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A continuous flow packed bed photocatalytic reactor for the destruction of 2-methylisoborneol and geosmin utilising pelletised TiO_2.

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Abstract

Taste and odour compounds, especially geosmin (GSM) and 2-methylisoborneol (2-MIB), cause major problems in both drinking water and aquaculture industries world-wide. Aquaculture in particular has experienced significant financial losses due to the accumulation of taint compounds prior to harvest resulting in consumer rejection. UV-TiO_2 photocatalysis has been demonstrated to remove GSM and 2-MIB at laboratory scale but the development of a continuous flow reactor suitable for use in water treatment has not been investigated. In this study, a pilot packed bed photocatalytic reactor was developed and evaluated for water treatment with both laboratory and naturally tainted samples. A significant reduction of both 2-MIB and GSM was achieved in both trials using the packed bed reactor unit. With the laboratory spiked water (100 ng L^{-1} of each compound added prior to treatment), detectable levels were reduced by up to 97% after a single pass through the unit. When the reactor was used to treat water in a fish farm where both compounds were being produced *in situ* (2-MIB: 19 ng L^{-1} and GSM: 14 ng L^{-1}) a reduction of almost 90% in taint compounds was achieved. These very encouraging promising results demonstrate the potential of this UV-TiO_2 photocatalytic reactor for water treatment in fish rearing systems and other applications.

Keywords: Packed bed photocatalytic reactor, TiO_2 pellets, water treatment; aquaculture; 2-methylisoborneol; Geosmin

1. Introduction

The two most prominent members of the group of taste and odour (off-flavour) compounds are 2-methylisoborneol (2-MIB) and geosmin (GSM), both compounds can have a significant financial impact on drinking water providers as well as fish farmers [1, 2]. They confer a musty-earthy flavour and smell to water and any produce grown in contaminated water, such as farmed fish [3, 4]. Significant financial losses are incurred by drinking water companies due to rejection of the product by customers and the need for additional treatment of water supplies [5]. Similar issues are also present in aquaculture, both in outdoor production ponds and in recirculation systems. Tainting caused from contamination with 2-MIB and GSM in aquaculture arises from the fact that even a relatively short contact time of a few hours is enough for measurable amounts to bioaccumulate in the tissue of the fish [4]. Depuration can take up to several days, provided uncontaminated water can be supplied to the fish in that period [3]. In the United States, research has mainly focused on channel catfish (*Ictalurus punctatus*) [6-8] where the problem has consistently increased production costs. Farmed rainbow trout and carp rearing (*Onchorhynchus mykiss* and *Cyprinus carpio*) in the UK and France have also been under investigation [9-11], as well as tilapia (*Oreochromis niloticus*) [12], 2000) and salmon (*Salmo salar*) [13]. The financial impact caused by the taste and odour compounds including 2-MIB and GSM cost the channel catfish rearing industry $ 15 to $ 23 million annually [2]. Therefore, it is important for the potable water and aquaculture industries to monitor and control the presence of both 2-MIB and GSM.

There are a number of treatment strategies depending on for what the water will be used. In aquaculture, recirculation systems, employing activated carbon filters [14], and purging [15] have been explored with little success. In water treatment applications, it has been found that conventional treatment methods are ineffective in removing 2-MIB and GSM from water [16] while chemical treatment of the water by oxidation of the compounds with chlorine or ozone does not always completely remove them [17]. Treatment with activated carbon has been successfully applied [18]. The drawback of the activated carbon method is the fact that the carbon eventually saturates especially where natural organic matter (NOM) levels are high and either needs to be regenerated or destroyed by incineration or deposited in a landfill [19,20]. A potential alternative, or indeed supplementary treatment, could be the implementation of titanium dioxide assisted photodegradation of 2-MIB and GSM. Promising results in a lab scale study have been achieved by Lawton *et al.* [21] where it was shown that titanium dioxide (nanoparticulate powder) successfully decomposed both 2-MIB and GSM within 60 minutes. Further studies by this group demonstrated that the pellet form of the photocatalyst also successfully degraded geosmin [22,23].

While a number of studies [21-24] have demonstrated the potential application of TiO_2 photocatalysis for taint removal in batch reactors, it is desirable to develop and evaluate a continuous flow reactor since batch treatment systems would be impractical for applied applications.

In developing a photocatalytic reactor for water treatment a number of key parameters, need to be considered [25]. These include the distribution of the photocatalyst and contaminant within the water matrix, the mass transfer of the target contaminant to the catalyst surface, the kinetics of the photocatalytic decomposition process at the catalyst surface. A particularly critical parameter is maximising the effective irradiation of the photocatalyst within the reactor unit, as the kinetics of the photocatalytic process are dependent on the irradiation intensity [25]. Where suspended catalyst reactors have been used in the past, a significant challenge has been separation of nanoparticulate TiO_2 from the treated water, which has greatly limited its application. Finally the capability of the unit to handle high throughputs of contaminated water has proven to be a particular challenge and this is strongly influenced by the parameters detailed above [25, 26].

This paper details the development and application of a simple modular photocatalytic water treatment unit allowing easy scalability for a wide range of applications, hence for the first time providing a practical solution for the removal of GSM and 2-MIB in water.

2. Experimental

2.1 *Materials*

The Hombikat K01/C titanium dioxide pellets were acquired from Sachtleben Chemie, Germany. These robust pellets are cylindrical in shape of between 8 and 15 mm in length with a diameter of ~5 mm with a surface area of 41 m^2g^{-1} [27]. The combined 2-methylisoborneol and geosmin standards were of analytical grade and obtained from Supelco, UK. All solvents used for the analysis were analytical grade supplied by Fisher Scientific, UK and of analytical grade.

2.2 *Construction of reactor for photocatalysis*

The reactor was constructed from a sheet of double walled Plexiglas Altop® (Evonik, Germany) with >97 % UV transmittance (12 x 2000 x 900 mm) and fifteen channels (c. 60 mm) running along the lengths of the sheet. To achieve the maximum path length (i.e. 30 m), 60 mm segments were removed from the inner vertical dividers on alternating ends of the sheet (Fig. 1). One end of the reactor was then sealed with the capping end-piece. The end-piece covering the nearest channel to the edge of the sheet was perforated to allow the outflow of the effluent. The reactor was filled with Hombikat K01/C titanium dioxide pellets (c. 22 kg). Once the catalyst was loaded into each channel the top was sealed with the capping end-pieces, only allowing one channel nearest the edge, diagonally opposite the outlet, to remain open to receive the tubing that would introduce the sample into the reactor (Fig. 1). The UV radiation was supplied by 12 UVB lamps (100 W per lamp, spectral output: 280 to 330 nm) placed near (c. 150 mm) the surface of the reactor. The reactor was mounted on marine ply cut to the same size as the reactor with a sheet of reflective acetate placed between the reactor and the ply to maximise reflective illumination within the reactor bed.

2.3 *Photocatalysis*

Accurately evaluating the actual removal of GSM and 2-MIB in water treatment systems is challenging, as these compounds can be lost to many surfaces [28]. To avoid sample loss due to non-specific binding (e.g. in pump tubing and plastic carboys), stainless steel pressure cans were used to hold the water prior to treatment and to apply the water to the reactor. For the laboratory evaluation 4 pressure cans were filled with 30 L each of Milli-RO water (Millipore) spiked with 2-MIB and GSM standard to achieve a concentration of 100 ng L^{-1} of each of the off-flavour compounds in the final solution. Triplicate samples (200 mL) were taken from each of the pressure cans to confirm the initial concentration of both analytes (T_0). Nitrogen gas was used as propellant to drive the water through the photocatalytic reactor at a flow rate of approximately 2 L min^{-1}. As there was limited back pressure due to the free flow of liquid through the reactor, only a small head pressure of 1-2 barr was required. Pressure was only applied immediately before treatment to prevent alteration in dissolved O_2 levels. Water (30 L) was passed through the reactor without illumination to determine system and dark adsorption with samples (triplicate 200 mL) collected directly from the outflow. To evaluate the photocatalytic removal of the 2-MIB and GSM, three 30 L batches were passed through the reactor at 2 L min^{-1} under constant illumination. Samples (200 mL) were collected in triplicate as each of the three batches passed through the reactor.

The photocatalytic reactor was designed for potential application in aquaculture settings hence naturally tainted water from a carp rearing raceway where 2-MIB and GSM were already present was used to evaluate the reactors performance. The selected sampling site was a 21 x 6 m indoor raceway (approximate depth 1.3 m) which had been in operation for carp rearing for 2.5 years located in central Scotland. Both GSM and 2-MIB had been previously detected at this site. The water was collected 09.03.2012 and placed directly into four 30 L stainless steel pressure cans. The experimental procedure was followed as per the laboratory testing with spiked purified water.

2.4 *2-MIB and GSM Analysis*

Each sample was immediately pre-concentrated using C8 solid phase extraction (SPE) cartridges (Biotage, Upsala, Sweden) where the 200 mL water sample was applied to the conditioned cartridge with subsequent elution in ethyl acetate (Table 1). Quantitative analysis of the samples was then carried out using a pulsed splitless injection GC-MS method (Table 2) where the analytes were detected in SIM mode [29].

3. Results and discussion

3.1 *Reactor Design*

The packed bed reactor configuration was designed with certain features that are important in ensuring large scale applications are viable. The photocatalytic reactor was constructed from Plexiglas which has a high transmission of UV light greater than the band gap energy required to activate the TiO_2 photocatalyst (380 nm [27]). The Plexiglas also facilitates effective transmission of UVB light. Furthermore, the reactor was designed with a relatively thin catalyst bed to further enhance effective light penetration throughout the unit. The way the photocatalyst was deployed within the channels allowed flow through the catalyst bed within the unit, which has been shown to enhance mass transport properties within photocatalytic reactors [25, 26, 30]. Although there was a relatively high loading of photocatalyst in the reactor unit (22 kg), the reactor was operated in a flow through mode pumping the water for treatment from a main reservoir. This is the type of configuration that would be adopted in a fish farm application. Using the pelletised photocatalyst material (Hombikat K01/C) the requirement for a catalyst separation step has been eliminated, which is required in packed bed units that utilise powder materials. Previous studies had demonstrated that this particular catalyst material and reactor configuration overcame the difficulties of catalyst water/separation encountered when employing nanoparticulate TiO_2 and was robust, not shedding significant quantities of powdered TiO_2 as has been observed for other particulate catalysts [31]. It had also previously been demonstrated that this catalyst performed well in an alternative batch reactor designed to evaluate the destruction of GSM [22]. The unpacked volume of the reactor was 21.6 L but when fully packed (22 kg of TiO_2

pellets = 17.6 L) the working fluid volume of the reactor was 4 L allowing a 2 minute residency at the flow rate applied (2 L min^{-1}).

3.2 *Reactor performance using laboratory water spiked with 2-MIB and GSM*

The investigation with spiked Milli-RO laboratory water demonstrates good removal of both 2-MIB and GSM (Fig. 2). Approximately 80 % and 88 % of the removal of 2-MIB and GSM respectively can be accounted for by dark adsorption to the pelleted titanium dioxide. This is significantly higher than that observed previously for GSM and the same catalyst (10-20% dark absorption [22]). One of the likely explanations for this significant difference could be the marked difference in catalyst load. In the work of Bellu and colleagues [22], the catalyst load related to the reaction volume was 0.75 kg L^{-1} compared to the current reactor with 5.5 kg L^{-1} providing significant increase in catalyst surface area. The flow through system also may favour dark adsorption due to the enhanced mass transport. Adsorption of the contaminant to the surface of the photocatalyst is an important first step in the photocatalytic decomposition process. It has previously been reported that for the photocatalytic destruction of microcystins, the materials that demonstrated the highest dark adsorption to the photocatalyst also displayed the most efficient photocatalytic decomposition [32]. On irradiation of the reactor unit 96% of both compounds were removed from the contaminated water sample. The photocatalyst materials were reused for treating different water samples and similar levels of dark adsorption and subsequent photocatalytic decomposition were achieved, demonstrating that the removal of both taint compounds was not purely an adsorption process; the adsorbed materials underwent subsequent photocatalytic decomposition. Bellu [33] has also observed the destruction of GSM in a bench top TiO_2-UV flow-through reactor. In Bellu's [33] design the lowest flow rate (0.05 L min^{-1}) achieved 67 %

removal of the original spike (100 ng L^{-1}) for GSM with the same catalyst (Hombikat K01/C). However, when the flow rate was increased to 0.2 L min^{-1}, a tenth of the flow rate used in the current study, the removal efficiency dropped to only 19%. Some of the key differences between the two systems are the much lower catalyst load (0.842 kg) and the UV irradiation, which was a single UV black lamp tube (40 Watt).

One of the only other studies which evaluate TiO_2 photocatalysis of both 2-MIB and GSM is an investigation by Lawton *et al.* [21] which reports that nanoparticulate Degussa P25 successfully degraded > 99 % of 2-MIB within 30 mins, however, the complete removal of GSM took 60 mins. This is somewhat different to the identical removal rates observed here for both compounds and interestingly it is the GSM that was observed to show the highest dark absorption. Typically, the higher the dark adsorption of a compound, the more efficient the photocatalytic removal of that compound. It is also worth noting that the removal rates that were observed were highly reproducible between each batch of spiked water applied to the reactor (Fig. 2).

3.3 *Reactor performance using fish farm water with naturally occurring 2-MIB and GSM*

Following this successful laboratory, test investigations were carried out to evaluate the performance of the reactor using a sample typical of that which may require treatment to remove naturally occurring taint. Water was sampled from a carp rearing raceway that has been in operation for more than two years and was known to contain naturally occurring amounts of 2-MIB and GSM. As expected both compounds were detected by SPE-GC/MS in the water prior to treatment, with GSM levels (18.5 ng L^{-1}) being slightly higher than the level of 2-MIB (14 ng L^{-1}). The water had not been pre-filtered prior to treatment so contained both dissolved and suspended matter. The reactor successfully removed the majority of the 2-MIB and GSM present in the fish farm samples (figure 3). As might be anticipated the dark adsorption, 71% for 2-MIB and 67% for GSM, is lower than that observed for the spiked laboratory water (2-MIB: 80 % and GSM: 88 %). Although the amount of the analytes in the water from the fish farm is lower (14 and 18.5 compared to 100 ng L^{-1}) the reduced dark adsorption can be explained by the presence of natural organic matter (NOM) competing for the binding sites on the catalyst and hence competing in the photocatalytic decomposition process. Newcombe *et al.* [34, 35] have conducted a study that investigated the competition between 2-MIB and natural organic matter (NOM) for binding sites on activated carbon. It was found that NOM actively competes with 2-MIB for binding places on the activated carbon, a similar process is very likely to be happening with 2-MIB, GSM and the NOM present in the fish farm samples as they compete for sites on the TiO_2. Doll and Frimmel [36] proposed that the presence of NOM and other organic substances would reduce the photocatalytic efficiency due to the obvious direct competition for active sites but also due to attenuation of the UV radiation and possibly catalyst surface deactivation.

UV Irradiation of the water as it passed through the reactor resulted in the successful elimination of 91% of the GSM (1.7 ng L^{-1} remaining) and 84% (2.2 ng L^{-1} remaining) of the 2-MIB. Bellu and co-workers [33] found that their flow reactor design applied to waters from a Danish eel farm could only remove 33 % of the GSM present (7 ng L^{-1}) in one pass through their reactor. Bellu [33] also proposed NOM as a competitor for the photocatalytic decomposition of GSM. In that study, significant removal was only achieved after 3 passes through a catalyst filled glass coil resulting in a total contact time of 60 mins. The reactor in the present study showed significant improvement in treatment efficiency, achieving almost complete removal with one pass through the reactor, which took 2 mins. The performance of this reactor reduced both GSM and 2-MIB to below the level that would be likely to cause taste and odour problems in aquaculture and drinking water, where the threshold for human detection MIB/geosmin can range from 4 to 20 ng/L [37, 38].

Analysis of the treated water samples, both in lab grade water and that from the fish farm, revealed no significant detectable by-products. Few studies have been published that explore the reaction by-products of 2-MIB and GSM following oxidation processes. Recently, Qi and co-workers [39] reported the production of ketoaldehydes during the ozonolysis of 2-MIB and trichloroanisole (TCA) in water. However, the yield of by-products was dependent on ozone dosage, temperature, pH and reaction matrix as might be expected. In the present study, the lack of detectable by-products may highlight the suitability of this systems design. The high catalyst load and flow through pattern allows the degradation of the parent compounds followed by adsorption and degradation of by-products. Other possible explanations include that the processing (SPE sample concentration) and GC-MS detection method were not optimised for by-product detection or that the activity of hydroxyl radicals result in lower yield of aldehydes [38].

4. Conclusion

The modular continual-flow reactor design, which is readily scalable to treat larger volumes, has successfully demonstrated the removal of both 2-MIB and GSM under both laboratory conditions and in the field with a contact time of only 2 mins. This type of reactor design is a particularly effective way to deploy the catalyst in a contained unit together with the control over flow rates, mass transport limitations may be minimised. This is a particularly important consideration when new more effective photocatalysts are developed as the system should not depend on mass transport limitations and hence any benefits of enhanced photocatalytic activity with the new materials may be maximised. This design of reactor could be added within the flow stream of a typical recirculation system used in the culture of fish and evaluation of its potential application in potable water treatment should be explored. Further development and application of this technology will now be explored to evaluate the removal of other pollutants and to optimise relevant treatment parameters.

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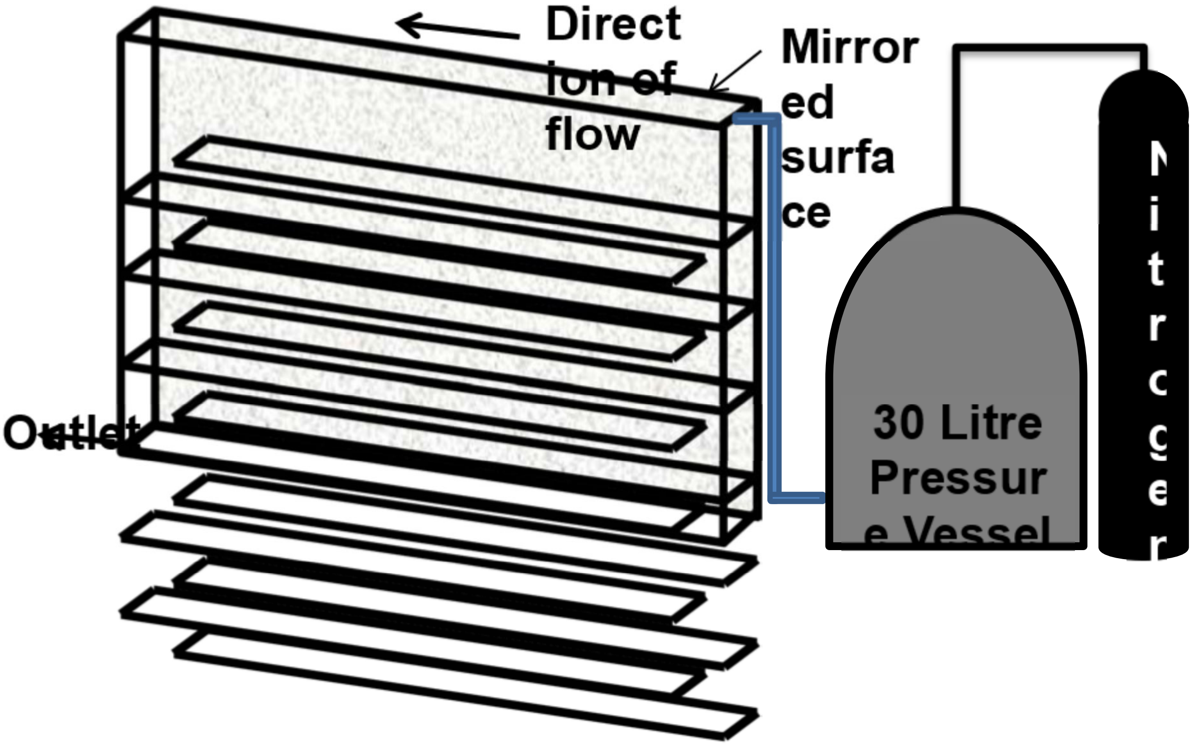
Fig. 1 a). Photocatalytic reactor used for the photocatalysis of 2-MIB and GSM over titanium dioxide in pellet form, for both spiked laboratory and environmental (fish farm) samples. b) Side cross section view of reactor.

Fig. 2. Laboratory test of photocatalytic reactor. 2-MIB (⊡) and GSM (▨) concentrations at T_0 and after one pass through the photocatalytic reactor. Sample 1: no irradiation, samples 2-4: irradiation. Initial concentration of 2-MIB and GSM: 100 ng L^{-1}. Error bars=1 SD; n=3.

Fig. 3. Results of the fish farm test of the photocatalytic reactor. 2-MIB (⊡) and GSM (▨) concentrations at T_0 and after one pass through the photocatalytic reactor. Sample 1: no irradiation, samples 2-4: irradiation. Error bars=1 SD; n=3.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Nitroger

Fig 1 a)

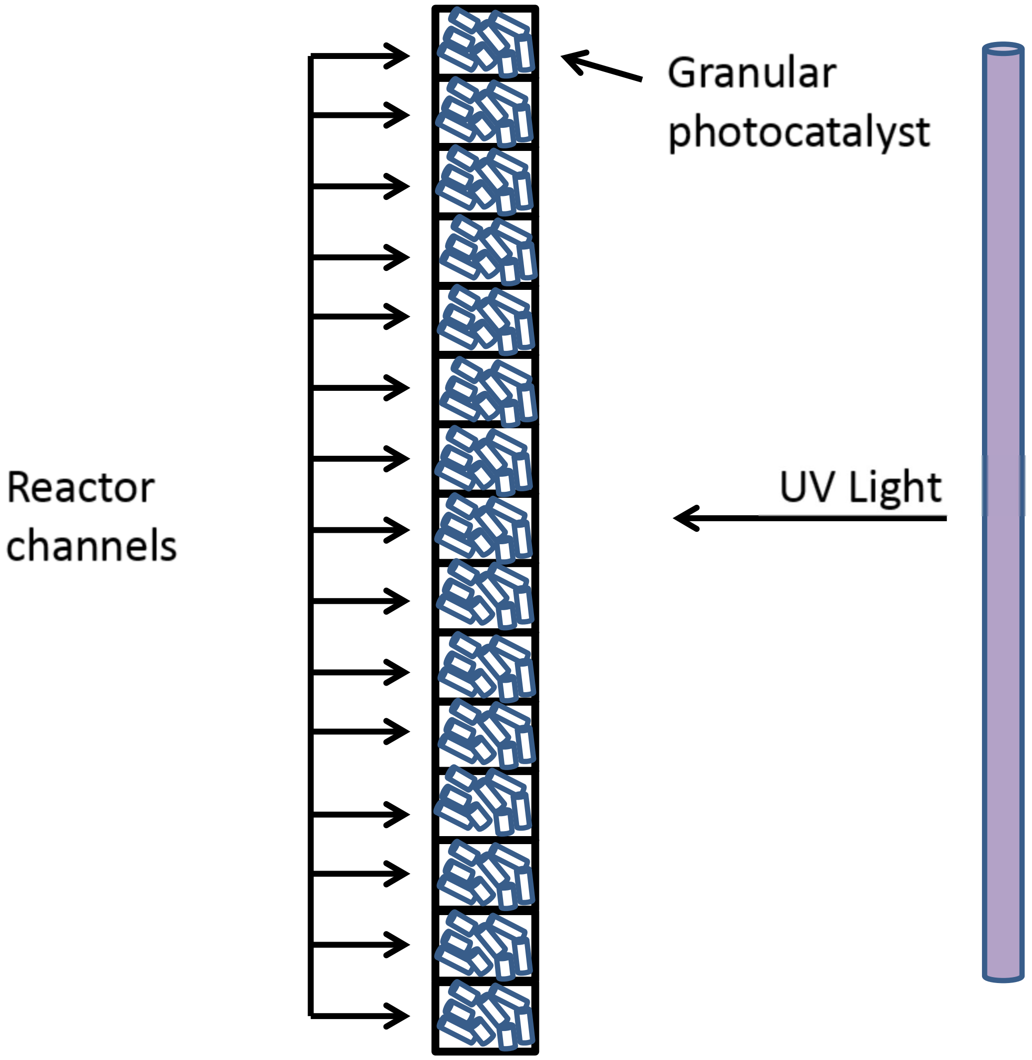
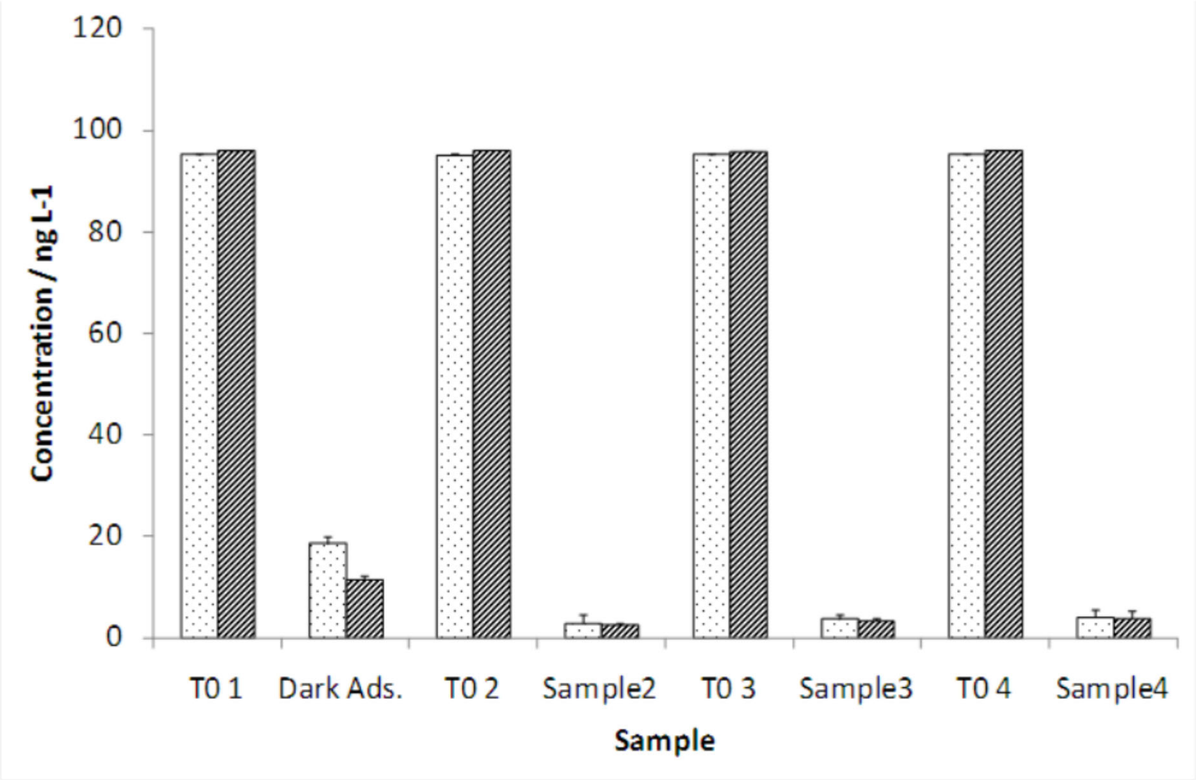


Fig 1 b)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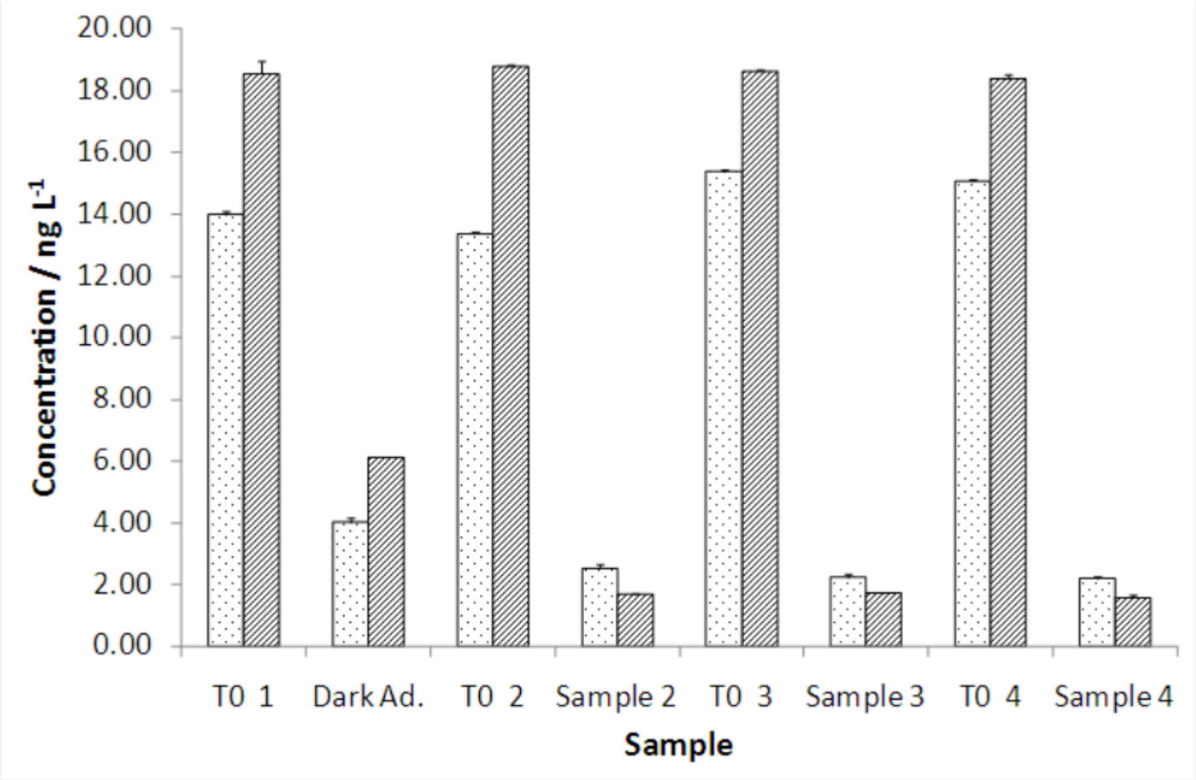

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10.00
8.00
6.00
4.00
2.00
0.00
Concentration / ng L-1
T0 1
Dark Ad.
T0 2
Sample 2
T0 3
Sample 3
T0 4
Sample 4
Sample

Fig 3.

Table 1 SPE method for the pre-concentration of 2-MIB and GSM

SPE parameter	*Applied in this method*
Sorbent material	**C8 (Biotage)**
Sorbent load	**100 mg**
Cartridge volume	**1 mL**
End-capped	**Yes**
Conditioning	**2 mL: Hexane, Acetone, Methanol; 10 mL: Milli-Q**
Mode of loading	**PTFE tubing with vacuum suction**
Sample volume	**200 mL**
Drying time	**5 min**
Elution solvent	**Ethyl acetate**
Elution solvent volume	**0.5 ml (+0.05 mL TCA internal standard)**
Concentration achieved	**363:1**

Table 2 Parameters for GC-MS (Agilent 6890A).

Parameter	*Optimised method*
Front inlet parameters	
Injection mode	Pulsed splitless
Injection temperature	250 °C
Inlet pressure	10 psi
Injection (pulsed) pressure	25 psi
Pulse time	0.5 min
Injection volume	3 µL
Gas type	Helium
Column	
Column type	Capillary column
Column length	30 m
Column diameter	250 µm
Film thickness	25 µm
Pressure	10 psi
Mass spectrometer – quantification ions (SIM)	
2-methylisoborneol	95, 107, 135
Trichloroanisole (Internal Standard)	167, 195, 210
Geosmin	112, 125, 182
Temperature program	
Initial temperature	60 °C
0 - 1 min	60 °C
2 - 3 min	20 °C min^{-1} (to reach 100 °C)
4 - 10 min	7.5 °C min^{-1} (to reach 152 °C)
10 - 12 min	Hold temperature (152 °C)