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1 **A continuous flow packed bed photocatalytic reactor for the destruction of 2-**
2 **methylisoborneol and geosmin utilising pelletised TiO₂.**

3 Carlos J. Pestana^a, Peter J. K. Robertson^{a*}, Christine Edwards^a, Willem Wilhelm^b,
4 Craig McKenzie^a, Linda A. Lawton^a

5 ^aInnovation, Design and Sustainability (IDeaS) Research Institute, Robert Gordon
6 University, Schoolhill, Aberdeen AB10 1FR, UK

7 ^bWAE, Eisenhowerlaan 66, NL – 2625 GK, Delft, The Netherlands

8

9 *corresponding author: Tel: +44 1224 263750, Fax: +44 1224 262757

10 Email: peter.robertson@rgu.ac.uk (PKJ Robertson)

11

12 **Abstract**

13 Taste and odour compounds, especially geosmin (GSM) and 2-methylisoborneol (2-
14 MIB), cause major problems in both drinking water and aquaculture industries world-
15 wide. Aquaculture in particular has experienced significant financial losses due to the
16 accumulation of taint compounds prior to harvest resulting in consumer rejection.
17 UV-TiO₂ photocatalysis has been demonstrated to remove GSM and 2-MIB at
18 laboratory scale but the development of a continuous flow reactor suitable for use in
19 water treatment has not been investigated. In this study, a pilot packed bed
20 photocatalytic reactor was developed and evaluated for water treatment with both
21 laboratory and naturally tainted samples. A significant reduction of both 2-MIB and
22 GSM was achieved in both trials using the packed bed reactor unit. With the
23 laboratory spiked water (100 ng L⁻¹ of each compound added prior to treatment),
24 detectable levels were reduced by up to 97% after a single pass through the unit.
25 When the reactor was used to treat water in a fish farm where both compounds were
26 being produced *in situ* (2-MIB: 19 ng L⁻¹ and GSM: 14 ng L⁻¹) a reduction of almost
27 90% in taint compounds was achieved. These very encouraging promising results
28 demonstrate the potential of this UV-TiO₂ photocatalytic reactor for water treatment
29 in fish rearing systems and other applications.

30 **Keywords:** Packed bed photocatalytic reactor, TiO₂ pellets, water treatment;
31 aquaculture; 2-methylisoborneol; Geosmin

32

33 1. Introduction

34 The two most prominent members of the group of taste and odour (off-flavour)
35 compounds are 2-methylisoborneol (2-MIB) and geosmin (GSM), both compounds
36 can have a significant financial impact on drinking water providers as well as fish
37 farmers [1, 2]. They confer a musty-earthy flavour and smell to water and any
38 produce grown in contaminated water, such as farmed fish [3, 4]. Significant financial
39 losses are incurred by drinking water companies due to rejection of the product by
40 customers and the need for additional treatment of water supplies [5]. Similar issues
41 are also present in aquaculture, both in outdoor production ponds and in recirculation
42 systems. Tainting caused from contamination with 2-MIB and GSM in aquaculture
43 arises from the fact that even a relatively short contact time of a few hours is enough
44 for measurable amounts to bioaccumulate in the tissue of the fish [4]. Depuration can
45 take up to several days, provided uncontaminated water can be supplied to the fish
46 in that period [3]. In the United States, research has mainly focused on channel
47 catfish (*Ictalurus punctatus*) [6-8] where the problem has consistently increased
48 production costs. Farmed rainbow trout and carp rearing (*Onchorhynchus mykiss*
49 and *Cyprinus carpio*) in the UK and France have also been under investigation [9-
50 11], as well as tilapia (*Oreochromis niloticus*) [12], 2000) and salmon (*Salmo salar*)
51 [13]. The financial impact caused by the taste and odour compounds including 2-MIB
52 and GSM cost the channel catfish rearing industry \$ 15 to \$ 23 million annually [2].
53 Therefore, it is important for the potable water and aquaculture industries to monitor
54 and control the presence of both 2-MIB and GSM.

55

56 There are a number of treatment strategies depending on for what the water will be
57 used. In aquaculture, recirculation systems, employing activated carbon filters [14],
58 and purging [15] have been explored with little success. In water treatment
59 applications, it has been found that conventional treatment methods are ineffective in
60 removing 2-MIB and GSM from water [16] while chemical treatment of the water by
61 oxidation of the compounds with chlorine or ozone does not always completely
62 remove them [17]. Treatment with activated carbon has been successfully applied
63 [18]. The drawback of the activated carbon method is the fact that the carbon
64 eventually saturates especially where natural organic matter (NOM) levels are high
65 and either needs to be regenerated or destroyed by incineration or deposited in a
66 landfill [19,20]. A potential alternative, or indeed supplementary treatment, could be
67 the implementation of titanium dioxide assisted photodegradation of 2-MIB and
68 GSM. Promising results in a lab scale study have been achieved by Lawton *et al.*
69 [21] where it was shown that titanium dioxide (nanoparticulate powder) successfully
70 decomposed both 2-MIB and GSM within 60 minutes. Further studies by this group
71 demonstrated that the pellet form of the photocatalyst also successfully degraded
72 geosmin [22,23].

73

74 While a number of studies [21-24] have demonstrated the potential application of
75 TiO₂ photocatalysis for taint removal in batch reactors, it is desirable to develop and
76 evaluate a continuous flow reactor since batch treatment systems would be
77 impractical for applied applications.

78 In developing a photocatalytic reactor for water treatment a number of key
79 parameters, need to be considered [25]. These include the distribution of the

80 photocatalyst and contaminant within the water matrix, the mass transfer of the
81 target contaminant to the catalyst surface, the kinetics of the photocatalytic
82 decomposition process at the catalyst surface. A particularly critical parameter is
83 maximising the effective irradiation of the photocatalyst within the reactor unit, as the
84 kinetics of the photocatalytic process are dependent on the irradiation intensity [25].
85 Where suspended catalyst reactors have been used in the past, a significant
86 challenge has been separation of nanoparticulate TiO_2 from the treated water, which
87 has greatly limited its application. Finally the capability of the unit to handle high
88 throughputs of contaminated water has proven to be a particular challenge and this
89 is strongly influenced by the parameters detailed above [25, 26].

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

94

95 **2. Experimental**

96 *2.1 Materials*

97 The Hombikat K01/C titanium dioxide pellets were acquired from Sachtleben
98 Chemie, Germany. These robust pellets are cylindrical in shape of between 8 and
99 15 mm in length with a diameter of ~5 mm with a surface area of 41 m²g⁻¹ [27]. The
100 combined 2-methylisoborneol and geosmin standards were of analytical grade and
101 obtained from Supelco, UK. All solvents used for the analysis were analytical grade
102 supplied by Fisher Scientific, UK and of analytical grade.

103

104 *2.2 Construction of reactor for photocatalysis*

105 The reactor was constructed from a sheet of double walled Plexiglas Altop[®] (Evonik,
106 Germany) with >97 % UV transmittance (12 x 2000 x 900 mm) and fifteen channels
107 (c. 60 mm) running along the lengths of the sheet. To achieve the maximum path
108 length (i.e. 30 m), 60 mm segments were removed from the inner vertical dividers on
109 alternating ends of the sheet (Fig. 1). One end of the reactor was then sealed with
110 the capping end-piece. The end-piece covering the nearest channel to the edge of
111 the sheet was perforated to allow the outflow of the effluent. The reactor was filled
112 with Hombikat K01/C titanium dioxide pellets (c. 22 kg). Once the catalyst was
113 loaded into each channel the top was sealed with the capping end-pieces, only
114 allowing one channel nearest the edge, diagonally opposite the outlet, to remain
115 open to receive the tubing that would introduce the sample into the reactor (Fig. 1).
116 The UV radiation was supplied by 12 UVB lamps (100 W per lamp, spectral output:
117 280 to 330 nm) placed near (c. 150 mm) the surface of the reactor. The reactor was
118 mounted on marine ply cut to the same size as the reactor with a sheet of reflective

119 acetate placed between the reactor and the ply to maximise reflective illumination
120 within the reactor bed.

121

122 *2.3 Photocatalysis*

123 Accurately evaluating the actual removal of GSM and 2-MIB in water treatment
124 systems is challenging, as these compounds can be lost to many surfaces [28]. To
125 avoid sample loss due to non-specific binding (e.g. in pump tubing and plastic
126 carboys), stainless steel pressure cans were used to hold the water prior to
127 treatment and to apply the water to the reactor. For the laboratory evaluation 4
128 pressure cans were filled with 30 L each of Milli-RO water (Millipore) spiked with 2-
129 MIB and GSM standard to achieve a concentration of 100 ng L⁻¹ of each of the off-
130 flavour compounds in the final solution. Triplicate samples (200 mL) were taken from
131 each of the pressure cans to confirm the initial concentration of both analytes (T₀).
132 Nitrogen gas was used as propellant to drive the water through the photocatalytic
133 reactor at a flow rate of approximately 2 L min⁻¹. As there was limited back pressure
134 due to the free flow of liquid through the reactor, only a small head pressure of 1-2
135 barr was required. Pressure was only applied immediately before treatment to
136 prevent alteration in dissolved O₂ levels. Water (30 L) was passed through the
137 reactor without illumination to determine system and dark adsorption with samples
138 (triplicate 200 mL) collected directly from the outflow. To evaluate the photocatalytic
139 removal of the 2-MIB and GSM, three 30 L batches were passed through the reactor
140 at 2 L min⁻¹ under constant illumination. Samples (200 mL) were collected in triplicate
141 as each of the three batches passed through the reactor.

142

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

152

153 *2.4 2-MIB and GSM Analysis*

154 Each sample was immediately pre-concentrated using C8 solid phase extraction
155 (SPE) cartridges (Biotage, Upsala, Sweden) where the 200 mL water sample was
156 applied to the conditioned cartridge with subsequent elution in ethyl acetate (Table
157 1). Quantitative analysis of the samples was then carried out using a pulsed splitless
158 injection GC-MS method (Table 2) where the analytes were detected in SIM mode
159 [29].

160

161

162 **3. Results and discussion**

163 *3.1 Reactor Design*

164 The packed bed reactor configuration was designed with certain features that are
165 important in ensuring large scale applications are viable. The photocatalytic reactor
166 was constructed from Plexiglas which has a high transmission of UV light greater
167 than the band gap energy required to activate the TiO₂ photocatalyst (380 nm [27]).
168 The Plexiglas also facilitates effective transmission of UVB light. Furthermore, the
169 reactor was designed with a relatively thin catalyst bed to further enhance effective
170 light penetration throughout the unit. The way the photocatalyst was deployed within
171 the channels allowed flow through the catalyst bed within the unit, which has been
172 shown to enhance mass transport properties within photocatalytic reactors [25, 26,
173 30]. Although there was a relatively high loading of photocatalyst in the reactor unit
174 (22 kg), the reactor was operated in a flow through mode pumping the water for
175 treatment from a main reservoir. This is the type of configuration that would be
176 adopted in a fish farm application. Using the pelletised photocatalyst material
177 (Hombikat K01/C) the requirement for a catalyst separation step has been
178 eliminated, which is required in packed bed units that utilise powder materials.
179 Previous studies had demonstrated that this particular catalyst material and reactor
180 configuration overcame the difficulties of catalyst water/separation encountered
181 when employing nanoparticulate TiO₂ and was robust, not shedding significant
182 quantities of powdered TiO₂ as has been observed for other particulate catalysts
183 [31]. It had also previously been demonstrated that this catalyst performed well in an
184 alternative batch reactor designed to evaluate the destruction of GSM [22]. The
185 unpacked volume of the reactor was 21.6 L but when fully packed (22 kg of TiO₂

186 pellets = 17.6 L) the working fluid volume of the reactor was 4 L allowing a 2 minute
187 residency at the flow rate applied (2 L min⁻¹).

188 3.2 Reactor performance using laboratory water spiked with 2-MIB and GSM

189 The investigation with spiked Milli-RO laboratory water demonstrates good removal
190 of both 2-MIB and GSM (Fig. 2). Approximately 80 % and 88 % of the removal of 2-
191 MIB and GSM respectively can be accounted for by dark adsorption to the pelleted
192 titanium dioxide. This is significantly higher than that observed previously for GSM
193 and the same catalyst (10-20% dark absorption [22]). One of the likely explanations
194 for this significant difference could be the marked difference in catalyst load. In the
195 work of Bellu and colleagues [22], the catalyst load related to the reaction volume
196 was 0.75 kg L⁻¹ compared to the current reactor with 5.5 kg L⁻¹ providing significant
197 increase in catalyst surface area. The flow through system also may favour dark
198 adsorption due to the enhanced mass transport. Adsorption of the contaminant to
199 the surface of the photocatalyst is an important first step in the photocatalytic
200 decomposition process. It has previously been reported that for the photocatalytic
201 destruction of microcystins, the materials that demonstrated the highest dark
202 adsorption to the photocatalyst also displayed the most efficient photocatalytic
203 decomposition [32]. On irradiation of the reactor unit 96% of both compounds were
204 removed from the contaminated water sample. The photocatalyst materials were
205 reused for treating different water samples and similar levels of dark adsorption and
206 subsequent photocatalytic decomposition were achieved, demonstrating that the
207 removal of both taint compounds was not purely an adsorption process; the
208 adsorbed materials underwent subsequent photocatalytic decomposition. Bellu [33]
209 has also observed the destruction of GSM in a bench top TiO₂-UV flow-through
210 reactor. In Bellu's [33] design the lowest flow rate (0.05 L min⁻¹) achieved 67 %

211 removal of the original spike (100 ng L^{-1}) for GSM with the same catalyst (Hombikat
212 K01/C). However, when the flow rate was increased to 0.2 L min^{-1} , a tenth of the flow
213 rate used in the current study, the removal efficiency dropped to only 19%. Some of
214 the key differences between the two systems are the much lower catalyst load
215 (0.842 kg) and the UV irradiation, which was a single UV black lamp tube (40 Watt).

216

217 One of the only other studies which evaluate TiO_2 photocatalysis of both 2-MIB and
218 GSM is an investigation by Lawton *et al.* [21] which reports that nanoparticulate
219 Degussa P25 successfully degraded $> 99 \%$ of 2-MIB within 30 mins, however, the
220 complete removal of GSM took 60 mins. This is somewhat different to the identical
221 removal rates observed here for both compounds and interestingly it is the GSM that
222 was observed to show the highest dark absorption. Typically, the higher the dark
223 adsorption of a compound, the more efficient the photocatalytic removal of that
224 compound. It is also worth noting that the removal rates that were observed were
225 highly reproducible between each batch of spiked water applied to the reactor (Fig.
226 2).

227 3.3 Reactor performance using fish farm water with naturally occurring 2-MIB and 228 GSM

229 Following this successful laboratory, test investigations were carried out to evaluate
230 the performance of the reactor using a sample typical of that which may require
231 treatment to remove naturally occurring taint. Water was sampled from a carp
232 rearing raceway that has been in operation for more than two years and was known
233 to contain naturally occurring amounts of 2-MIB and GSM. As expected both
234 compounds were detected by SPE-GC/MS in the water prior to treatment, with GSM

235 levels (18.5 ng L^{-1}) being slightly higher than the level of 2-MIB (14 ng L^{-1}). The
236 water had not been pre-filtered prior to treatment so contained both dissolved and
237 suspended matter. The reactor successfully removed the majority of the 2-MIB and
238 GSM present in the fish farm samples (figure 3). As might be anticipated the dark
239 adsorption, 71% for 2-MIB and 67% for GSM, is lower than that observed for the
240 spiked laboratory water (2-MIB: 80 % and GSM: 88 %). Although the amount of the
241 analytes in the water from the fish farm is lower (14 and 18.5 compared to 100 ng L^{-1})
242 the reduced dark adsorption can be explained by the presence of natural organic
243 matter (NOM) competing for the binding sites on the catalyst and hence competing in
244 the photocatalytic decomposition process. Newcombe *et al.* [34, 35] have conducted
245 a study that investigated the competition between 2-MIB and natural organic matter
246 (NOM) for binding sites on activated carbon. It was found that NOM actively
247 competes with 2-MIB for binding places on the activated carbon, a similar process is
248 very likely to be happening with 2-MIB, GSM and the NOM present in the fish farm
249 samples as they compete for sites on the TiO_2 . Doll and Frimmel [36] proposed that
250 the presence of NOM and other organic substances would reduce the photocatalytic
251 efficiency due to the obvious direct competition for active sites but also due to
252 attenuation of the UV radiation and possibly catalyst surface deactivation.

253

254 UV Irradiation of the water as it passed through the reactor resulted in the successful
255 elimination of 91% of the GSM (1.7 ng L^{-1} remaining) and 84% (2.2 ng L^{-1} remaining)
256 of the 2-MIB. Bellu and co-workers [33] found that their flow reactor design applied
257 to waters from a Danish eel farm could only remove 33 % of the GSM present (7 ng
258 L^{-1}) in one pass through their reactor. Bellu [33] also proposed NOM as a competitor
259 for the photocatalytic decomposition of GSM. In that study, significant removal was

260 only achieved after 3 passes through a catalyst filled glass coil resulting in a total
261 contact time of 60 mins. The reactor in the present study showed significant
262 improvement in treatment efficiency, achieving almost complete removal with one
263 pass through the reactor, which took 2 mins. The performance of this reactor
264 reduced both GSM and 2-MIB to below the level that would be likely to cause taste
265 and odour problems in aquaculture and drinking water, where the threshold for
266 human detection MIB/geosmin can range from 4 to 20 ng/L [37, 38].

267

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

281 **4. Conclusion**

282 The modular continual-flow reactor design, which is readily scalable to treat larger
283 volumes, has successfully demonstrated the removal of both 2-MIB and GSM under

284 both laboratory conditions and in the field with a contact time of only 2 mins. This
285 type of reactor design is a particularly effective way to deploy the catalyst in a
286 contained unit together with the control over flow rates, mass transport limitations
287 may be minimised. This is a particularly important consideration when new more
288 effective photocatalysts are developed as the system should not depend on mass
289 transport limitations and hence any benefits of enhanced photocatalytic activity with
290 the new materials may be maximised. This design of reactor could be added within
291 the flow stream of a typical recirculation system used in the culture of fish and
292 evaluation of its potential application in potable water treatment should be explored.
293 Further development and application of this technology will now be explored to
294 evaluate the removal of other pollutants and to optimise relevant treatment
295 parameters.

296

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303

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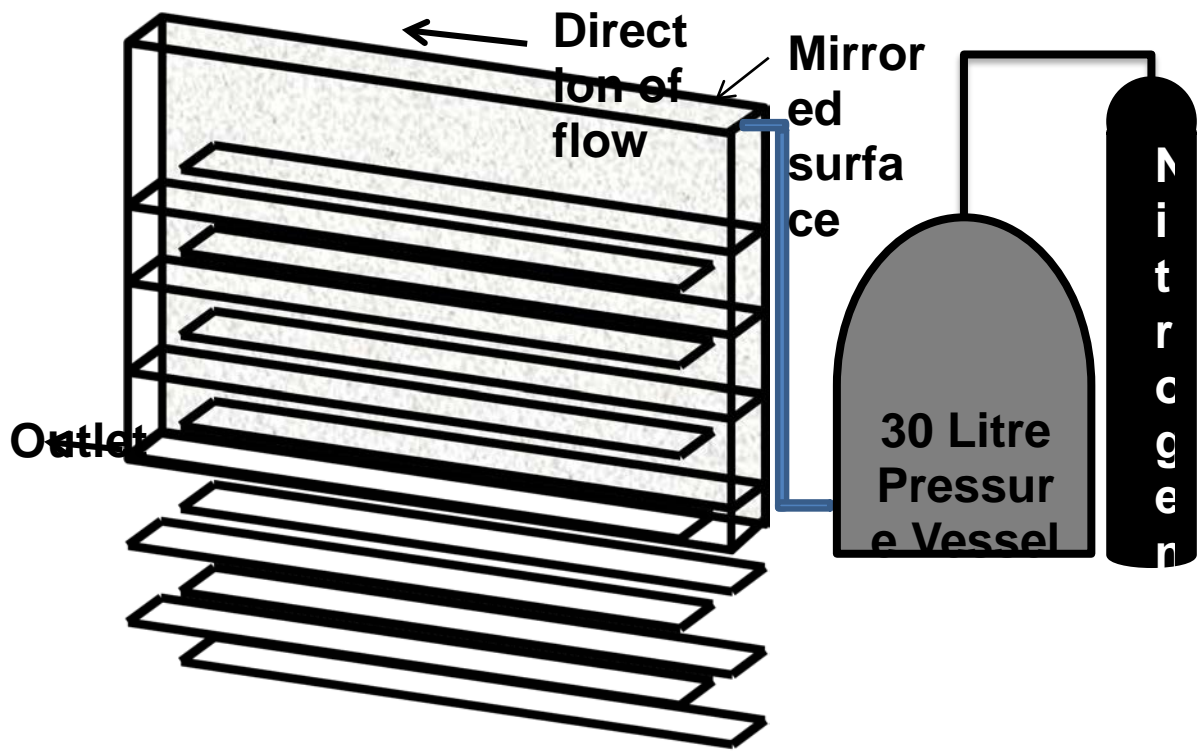
447 **Fig. 1 a).** Photocatalytic reactor used for the photocatalysis of 2-MIB and GSM over
448 titanium dioxide in pellet form, for both spiked laboratory and environmental (fish
449 farm) samples. b) Side cross section view of reactor.

450 **Fig. 2.** Laboratory test of photocatalytic reactor. 2-MIB (□) and GSM (▨)
451 concentrations at T_0 and after one pass through the photocatalytic reactor. Sample
452 1: no irradiation, samples 2-4: irradiation. Initial concentration of 2-MIB and GSM:
453 100 ng L^{-1} . Error bars=1 SD; n=3.

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

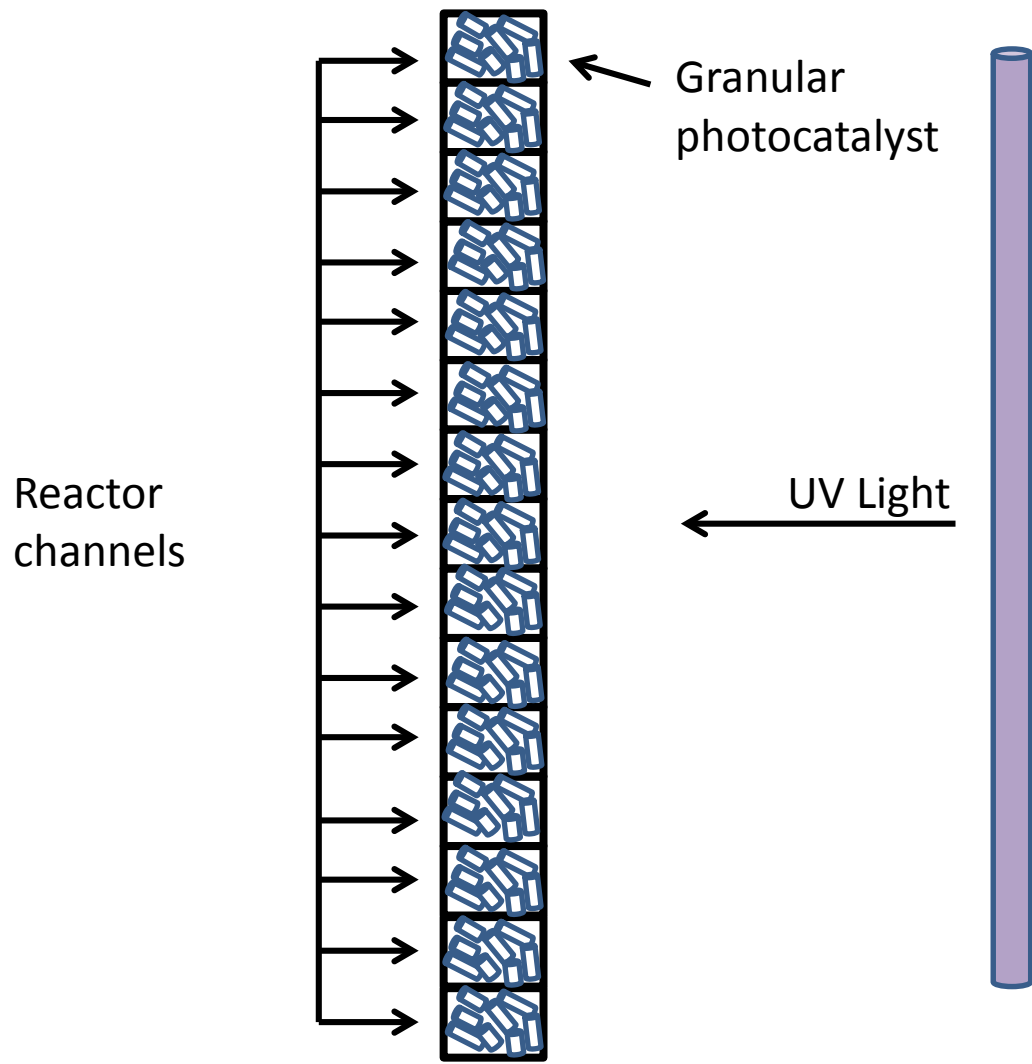
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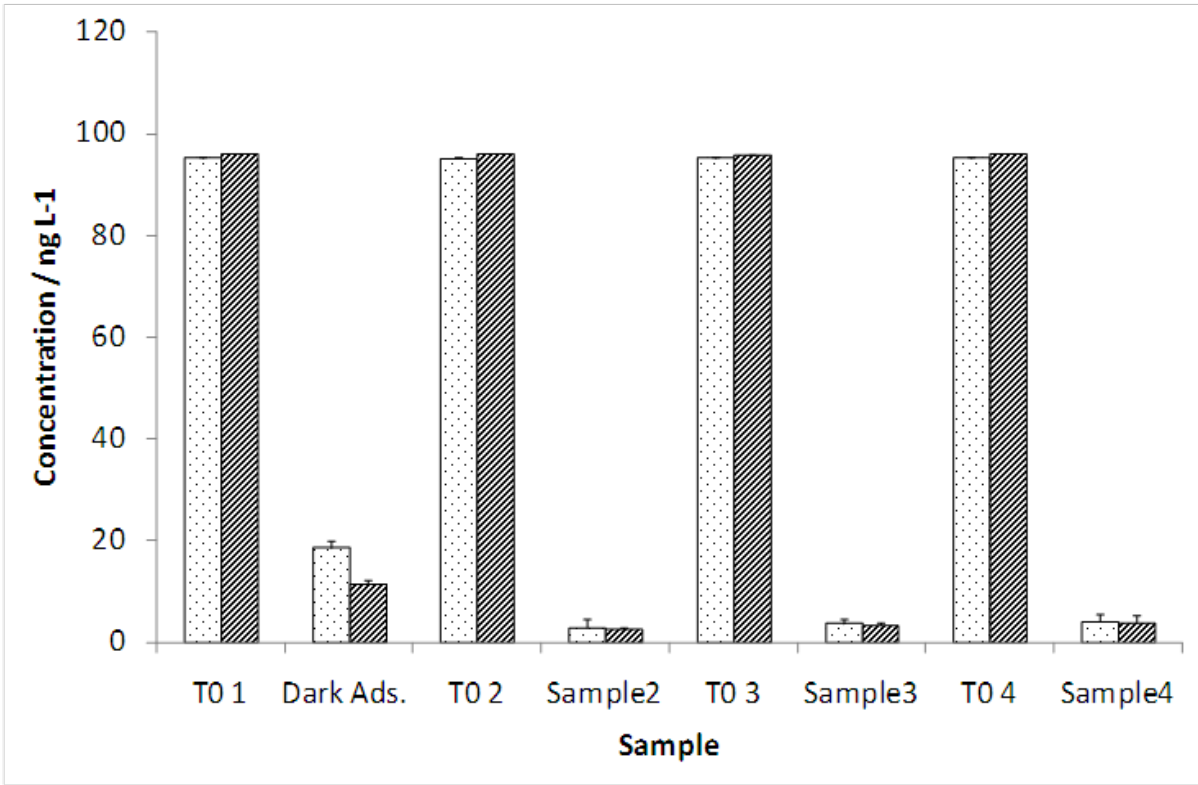
460 Fig 1 a)



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462 **Fig 1 b)**

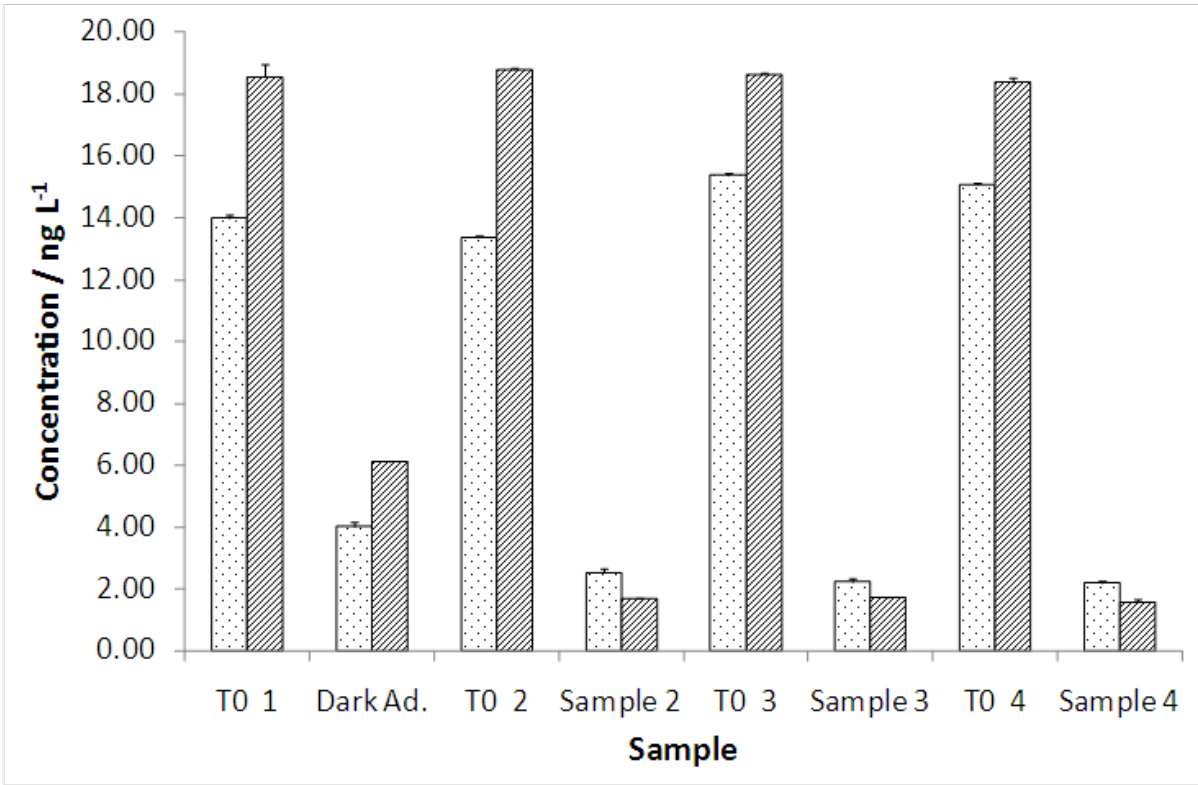
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465 **Fig 2.**

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468 **Fig 3.**

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

<i>SPE parameter</i>	<i>Applied in this method</i>
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

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

<i>Parameter</i>	<i>Optimised method</i>
<i>Front inlet parameters</i>	
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
<i>Column</i>	
Column type	Capillary column
Column length	30 m
Column diameter	250 µm
Film thickness	25 µm
Pressure	10 psi
<i>Mass spectrometer – quantification ions (SIM)</i>	
2-methylisoborneol	95, 107, 135
Trichloroanisole (Internal Standard)	167, 195, 210
Geosmin	112, 125, 182
<i>Temperature program</i>	
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)

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