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Photocatalytic Destruction of Geosmin Using Novel Pelleted Titanium Dioxide

Edmund Bellu[a], **Linda A. Lawton***[a, b], **and Peter K. J. Robertson**[a]

[a]Centre for Research in Energy and the Environment, The Robert Gordon University, Schoolhill, Aberdeen, AB10 1FR, U.K
[b]School of Pharmacy and Life Sciences, The Robert Gordon University, St Andrew Street, Aberdeen, AB25 1HG, U.K

Abstract**:** Geosmin is produced by cyanobacteria and actinomycetes in surface waters. It causes undesirable earthy off-flavours in freshwater fish and is a major concern for the drinking water industry. This paper presents the first published study on the use of the novel pelleted TiO_2 photocatalyst, Hombikat K01/C, for the removal of geosmin from water. TiO_2 in pelleted form eliminates the requirement for the separation of the catalyst from the water following treatment which is normally the case with the widely used powdered catalysts. A laboratory reactor was designed to limit system loss since the compound adsorbs to a wide range of surfaces. Initial concentration, aeration rate and irradiation were evaluated. It was found that degradation of geosmin followed the Langmuir-Hinshelwood model. Elevated aeration had no effect on the photocatalytic removal of geosmin, but increasing irradiation was found to increase degradation rates. The catalyst proved effective within 10 min under optimum conditions.

Introduction

Geosmin, an alicyclic alcohol, is a semi-volatile compound that is produced by microorganisms in surface waters, namely cyanobacteria and actinomycetes. Geosmin causes undesirable earthy off-flavours in freshwater fish as well as causing major concern for the drinking water industry due to seasonal taste and odour episodes (*1*). The problem is exacerbated by the low threshold of detection level of geosmin (0.015 $\mu g\ L^{-1}$) by humans (*2*).

Although non-toxic, the presence of geosmin in drinking water results in consumer rejection and an association with inadequate water quality by the public (*3*). The compound's lipophilic nature is the source of problems in aquaculture. Geosmin rapidly accumulates in fish flesh, thereby resulting in poor flavour quality and subsequent delays in harvesting due to rejection of the cultured fish by processors (*4*). Off-flavours add $15 to $23 million annually to catfish production costs in the USA and is a significant problem to aquaculture worldwide (*5*). Off-flavour problems are likely to increase worldwide due to the greater demand for aquaculture products by consumers and an increase in eutrophication of water bodies by human activities (e.g. agriculture), which can promote the growth of the geosmin-producing cyanobacterial species. Two main strategies exist for dealing with off-flavours: 1. reduction or removal of the microorganism producing off-flavour compounds by algicides; and/or 2. reduction or removal of the off-flavour compound using water treatment technologies. Copper-based algicides are commonly used by the catfish industry to control cyanobacterial blooms in production ponds. These algicides have a number of drawbacks ranging from toxicity to the catfish at elevated concentrations to the selection of copper-tolerant cyanobacteria (*5, 6*). Also, the application of algicides causes the cyanobacterial cells to lyse upon death and therefore release additional geosmin into the water. Increased restrictions on the use of algicides have led to considerable interest in replacement technologies to either prevent cyanobacterial growth or eliminate unwanted metabolites during water purification. In nature, degradation of geosmin is slow with the main route via microbial degradation (*7*).

Current water treatment methods for the removal of geosmin include the use of ozonation (*8*) and powdered activated carbon (PAC) (*9*). Photocatalysis offers a possible alternative and improvement to these treatment methods. TiO_2 photocatalysis has proved its effectiveness in the destruction of a wide range of organic contaminants (*10, 11*) and previous work (*12*) has demonstrated the successful destruction of geosmin using the powdered TiO_2 photocatalyst Degussa P25. In that study complete removal took 60 minutes and difficulties inherent in using powdered catalysts such as post-treatment catalyst removal were encountered. In this study we investigate and determine the optimal conditions for the use of a novel pellet-form catalyst Hombikat K01/C for geosmin removal in water.

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*Corresponding author; E-mail: l.lawton@rgu.ac.uk
Tel.: +44 1224 262823; Fax: +44 1224 262828

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Experimental

Materials

Geosmin (±) (Sigma, UK) was dissolved in methanol in a glass vial with a gas tight PTFE lined silicon septa and stored at -20 °C. Hombikat K01/C titanium dioxide (Sachtleben Chemie, Germany) was used as received. All solutions were prepared in Milli-Q water (Millipore, Waterford, UK), and all other reagents and solvents used were analytical grade.

Reactor Development.

Development of a suitable reactor to evaluate the efficacy of Hombikat K01/C TiO_2 in the degradation of geosmin was essential. Geosmin readily adsorbs to a wide range of materials commonly used in laboratory reactor designs. Three reactor designs were iteratively developed to limit system loss. The first reactor design which consisted of a glass vessel fed from a glass reservoir by a peristaltic pump experienced geosmin losses of 70% after one hour under control conditions (i.e. no photocatalysis). Losses were traced to adsorption of geosmin onto the silicon peristaltic pump tubing. The second reactor design replaced the majority of the peristaltic tubing with glass tubing. This reduced system loss to 40% after one hour, which was traced to adsorption to the remaining short section of silicon pump tubing. To eliminate system loss the peristaltic pump was removed resulting in the final reactor design shown in Figure 1. The bubbles from the air pump mixed the solution and had the added benefit of aerating the reaction solution. A rotameter allowed the air flow to be controlled and during evaluation a flow rate of 30 mL min^{-1} ±5% was found to be sufficient to aerate and mix test solutions. Teflon tubing (Fisher, UK) was used to connect the apparatus as it had been previously shown (*13*) that adsorption of geosmin to Teflon was minimal. The final reactor design was found to reduce loss of geosmin to ~20% after 1 hr under control conditions which was thought to be due to adsorption onto the catalyst surface (dark adsorption).

Sample Preparation

While it was necessary to initially dissolve geosmin in methanol to provide a stock solution of known concentration and to facilitate storage, it was also important to remove methanol prior to preparation of solutions for photocatalysis. The required amount of geosmin in methanol (typically 10 – 50 µL) was placed in a glass vial and evaporated to dryness under a stream of nitrogen gas. Geosmin was exhaustively re-suspended in Milli-Q water (Millipore, UK) prior to photocatalysis. Tests confirmed no significant loss of geosmin during the drying and re-suspension step.

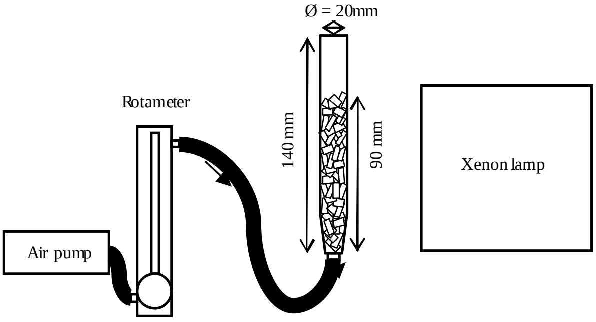

Figure 1. (not to scale): Diagram of small scale photocatalytic reactor v3.0 with arrows indicating direction of air flow. The main body of the reactor was constructed from glass and all tubing was Teflon.

Photocatalysis

Aqueous solutions (20 mL) of geosmin with 15 g Hombikat K01/C TiO_2 were illuminated in the presence of air with a 400 W xenon lamp (Uvalight Technology Ltd.; spectral output 330-500 nm). Reactions were carried out in a glass batch reactor with a constant air flow provided (30 mL min^{-1} ±5%) via the bottom of the reactor (Figure 1). The light intensity from the xenon lamp was 690 µmol s^{-1} m^{-2} and the temperature was 30 °C. Samples (1 mL) were removed at timed intervals over a 25 minute irradiation period and analyzed for geosmin. The concentration of geosmin used in this study, 1 µg mL^{-1} unless stated, was higher than might be encountered in the natural environment. This was to enable the degradation process to be followed without the need for time consuming sample concentration which also increases sampling errors. All experiments were repeated twice.

Influence of Irradiation and Aeration

Geosmin was irradiated over a range of light intensities, 199, 319, 690, 1735 µmol s^{-1} m^{-2} achieved by altering the distance between the light source and the reactor. A light meter (LI-250A light meter with LI-190SA quantum sensor, Li-COR Bioscience, USA) was used to measure photonic intensity and to attain the desired light intensities.

Photocatalysis of geosmin at aeration rates of 30, 60, 120 and 150 mL min^{-1} was conducted with a geosmin concentration of 1 µg mL^{-1}. Controls were carried out at each of the different aeration rates with no illumination.

Effect of Concentration on the Photocatalysis of Geosmin

A range of geosmin concentrations (5, 1, 0.5 and 0.1 µg mL^{-1}) were prepared to evaluate the effect initial concentration had on the efficacy of photocatalysis.

Controls consisting of geosmin solutions at each concentration were also aerated in the presence of catalyst with the xenon lamp off.

GC-MS Analysis

Aqueous samples from the reactor were treated to remove water, replacing it with a solvent (methanol) compatible GC-MS analysis. C8 SPE columns (25 mg sorbent mass and 1 mL reservoir volume) on a vacuum manifold system were used to extract geosmin from aqueous samples. The columns were preconditioned by solvating with methanol (4 mL) followed by water (4 mL). Each sample (1 mL) was applied to a preconditioned column then air drawn through the cartridge for 20 s to minimize the carry over of water. Finally, the geosmin was eluted with 1 mL of methanol. Laboratory evaluation of this procedure indicated a recovery of geosmin of 93% ±2.3%.

The GC-MS system used in this study consisted of an Agilent 6890 GC coupled with a 5975 Mass spectrometer. The column used was a DB-5 MSD (30 m x 0.25 μm x 0.25 mm, J&W Scientific, UK) and the injection volume was 1 μL. A GC temperature gradient was programmed from 60°C (held for 2 min) followed by an increase to 130 °C (20 °C min^{-1}), then an increase to 152 °C (7.5 °C min^{-1}) and finally an increase to 280 °C (held for 1 min). The system was operated in simultaneous full scan/SIM mode, with the mass range for full scan set between 50 and 300 and the same ion selected for SIM (m/z 112). Chemstation software workstation was used for the GC-MS control, data acquisition and data processing. A calibration was performed daily using standard solutions of geosmin. Limit of quantitation was 0.01 μg mL^{-1}.

Results and Discussion

Geosmin was rapidly degraded on exposure to the TiO_2 photocatalyst. No geosmin was detectable at 25 minutes under any of the conditions investigated and adopting optimum conditions no geosmin was detectable after 10 minutes. This is considerably faster than previously reported using the powered catalyst P-25 where total destruction was observed at 60 minutes (*12*).

The rate of destruction of geosmin was found to increase as light intensity increased. At the highest light intensity used 50% of the geosmin was eliminated in less than 4 minutes while none could be detected after 10 minutes exposure. This rapid degradation rate suggests that the use of pelleted TiO_2 photocatalysis has significant potential in treating contaminated water supplies. Incident light is an important factor in influencing photocatalytic activity and normally a

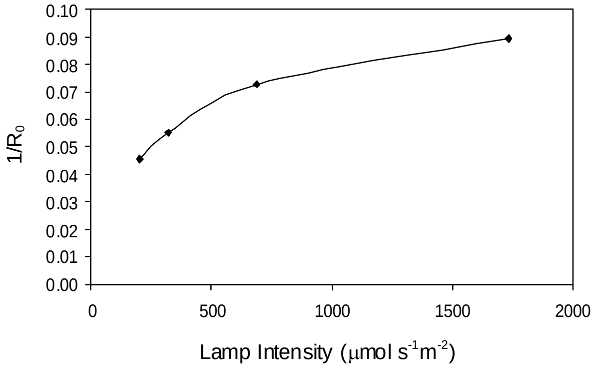

Figure 2. Relationship between reciprocal Initial Rate ($1/R_0$) and lamp (400 W UVASpot 400 lamp; spectral output 330 – 450 nm) intensity for destruction of geosmin (1 μg ml^{-1}) using Hombikat K01/C.

linear relationship between destruction rate and light intensity at low light intensity and square root relationship at high light intensity is observed. A similar relationship has been observed by other workers (*11, 14, 15*). A plot of the reciprocal initial rate of geosmin destruction (R_0) against light intensity demonstrates that the increase in geosmin destruction is linear at low light intensities, but reducing at the higher light intensities, possibly moving into a square root relationship between light intensity and geosmin destruction (Figure 2). A similar relationship has been observed by other workers.

Previous studies (*14-16*) of the effect of light intensity on the kinetics of the photocatalysis process indicated that at low light intensities (0-20 W cm^{-2}), and mass transfer dependant, the reaction rate would increase linearly with increasing light intensity (first order). At intermediate intensity levels (~20 W cm^{-2}), the reaction rate increases with the square root of light intensity. At high light intensities the rate is independent of light intensity. This is probably caused by the competition of electron-hole pair separation and recombination, resulting in a reduced effect of light intensity on the reaction rate. At low light intensities electron-hole recombination is negligible. The work conducted here clearly demonstrates a similar relationship between the rate of geosmin destruction and increasing light intensity.

An increase in aeration rate was found to increase the rate of geosmin removal, which levelled off at an air flow rate of 120 mL min^{-1} (Figure 3). However, it was also noted that geosmin removal also increased in the controls as aeration rates increased. Adjusting geosmin loss, by subtracting geosmin loss under control conditions (no light) from the geosmin reduction under photocatalytic conditions, indicated there was a negligible difference in the rate of geosmin

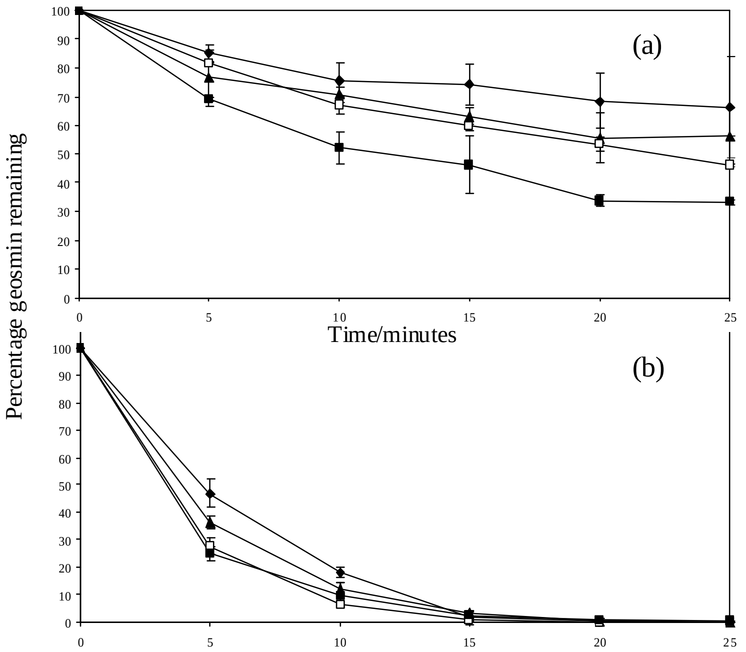

Figure 3. Influence of aeration rate (150 —■—; 120 —□—; 60 —▲— and 30 mL min^{-1} —◆—) on the photocatalysis of geosmin (1 µg mL^{-1}) **(a)** Dark control **(b)** Removal of geosmin by TiO_2 photooxidation. Geosmin monitored by GC-MS. Bars equivalent to 1 SD (n=2).

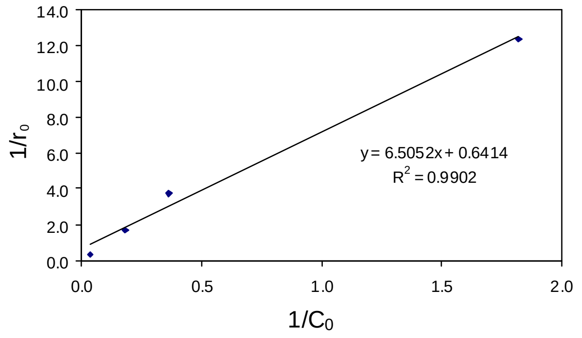

Figure 4. Reciprocal initial rate ($1/r_0$) of geosmin destruction vs. reciprocal initial concentration ($1/C_0$) of Geosmin.

destruction. For the flow rates of 30, 60, 120, and 150 mL min^{-1}, adjusted geosmin loss was 48, 46, 49, and 44 % respectively after 5 minutes.

Although previous studies suggest that air stripping is unlikely to remove geosmin from water (*17*), results in this study appear to show that an increase in aeration rate does have an effect on the volatilization of geosmin. This effect is most pronounced when comparing the aeration rates of 30 mL min^{-1}, the standard air flow rate used in this study for the photocatalysis of geosmin, and the 150 ml min^{-1} flow rate, under control conditions (Figure 3). Geosmin losses with aeration and no illumination were 34 and 67% for the 30 and 150 mL min^{-1} respectively after 25 minutes. Although a proportion of these losses can be associated with dark adsorption onto the catalyst surface, it is clear that a significant proportion of the geosmin loss observed at the 150 mL min^{-1} flow rate is caused by volatilization.

The Langmuir-Hinshelwood rate expression has been successfully applied to the heterogeneous photocatalytic degradation of a wide variety of organic compounds (*11, 18, 19*), describing the relationship between initial degradation and initial concentration. By plotting reciprocal initial rate against reciprocal initial concentration a linear expression can be obtained (*20*). A linear fit was achieved (R^2 = 0.9901) with values of 1.56 µM min^{-1} and 0.098 $µM^{-1}$, for *k* and *K* respectively (Figure 4). This would suggest that degradation of geosmin obeys the Langmuir-Hinshelwood model and that geosmin degradation occurs on the TiO_2 surface. However, when the overall degradation characteristics were followed until complete removal occurred, it was observed that there was little difference between highest three concentrations (5, 1 and 0.5 µg mL^{-1}, data not shown). This may suggest that degradation is also taking place in solution.

Table 1 compares the values determined for *k* and *K* for the destruction of geosmin using the Langmuir-Hinshelwood model in this study with the values for geosmin destruction using P-25 titanium dioxide (*12*). The rate of geosmin degradation is considerably faster than previously found with P-25 (Table 1) with removal of 50% of the geosmin taking ~5 minutes, compared with ~12 minutes for P-25.

Previous work has demonstrated that organic compounds appear to be more strongly adsorbed to TiO_2

Table 1. Comparison of rate and adsorption constants for the photocatalytic destruction of geosmin by Hombikat 01/C with P-25 data from Lawton and co-workers (*12*). Constants *k* and *K* determined using simple Langmuir-Hinshelwood model.

TiO_2 Catalyst	*k* [μM min^{-1}]	*K* [μM^{-1}]
Hombikat 01/C	1.56	0.099
Degussa P-25	0.0048	24.55

dispersions than film forms of TiO_2. The Hombikat K01/C catalyst has greater photocatalytically available surface area than a thin film, but less than powdered TiO_2, this is reflected in the *K* values in Table 1, with adsorption of geosmin onto dispersed P-25 250 times greater than adsorption onto Hombikat K01/C. These data would initially suggest that surface adsorption of geosmin onto Hombikat K01/C TiO_2 was not essential for the degradation of geosmin.

Ollis has recently proposed a steady state model for liquid phase kinetics of photocatalytic reactions (*21, 22*). This model has been developed following from the observation that the value of K calculated for the photocatalytic processes was not a true representation of the dark adsorption constant for the process. In fact with the re-evaluation of the mechanism of the photocatalytic reactions it would appear that the K like k is dependent on the light intensity. A more detailed study of this model was subsequently reported by Mills and Ollis (*22*) where the data for the kinetic data for the photocatalytic destruction of a number of substrates were applied to the steady state model and a good agreement with experimental observations was obtained. The system under investigation in this paper is however slightly more complicated by the nature of the catalyst. Most investigations of the kinetics of photocatalytic processes have involved the use of either powder suspensions or immobilized films. The granular material used in this study acts as neither a suspended powder system nor an immobilized film process so the applicability of a pure Langmuir-Hinshelwood model may not be appropriate.

This study demonstrates good performance of the Hombikat K01/C TiO_2 catalyst for geosmin destruction and its potential for treating tainted water supplies. Furthermore, as a pelleted catalyst it eliminates the need for the challenging processing required to remove powdered catalysts such as P-25 from water suspensions, while at the same time providing a considerably larger surface area compared to thin-film reactors. Future work is now required to evaluate catalyst performance in a range of natural waters and to design appropriate treatment scale reactors.

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