

**The Destruction of 2-Methylisoborneol and Geosmin using Titanium Dioxide
Photocatalysis**

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Abstract

Geosmin (GSM) and 2-methylisoborneol (MIB) are semi-volatile compounds produced by cyanobacteria in surface waters. These compounds present problems to the drinking water industry and in aquaculture because they can taint water and fish producing an earthy-musty flavour. This paper presents an initial study on the use of TiO₂ photocatalysis for the destruction of these compounds in water. The process proved effective with the complete destruction of MIB and GSM being achieved within 60 minutes. These results suggest that TiO₂ photocatalysis will be a successful method for removal of taint compounds from potable water supplies and fish farms.

Keywords: Geosmin, 2-methylisoborneol, cyanobacteria, TiO₂, photocatalysis, aquaculture, potable water.

1. Introduction

Geosmin (GSM) and 2-methylisoborneol (MIB) are bicyclic tertiary alcohols (Figure 1) produced by microorganisms, namely actinomycetes and cyanobacteria. Both compounds cause undesirable tastes and odours, and have a relatively low threshold of detection in humans (1.3 and 6.3 ng/l by odour for GSM and MIB respectively [1]). The global increase in nutrient-rich water bodies promotes the growth of many of the cyanobacterial species that produce these compounds and subsequently increase the occurrence of GSM and MIB in water resources. GSM is reported to cause an earthy-muddy taint whereas MIB imparts a musty taste and odour [2]. These taints have long been recognised as a significant problem in drinking water and although both compounds are non-toxic their presence results in consumer rejection and are subsequently associated with poor water quality by the public [3]. Likewise in aquaculture these taint compounds can rapidly accumulate from water into fish flesh due to their lipophilic nature thus resulting in quality problems and reduced marketability [4]. It is estimated that taint problems, due to the accumulation of cyanobacterial taints in catfish farms located in the USA, costs producers tens of millions of dollars per annum [4,5].

A number of water treatment strategies have been investigated to remove cyanobacteria and/or taint compounds from water. These include the reduction of cyanobacteria through the application of algicides, however, this can be of limited efficacy since it results in the lysis of the cyanobacterial cells and subsequent release of GSM or MIB into the water. Furthermore, many of the algicidal preparations contain significant quantities of copper that can be harmful to a wide range of aquatic

organisms and in many countries its use may be severely limited or prohibited. Prolonged treatment with copper sulphate has also been observed to select the growth of more copper tolerant cyanobacteria, resulting in a 15-fold increase in algicide treatment dosage [4]. Natural degradation of MIB and GSM is relatively slow with the main route for its removal being identified as microbial biodegradation. A biodegradation rate of around three days has been reported for GSM [7] whereas MIB appears to be considerably more resistant with a degradation time ranging from 5 to 14 days [7]. It is therefore important that reliable physical or chemical methods are available to ensure the removal of these taint compounds from both drinking water and water used within the aquaculture industry.

While a number of treatment methods, including the use of granular activated carbon (GAC) [8] and ozonation [9], have been shown to successfully deplete levels of taint in drinking water, it is important we evaluate new advanced oxidation technologies. TiO₂ photocatalysis has been successfully used to destroy a wide range of organic contaminants [10-12] and we have demonstrated its efficacy in the removal of a number of problematic cyanobacterial metabolites, i.e. microcystins and anatoxin-a [13,14]. In this investigation we demonstrate the rapid destruction of both MIB and GSM using TiO₂ photocatalysis.

2. Experimental

2.1. Chemicals

Geosmin, 2-methylisoborneol (both Supelco, Sigma Aldrich Ltd) and titanium dioxide (P-25, Degussa, UK) were used as received. All solutions were prepared

using Milli-Q water (Millipore, Watford, UK).

2.2. Dark adsorption

Dark adsorption was determined for a range of concentrations for both target molecules (5.95, 11.90, 17.85, and 23.8 nM for MIB, and 5.49, 10.98, 16.47 and 21.96 nM GSM). Aliquots (20 ml) of each concentration were placed in a 20 ml glass vial together with 1% TiO₂, sealed with a PTFE-lined cap and protected from light by covering with aluminium foil. Vials were placed on a shaker at 700 oscillations per minute for 21 hours at room temperature after which time TiO₂ was removed by centrifugation prior to quantification by GS-MS. Control samples were prepared and treated in an identical manner in the absence of TiO₂. All samples were prepared in duplicate.

2.3 Photocatalysis

The TiO₂ photocatalytic destruction of MIB (11.90 nM) and GSM (10.98 nM) was examined by placing 20 ml solutions in thin-walled glass vials in the presence of 1% catalyst, which were irradiated with a 280 W xenon lamp (Uvalight Technology; spectral output 330-500 nm). The concentrations of both compounds examined represent levels of environmental significance to the aquaculture industry. The photonic output of the lamp was determined to be 2.15×10^{-5} einstein min⁻¹ using ferrioxalate actinometry. Samples were irradiated in air for, 0, 5, 10, 15 and 30 min and were stirred continuously throughout. TiO₂ was removed by centrifugation prior to quantification by GC-MS and all samples were prepared in duplicate.

The initial reaction rate for the photocatalytic destruction of the two taint compounds

was determined using a range of concentrations (6.31, 12.08, 17.44, 21.25 and 32.97 nM for MIB, and 9.94, 19.19, 29.00, 38.64 and 50.32 nM for GSM). Aliquots (30 ml) of each solution were placed in thin-walled glass vials and mixed with 1% TiO₂ for 5 minutes after which 14 ml was removed, centrifuged and analysed by GC-MS. The remaining solution was irradiated for 5 min, centrifuged and analysed by GC-MS. All samples were prepared in duplicate.

2.4. Analytical method

GSM and MIB were extracted from aqueous solution using the solid-phase microextraction (SPME) procedure described by Watson *et al* [15]. Samples (10 ml) were placed in screw-capped, straight-sided headspace vials with a PTFE-faced silicone septum. Sodium chloride (3 g) and a PTFE stirrer bar was added then the sealed vial placed in a 65 °C hot-block. The SPME fibre was extended into the headspace of the vial then exposed for 15 min while the sample was constantly stirred and maintained at 65 °C. After this time the fibre was retracted and transferred to the injector of the GC/MS where the sample was thermally desorbed (270 °C for 5 min). A GC temperature gradient from 80 °C (held for 1 min) to 100 °C (20 °C/min) followed by an increase to 152 °C (7.5 °C/min) then 250 °C (65 °C/min) was used to separate GSM and MIB [16]. The GC-MS system used throughout was a Hewlett Packard model 5890 series II GC connected to a Hewlett Packard model 5971A mass selective detector. This was operated in selective ion monitoring (SIM) mode for quantification. The column used was a 30 m x 0.25 µm x 0.25 mm ZB-5 column (Phenomenex, U.K.). A calibration was performed daily using standard solutions of MIB and GSM.

3. Results and Discussion

Both GSM and MIB were rapidly degraded by the TiO₂ photocatalyst with over 99% decomposition of both compounds achieved within 60 minutes (Figure 2). No destruction was observed with either control i.e. under dark conditions or UV in absence of TiO₂. A linear plot was obtained in both cases when plots of $\ln C_0/C$ vs. time were prepared indicating pseudo first order kinetics for both processes, which is typical of most photocatalytic processes. The pseudo first order rate constants for MIB and GSM determined from these plots were found to be 0.1979 min⁻¹ and 0.0833 min⁻¹ respectively. The photonic efficiencies for the photocatalytic destruction of MIB and GSM were calculated to be 1.06×10^{-3} and 2.24×10^{-4} respectively. These figures appear rather low although are comparable to the figure obtained by Coleman *et al.* [17]. It should however be noted that they represent formal photonic efficiencies since a polychromatic light source was used in this study. As pointed out by Mills and Le Hunte [12] the formal photonic efficiency is frequently lower than the actual photonic efficiency calculated when monochromatic irradiation sources are used. The source used in this study has a significant output above 400nm where TiO₂ scatters or reflects over 90% of the incident radiation. Since a significant quantity of light is not directly involved in activating the photocatalyst the resulting modest photonic efficiency figures. The formal photonic efficiencies are however of use when comparing the photocatalytic destruction of other compounds under similar conditions.

The rate of destruction of both compounds was found to increase with increasing concentration as expected (figure 3). As Matthews discussed where there are concentration dependencies on photocatalytic decomposition reactions on TiO₂ the

system can be described using a Langmuir adsorption isotherm [18]. Consequently concentration effects will have a strong influence on the rate of destruction and knowledge of Langmuir-Hinshelwood kinetics for the compound in question is important if any estimates are to be made for rates of destruction. This is particularly important when considering reactor design, configuration and operating parameters for any practical water treatment unit.

The Langmuir-Hinshelwood kinetic rate model has been widely applied to the initial rate of the photocatalytic destruction of a wide series of compounds [18,19]. This describes the rate law for surface catalysed reactions, where the overall reaction rate is proportional to the surface coverage of the substrate over the catalyst. The basic Langmuir-Hinshelwood rate equation is shown in Equation 1 where r_o is the initial rate of disappearance of the substrate and C_o is the initial substrate concentration, k is the rate constant of the reaction and K is the Langmuir adsorption constant.

$$r_o = \frac{kKC_o}{1 + KC_o} \quad (1)$$

If the system obeys the Langmuir-Hinshelwood model a double reciprocal plot of initial rate versus initial concentration, with the intercept of the line provides us with $1/k$ while the slope is equal to $1/kK$ where k is the rate constant of the reaction and K is the Langmuir adsorption constant.

As shown in figure 3 linear relationships were obtained for the double reciprocal plot of initial rate vs. initial concentration for both MIB and GSM suggesting the photocatalytic destruction of both species does indeed follow the Langmuir-Hinshelwood Model. Table 1 presents the values determined from figure 3 for k and K

for the destruction of MIB and GSM together with data reported for other compounds obtained using this model. The values obtained for MIB and GSM are significantly different from those reported in other studies with the exception of work by Coleman *et al.* [17]. It has been demonstrated by other workers that the values of k and K obtained for photocatalytic systems are, however, greatly affected by experimental conditions including initial substrate concentration and light intensity so direct comparison of data is difficult.

Several groups, including our own have reported in the past a discrepancy between the value of K obtained using the Langmuir-Hinshelwood analysis of the photocatalytic process with that obtained from dark adsorption isotherms [20,21]. To examine the magnitude of discrepancy in this case dark adsorption isotherms, for the adsorption of MIB and GSM on TiO_2 , were prepared (figure 4). Values of $5.95 \times 10^{-5} \mu\text{M}^{-1}$ and $2.84 \times 10^{-4} \mu\text{M}^{-1}$ were determined for K for GSM and MIB respectively from these isotherms. These values are several orders of magnitude lower than those obtained using the Langmuir-Hinshelwood analysis of the photocatalytic degradation (Table 1). Similar discrepancies have been observed by Cunningham and Al-Sayed [20] for benzoic acids, Mills and Morris [21] for chlorophenol and our group for microcystin-LR [13]. It has been suggested that these discrepancies may be due to adsorbed substrate radical cations undergoing mineralisation enhancing electron-hole recombination. Alternatively if the photodegradation does not occur at the TiO_2 surface but occurs via released hydroxyl radicals there would be a further discrepancy in the Langmuir-Hinshelwood data [20].

Turchi and Ollis [22] examined this discrepancy and consequently developed the

basic Langmuir-Hinshelwood model. In this paper they proposed the photocatalytic decomposition of the substrate could take place by four potential mechanisms via hydroxyl radical attack either on the catalyst surface or in the bulk of the solution. The Langmuir-Hinshelwood model could be applied to all of these mechanisms, however in each case the essential definition of K was different and did not simply represent the Langmuir adsorption constant. In the Ollis model, k depended on the physical and electronic properties of the catalyst and was influenced by light intensity. This modified model provided a better representation of the photocatalytic process than the traditional model since it accounted for both light intensity effects and adsorption of breakdown products, neither of which are accounted for by the basic model.

A recent paper by Xu and Langford [23] reported a detailed investigation of the effect of light intensity of K for the photocatalytic degradation of acetophenone on TiO_2 . It was reported that K decreased with light intensity. As discussed by these authors the surface electronic properties of the photocatalyst will change significantly when irradiated and this in turn will influence the adsorption properties of the target compound. They suggested the inverse relationship between K and I may relate to the distribution of adsorption sites varying with light intensity. It should also be remembered that the rate of many photocatalytic processes have been reported to vary initially with I^1 while at higher intensities the rate varies with $I^{0.5}$. Perhaps this variation may also be due to a reduction in extent of adsorption as a further consideration to the enhanced e-h recombination of OH-OH interaction suggested by other workers [24-26]. Further work on the influence of light on K will be necessary to further elucidate the photocatalytic process. The validity of the Ollis model for the decomposition of GSM and MIB will also have to be investigated with a detailed

study of the breakdown product of this process. A full understanding of the photocatalytic process is necessary when developing a practical system for use as a water treatment method.

4. Conclusion

The present study is the first to demonstrate the removal of these compounds that have been problematic in water supplies for a considerable time. Although the kinetic study detailed in this report has provided important information required for developing practical reactors, extensive work is still necessary in order to elucidate and optimise the mechanism of the photocatalytic process in order to develop a commercial system. However, this initial study is extremely promising demonstrating a novel approach to this import challenge to the water and aquaculture industries.

Acknowledgement

This project was funded under the LINK Aquaculture programme by DEFRA with the British Trout Association as our industrial collaborators. We would also like to thank Professor Detlef Bahnemann of The University of Hannover for his useful comments on the preparation of this manuscript.

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Figure. 1. a) 2-Methylisoborneol, b) Geosmin.

Figure. 2 The destruction of 2-methylisoborneol (white) and geosmin (black) using a titanium dioxide photocatalyst. Bars represent one standard deviation, $n=2$.

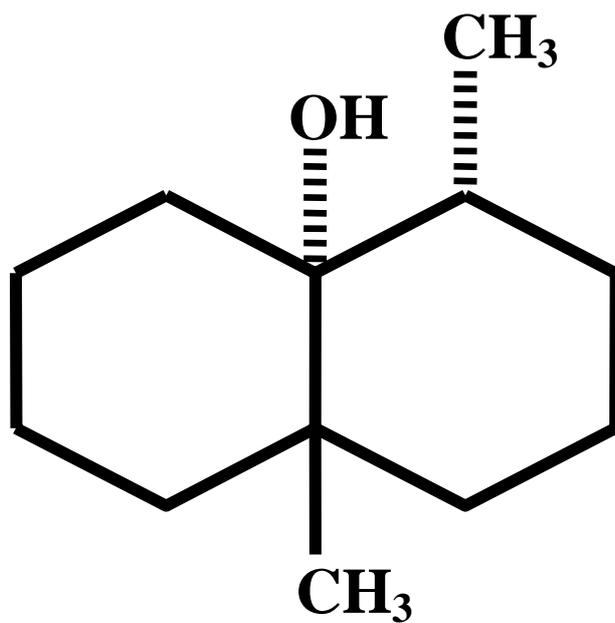
Figure 3. Relationship between initial rate and initial concentration of MIB and GSM

Figure. 4 Plot of the reciprocal of the initial rate ($1/r_0$) vs. the reciprocal of the initial concentration ($1/C_0$) for photocatalytic destruction of 2-methylisoborneol (\blacklozenge) and geosmin (\blacktriangle).

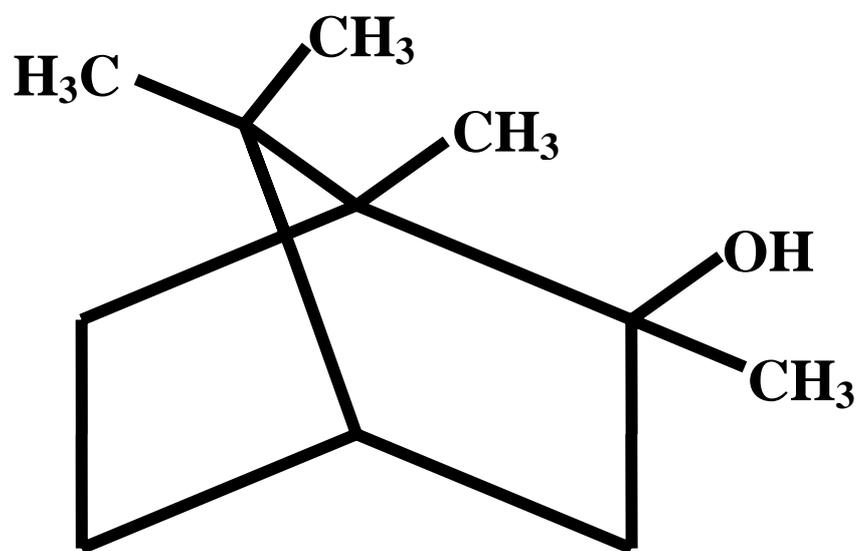
Figure. 5 Dark adsorption isotherm of 2-methylisoborneol (\blacksquare) and geosmin (\blacklozenge) on TiO_2 . The number of moles of taint compound attached per gram of TiO_2 is n_2^S while C_{eq} represents the equilibrium concentration of taint compound after 24 hours.

Compound	$k/\mu\text{M min}^{-1}$	$K/\mu\text{M}^{-1}$	Reference
2-Methylisoborneol	2.28×10^{-2}	9.10	this paper
Geosmin	4.8×10^{-3}	47.55	this paper
17 β -oestrodial	4.4×10^{-2}	3.47×10^{-1}	17
Microcystin-LR	19.2	2.90×10^{-2}	13
Benzene	39.0	1.80×10^{-2}	22
Perchloroethylene	34.0	8.60×10^{-3}	22
4-chlorophenol	79.3	4.88×10^{-3}	21
Phenol	12.9	2.19×10^{-2}	27

Table 1. Comparison of rate and adsorption constants of geosmin and 2-methylisoborneol with other organic compounds. Constants determined using the simple Langmuir-Hinshelwood model for photocatalytic destruction.



a



b