanol was calculated using the first 30 minutes of reaction time only to avoid potential interferences from intermediate products. Quantitative comparison was also made using the normalised reaction rate constant, $K = k/k'$, where $k'$ is the degradation rate constant in the absence of added alcohol.

In Figure 4, $K$ has been plotted for both geosmin and MIB as a function of $M$, which is the molar ratio of alcohol to geosmin or MIB, multiplied by $10^{-5}$. It can be seen that similarly to the case of adding sodium bicarbonate, increasing the alcohol concentration showed increasingly negative effects on the geosmin and MIB degradation and the curves for both geosmin and MIB were similar. It can also be seen that ethanol had a greater negative influence than methanol for the same $M$. In the case of adding methanol, $K$ remained at unity for $M$ at about 0.8 (methanol = 3.5 mg/L)$^1$ and decreased to 0.9 for $M$ at ten times higher (methanol = 35 mg/L). In the case of adding ethanol, $K$ was 0.96 for $M$ at about 0.8 (ethanol = 5 mg/L)

$^1$ Indicating that the methanol present in our stock solutions, at concentrations of less than 2 mg/L, should not have any noticeable effects on the degradation of either geosmin or MIB.

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**Effect of bicarbonate on degradation kinetics**

The rate constants for both geosmin and MIB degradation, given in Table 2, were found to be independent of initial concentration. Consequently, only an initial concentration of 250 ng/L was investigated. The rate constant of the geosmin and MIB degradation in the presence of sodium bicarbonate was calculated using the first 30 minutes of reaction time only to avoid potential interferences from intermediate products. Quantitative comparison was made using the normalised reaction rate constant, $K = k/k'$, where $k'$ is the degradation rate constant in the absence of added bicarbonate.

In Figure 3, $K$ has been plotted for both geosmin and MIB as a function of $M$, which is the molar ratio of bicarbonate to geosmin or MIB, multiplied by $10^{-5}$. It can be seen that increasing the bicarbonate concentration showed increasingly negative effects on the geosmin and MIB degradation and the curves for both geosmin and MIB were similar. For $M$ at about 0.7 (NaHCO$_3$ = 8 mg/L) $K$ decreased to 0.98. For a higher $M$ of 4.0 (NaHCO$_3$ = 50 mg/L) $K$ decreased to 0.94. At very high sodium bicarbonate concentrations ($M$ greater than 50) $K$ decreased to 0.9. Since bicarbonate concentration in natural surface waters is typically less than 50 mg/L NaHCO$_3$, its presence is therefore expected to have only a small negative influence on the photocatalytic removal of geosmin or MIB.

**Table 3 | Normalised FQE for geosmin and MIB**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Initial concentration (ng/L)</th>
<th>FQE</th>
<th>NFQE (L/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Geosmin</td>
<td>250</td>
<td>0.250 $\times$ 10$^{-6}$</td>
<td>182</td>
</tr>
<tr>
<td>Geosmin</td>
<td>500</td>
<td>0.481 $\times$ 10$^{-6}$</td>
<td>175</td>
</tr>
<tr>
<td>MIB</td>
<td>250</td>
<td>0.271 $\times$ 10$^{-6}$</td>
<td>182</td>
</tr>
<tr>
<td>MIB</td>
<td>500</td>
<td>0.481 $\times$ 10$^{-6}$</td>
<td>162</td>
</tr>
</tbody>
</table>

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and decreased to below 0.9 for $M$ at ten times higher (methanol = 35 mg/L).

Overall, the presence of either bicarbonate or alcohols was seen to have a negative influence on the degradation rate constants of geosmin and MIB. However, compared to sodium bicarbonate, the negative effects appeared to be more pronounced with methanol and ethanol.

Geosmin and MIB degradation mechanism

It has been found that geosmin and MIB do not adsorb onto the surface of the TiO$_2$ particles (Tran et al. 2009). On this basis it is more likely that the degradation mechanism is governed by HO$^-$ radicals rather than positively charged hole attack. This notion is supported by the bicarbonate and alcohol results of this study. Alcohols are known to be degraded by HO$^-$ radicals in photocatalytic reaction systems (Chen et al. 1999; Hatipoglu & Cinar 2003), and are likely to compete directly with geosmin and MIB for reactions with HO$^-$ radicals, thus reducing the degradation rates of geosmin and MIB. The bicarbonate ion is a known HO$^-$ radical scavenger (Morioka et al. 1993) and forms CO$_3^{2-}$ radicals according to the following reaction:

$$\text{HCO}_3^- + \text{HO}^- \rightarrow \text{CO}_3^{2-} + \text{H}_2\text{O}$$

The CO$_3^{2-}$ radicals are less reactive than HO$^-$ radicals (Wiszniowski et al. 2004), thus reducing the degradation efficiency for geosmin and MIB. Overall, the trend observed in this study of ethanol > methanol > bicarbonate reacting with HO$^-$ radicals is consistent with the corresponding rate constants of 185, 85, and $1.5 \times 10^7$ M$^{-1}$ s$^{-1}$ reported in the literature (Anbar et al. 1966; Weeks & Rabani 1996).

CONCLUSIONS

The degradation kinetics of both geosmin and MIB in the immobilised TiO$_2$ photoreactor was found to follow a first-order model, with the reaction rate constants being very similar. The introduction of sodium bicarbonate and alcohols had only a relatively small negative effect on the photocatalytic degradation performance. This behaviour was consistent with the notion that the degradation mechanism was that of attack involving HO$^-$ radicals. It was found that the normalised formal quantum efficiency values for geosmin and MIB were much lower for the immobilised system than those reported for suspended systems. Consequently, while immobilised systems may be the preferred ones in water treatment applications due to ease of recovery of the used photocatalysts, more work is needed to increase the activity of the photocatalytic coating.
REFERENCES


