

Photocatalytic Degradation of Geosmin: Intermediates and Degradation Pathway Analysis

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Photocatalysis is a promising technology for the treatment of taste and odour compounds in water. However, the intermediates formed during the degradation process and the degradation pathway for geosmin photocatalysis is yet to be established. In this study, the degradation profile as well as the intermediates formed during the photocatalytic degradation of geosmin was monitored in an effort to obtain a better understanding of the pathway of degradation. Photocatalysis of geosmin in the presence of radical scavengers reduced reaction rate constants from 0.09 min^{-1} to 0.055 min^{-1} , indicating that hydrogen radical induced degradation is dominant over reactive electron-hole pairs on the catalyst surface. Bicyclic compounds obtained from dehydration and dehydrogenation of geosmin (a bicyclic tertiary alcohol), were not observed from GC/MS analysis of intermediate products. Intermediates identified consisted of acyclic unsaturated alkenes, carbonyl compounds and some organic acids. Results suggest that bond fission resulting in ring opening of geosmin cyclic structure and that of dehydration/dehydrogenation products (if any) occur rapidly during photocatalysis. The intermediate products identified are of no environmental significance and would not pose any threat to either the aesthetic value of the water or the health of end users.

1. Introduction

The quality of potable water is often judged by its aesthetic value. The presence of taste and odour in water compromises the aesthetic value of the water often resulting in consumer rejection. Two compounds often responsible for earthy and musty taste and odour in drinking water supplies are *trans-1, 10-dimethyl-trans-9-decalol* (geosmin) and *2-methylisoborneol* (2-MIB). These compounds also cause taint problems in the aquaculture industry. Geosmin and 2-MIB are bicyclic tertiary alcohols produced as secondary metabolites of blue green algae (cyanobacteria) and actinomycetes (Tran et al., 2008; Lawton et al., 2003).

Effective treatment of taste and odour compounds - Geosmin and 2-methylisoborneol (2-MIB) in water to levels below the human detection threshold is a major challenge to the water industry. Treatment methods that have been investigated for the removal of taste and odour compounds from water include: ozonation (Ho et al., 2002), adsorption on powdered activated carbon (PAC) (Ng et al., 2002) or granular activated carbon

(GAC). Other treatment methods involve control of cyanobacteria by the use of algacides (Lawton et al., 2003) or by microbial oxidation (Saito et al., 1999). Conventional treatment methods such as chemical, biological and physical methods have limited success in treating taste and odour compounds (Tran et al., 2009).

On the other hand, the more recent advanced oxidation technologies have shown success with the degradation of these compounds, especially photocatalysis which achieves complete degradation in water within 40-60 minutes (Bamuza-Pemu and Chirwa 2010; Chirwa and Bamuza-Pemu, 2010; Lawton et al., 2003). Ultrasonic cavitation has also been reported for degradation of geosmin and MIB via predominantly pyrolytic bond cleavage (Song and O'Shea, 2007). Degradation in both systems obeys first order kinetics. Though, the efficiency of photocatalysis for degradation of taste and odour compounds have been established, the intermediates formed during the degradation process and the degradation pathway for geosmin photocatalysis is yet to be established. Degradation of organic compounds in solution can proceed via hydroxyl radicals, reactive holes and to some limited extent by photolytic cleavage. In this study, the degradation profile as well as the intermediates formed during the photocatalytic degradation of geosmin was monitored in an effort to obtain a better understanding of the pathway of degradation.

2. Experimental Procedure

2.1 Degradation Studies

Photocatalytic degradation of geosmin was conducted in batch systems at concentration of 10 ppb with solutions prepared by spiking ultrapure water with geosmin standards. The solutions were irradiated with a medium pressure 400W UV lamp in the absence of TiO_2 , and in the presence of TiO_2 . The photocatalytic experiment was repeated in the presence of tertiary butanol (t-BuOH), a radical scavenger. Temperature control in the reactor was achieved by circulating cold water through the outer jacket of the UV lamp sleeve. Reactor contents in all situations were continually aerated at a flow rate of 10 mL min^{-1} .

2.2 Analysis

Progress of geosmin degradation was monitored by GC/MS analysis with Clarus 600T (Perkin Elmer, Connecticut, USA). Sample extraction and introduction onto the GC column was achieved online by Turbo Matrix 40 Headspace equipped with a trap. Geosmin was extracted with headspace oven temperature of 80°C for 40 min at a vial pressure of 30 psi and desorbed onto the column at a pressure of 15 psi with helium as carrier gas. GC oven was programmed from 40 °C at 0 mins, ramped at 6°C min^{-1} to 150°C and at 15°C min^{-1} to 250°C. Concentrations of geosmin were obtained from calibration curve of standards. Degradation intermediates were obtained from MS analysis of intermediate peaks obtained in the chromatogram of geosmin samples during the course of degradation by spectral comparison with those in the NIST chemical spectral database (NIST, Gaithersburg, Maryland, USA).

3. Results and Discussion

Photocatalytic degradation of geosmin occurred rapidly achieving over 99% degradation in 60 minutes (fig 1). UV photolysis alone achieved only 86% degradation in 60 min. The introduction of radical scavengers during the photocatalytic degradation reduced degradation efficiency; reducing rate constants from 0.09 min^{-1} to 0.055 min^{-1} as obtained from the first order linear transforms of the data in figure 1 (Table 1).

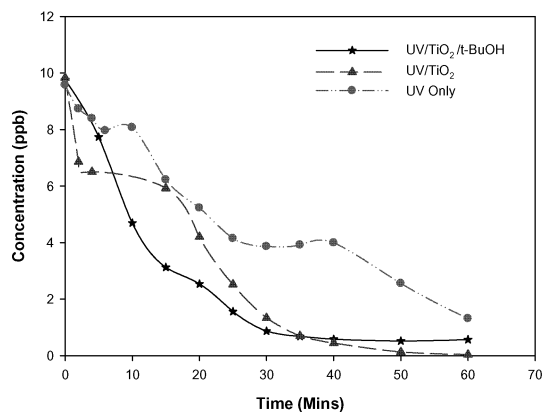


Figure 1: Degradation profile of geosmin 10 ppb.

Reduction in the degradation efficiency in the presence of a radical scavenger indicate that the hydroxyl radical initiated degradation is the dominant route over degradation by reactive electron-hole pairs on the catalyst surface and photolytic cleavage.

Table 1: Reaction rate constants

Reaction Condition	Rates	$k \text{ (min}^{-1}\text{)}$	% degraded after 60 min	r^2
TiO ₂ /UV	0.163	0.090	99.63	0.94
UV Only	0.138	0.030	86.31	0.95
TiO ₂ /UV/t-BuOH	0.153	0.055	94.18	0.89

3.1 Degradation pathways and intermediates formed

Intermediates formed during the photocatalytic degradation of geosmin were identified to gain a better understanding of the pathway during photocatalysis and to ascertain the intermediates formed during the process are not environmental threats. Possible reactive pathways to degradation of geosmin in solution include (i) oxidation by hydroxyl radicals; (ii) oxidation by reactive holes on the surface of the catalyst and (iii) photolytic cleavage by exposure to UV radiation. Geosmin is a bicyclic tertiary alcohol (fig 2) with mainly sp^3-sp^3 (C–C) bonds with bond energies of 83-85 kcal mol⁻¹; sp^3-O (C–O) bond with bond energies of 85-91 kcal mol⁻¹; sp^3-H (C–H) bond with bond energies of 96-99 kcal mol⁻¹ and an O–H bond with energies 110-111 kcal mol⁻¹ (Smith

and March, 2006). Since the energy of UV light with λ_{max} at 365 nm, its energy of 78.28 kcal mol⁻¹ is of the same order of magnitude and comparable with those of the bonds in geosmin and can cause cleavage with the most susceptible bonds been the C—O and the C—C bonds. Cleavage of the C—O would lead to a rather stable tertiary carbocation making it a most susceptible point of attack followed by an adjacent hydrogen abstraction leading to two possible dehydration products II and III.

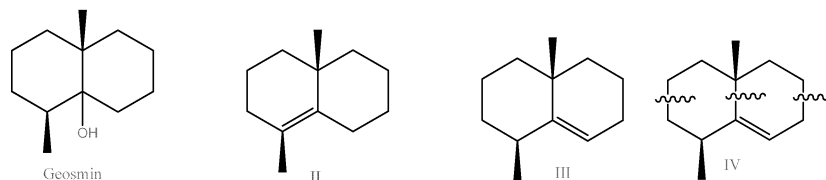


Figure 2: Structure of geosmin and possible dehydration Products II and III

Bond fission is possible at all C—C bond sites with subsequent opening of the ring structure of both geosmin and the dehydration products II and III leading to the formation of a collection of acyclic saturated and unsaturated compounds.

GC/MS data for geosmin and some of the identified intermediate compounds are presented in table 2. Degradation intermediates identified from GC/MS analysis include 3,5-dimethylhex-1-ene(V), which would most likely be a product of ring fission at positions indicated in figure 2(IV). Other intermediate products identified include 2,4-dimethylpentan-3-one (VI) (24.06 min), 2-methylethylpropanoate (VII) (24.06), and 2-heptanal (VIII) (15.64) (figure 3).

Table 2: GC/MS data of geosmin and some identified intermediate compounds

Chemical formula	Compound No. in figure 3	Retention Time (Min)	Match Probability	Major Ions for Identification
C ₁₂ H ₂₂ O (geosmin)		24.98	standard	112,41,55,111,125,43,97
C ₈ H ₁₆	V	15.64	824	41,31,55,57,70,83
C ₇ H ₁₄ O	VI	24.06	759	43,71,56,55,41,39
C ₆ H ₁₂ O ₂	VII	24.06	766	43,71,55,41,39
C ₇ H ₁₂ O	VIII	15.64	751	41,31,55,57,70,83

Dehydration products II and III were not identified during GC/MS analysis of intermediates. This suggests that bond fission resulting in ring opening of geosmin cyclic structure and that of dehydration/dehydrogenation products occurs rapidly during photocatalysis and the dehydration products are transient intermediate species due to the various possible points of bond fission for ring opening. Intermediates VII and VIII are most likely products obtained from ring opening of compound IX, which was not identified in the present study. However, the compound IX was identified as an intermediate product of microbial degradation of geosmin by Saito et al. (Saito et al., 1999).

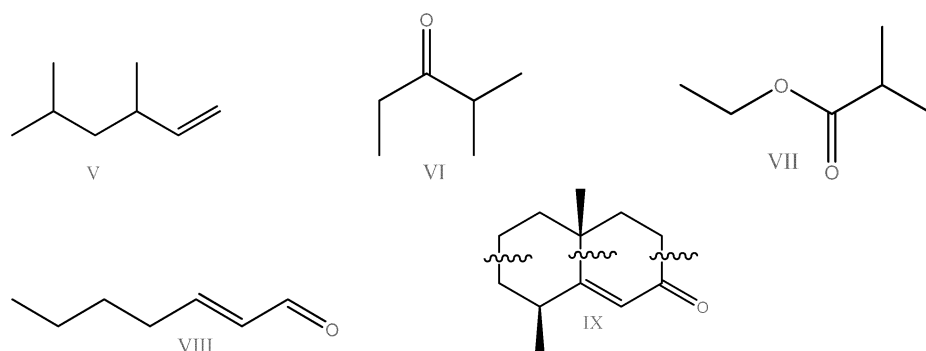


Figure 3: Structures of some identified degradation products

Earlier studies by this group with geosmin at environmentally significant levels resulted in total mineralisation of geosmin and degradation intermediates (Chirwa and Bamuzapemu, 2010). Less than optimal catalyst concentrations were used in current study, reaction conditions were chosen to enable the identification of intermediates formed during degradation. Though under the reaction conditions of the present study total mineralisation was not obtained, the intermediate products identified are not of environmental concern.

3.2 Predominant pathway of degradation

Degradation of organic compounds by photocatalysis is often attributed to reaction with highly reactive hydroxyl radicals generated in solution (Lawton et al. 2003), the current study indicates that there is synergic contribution of the three possible reactive paths leading to the rapid degradation of geosmin in solution. This can be attributed to the significant level of degradation achieved with UV radiation alone in the absence of the catalyst. However, reaction rate constants obtained for the reactions where hydroxyl radicals in solution were quenched by the introduction of tertiary butanol (table 1) indicate that the dominant reactive pathway is via oxidation by hydroxyl radicals in solution. This is consistent with findings by Tran et al on their study of effect of ionic species on the photocatalytic degradation efficiency of geosmin (Tran et al., 2009). This is due to the very high oxidative potential of hydroxyl radicals (2.8 V), which is higher than most other oxidants with the exception of fluorine. Presence of oxygenated degradation products (VI-VII); rather than only products from bond cleavage is also an indication of the presence of oxidative species in solution. Greater efficiency was probably obtained for the degradation in the presence of radical scavengers over the photolytic pathway due to the contribution from reactive positive holes in solution in synergy with photolysis from UV radiation.

4. Conclusion

Though photocatalytic degradation of geosmin and MIB has been reported, to the best of our knowledge studies on the intermediates formed during photocatalytic degradation and pathway studies are lacking. In this study, intermediate products obtained from

rapid photocatalytic degradation of geosmin in solution were identified by GC/MS analysis. Results show that geosmin undergoes rapid ring opening and subsequent bond cleavage at multiple sites to produce acyclic saturated and unsaturated compounds including some alkanones and esters. Complete mineralization of geosmin and intermediate compounds is possible thereby eliminating the risk of the degradation of a compound and the formation of more harmful intermediates and by-products. The dominant degradation pathway is the hydroxyl radical oxidation pathway over the photolytic cleavage and reaction with the reactive electron hole pair.

Acknowledgement

The research was funded by the Water Research Commission (WRC) of South Africa through the WRC Project No. K5/1717 awarded to Prof Evans M.N. Chirwa of the University of Pretoria.

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