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Photocatalytic degradation of water taste and odour compounds in the presence of polyoxometalates and TiO_2: Intermediates and degradation pathways

Theodora Fotiou[a], Theodoros M. Triantis[a], Triantafyllos Kaloudis[b], Elias Papaconstantinou[a], Anastasia Hiskia[a,*]

[a] *Laboratory of Catalytic – Photocatalytic Processes (Solar Energy – Environment), Institute of Advanced Materials, Physicochemical Processes, Nanotechnology & Microsystems, National Center for Scientific Research "Demokritos", Athens 15310, Greece*
[b] *Quality Control Department, Athens Water Supply and Sewerage Company (EYDAP SA), Oropou 156, 11146 Galatsi, Athens, Greece*

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ABSTRACT

Geosmin (GSM) and 2-methylisoborneol (MIB) are produced by several species of cyanobacteria and actinomycetes. These compounds can taint water and fish causing undesirable taste and odours. Studies have shown that GSM/MIB are resistant in standard water treatments. Polyoxometalates (POM) are efficient photocatalysts in the degradation and mineralization of a great variety of organic pollutants, presenting similar behaviour with the widely published titanium dioxide (TiO_2). Photocatalytic degradation of GSM and MIB under UV-A light in the presence of a characteristic POM photocatalyst, $SiW_{12}O_{40}{}^{4-}$, in aqueous solution has been studied and compared with the photodegradation by TiO_2 suspensions. GSM and MIB are effectively degraded in the presence of both photocatalysts. Addition of •OH radical scavengers (KBr and tertiary butyl alcohol, TBA) retards the photodegradation rates of both compounds, suggesting that photodegradation mechanism takes place via •OH radicals. Intermediates identified using GC–MS in the case of GSM and MIB, are mainly identical in the presence of both photocatalysts, also suggesting a common reaction mechanism. Possible photocatalytic degradation pathway for both GSM and MIB is proposed.

1. Introduction

Cyanobacteria cause many water-quality concerns, including potential production of toxins and taste and odour compounds. The most usually occurring taste and odour compounds produced by cyanobacterial blooms as secondary metabolites, are geosmin (GSM) and 2-methylisoborneol (MIB) [1]. They are often found in surface waters such as lakes, rivers and eutrophic drinking water reservoirs [2], indoor air [3], fish tissues [4,5] and foods [6–8]. GSM is a bicyclic tertiary alcohol produced by certain species of *Oscillatoria* [9,10], *Anabaena* [11] and actinomycetes [12]. MIB is a terpenoid also produced by the cyanobacterial species of *Oscillatoria* [9,10] and *Phormidium* [13]. Actinomycetes have also been shown to produce MIB [12]. GSM has a distinct earthy-muddy flavour and aroma, and is responsible for the earthy taste of beets and MIB gives a musty taste and odour to water. The human nose can detect the odour of GSM and MIB in water with odour concentrations reported to be 9 and 4 pg mL^{-1}, respectively [14,15].

Communities whose water supply depends on surface water periodically experience episodes of unpleasant tasting water. Upon cellular death of above bacteria, GSM/MIB are released into the local water supply, impacting greatly on the aesthetic quality and general consumer acceptability of drinking water. For these reasons, the removal of these compounds from water is very important for its use and consumption. In cyanobacteria bloom events when GSM and MIB are released, removal processes are required. Studies have shown that GSM and MIB are resistant in standard water treatments such as coagulation, sedimentation and filtration, especially at very low concentrations [16]. Common disinfectants and oxidants such as Cl_2, ClO_2 and $KMnO_4$ are also shown to be ineffective in their removal [17,18]. Even aeration (air stripping), that is generally effective for volatile compounds, is in this case not the treatment of choice, due to the low Henry's Law constant of GSM/MIB [19].

Currently, powdered activated carbon (PAC) is the treatment commonly used, with a number of studies reported for the removal

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* Corresponding author. Tel.: +30 2106503643; fax: +30 2106511766.
E-mail address: hiskia@chem.demokritos.gr (A. Hiskia).

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of organic pollutants such as seasonal tastes and odours in water. Cook et al. [20] applied adsorption of GSM/MIB in four raw waters, with GSM presenting better adsorption than MIB for all waters studied, attributed to GSM's lower molecular weight, solubility and flatter structure. Bruce et al. [16] using several different types of PAC studied GSM/MIB adsorption in natural water, with dissolved organic carbon (DOC) competing for adsorption sites. With similar results, Newcombe et al. [21,22] studied the simultaneous adsorption between MIB and natural organic matter (NOM). It was found that the presence of NOM of similar size with MIB resulted more in competition of adsorption sites. Granular activated carbon (GAC) was also studied by several authors for GSM/MIB removal [23–25] with efficiencies also influenced by NOM adsorption and reduced after several times of operation.

Biological activated carbon (BAC) was also used in several studies for GSM/MIB removal [26–29], presenting satisfactory results with several parameters like temperature, media type etc. affecting biofilter performance. Ho et al. [30] using a biologically active sand filter, indicated that four different bacteria, i.e. *Pseudomonas* sp., *Alphaproteobacterium*, *Sphingomonas* sp. and *Acidobacteriaceae*, were responsible for the biodegradation of GSM/MIB.

In a recent review [31] on advanced oxidation processes (AOPs) for the removal of taste and odour compounds from aqueous media, processes such as ozone (O_3), UV/O_3 and UV/O_3/H_2O_2 have been used for the removal of GSM/MIB. O_3 [32,33] was found to be ineffective, showing low removal rates. When UV illumination or H_2O_2 were used in combination with O_3 higher removal efficiencies were achieved [32,33]. Other AOP applied for GSM/MIB destruction were ultrasonic [34] and UVC radiation [35]. Lawton et al. [36] reported rapid degradation of both GSM/MIB with more than 99% removal within 60 min of illumination in the presence of suspended TiO_2. Bellu et al. [37], using a pellet form of TiO_2 completely removed GSM within 25 min of treatment. In a later study using the same material in a heavy water solvent, an isotopic effect was observed upon GSM destruction. The results of the study showed the dependence on the photocatalyst material used and also suggested that the photocatalytic degradation took place on the catalysts surface with $^{\bullet}OH$ radicals generation being the rate determining step [38]. In another study, TiO_2 entrapped into EFAL (extra-framework-aluminium)-removed Y-zeolites was applied for MIB degradation presenting enhanced photocatalytic activity. This was due to modification of the surface states of TiO_2 that leads to enhancement of the photocalyst adsorption capability [39]. A preliminary study was also performed by Pemu et al. [40] using TiO_2 photocatalysis of GSM in which few intermediate products were identified.

Polyoxometalates (POM) have previously been used for degradation of several organic pollutants in water [41–45]. In almost all cases final degradation products were CO_2, H_2O and inorganic anions. POM are acid condensation products, mainly of molybdenum and tungsten [46–48], that upon excitation with near visible and UV light become powerful oxidizing reagents capable of destroying a great variety of organic compounds in aqueous solutions through a hole–electron ($h^+ + e^-$) mechanism [49–51]. Hydroxyl radicals ($^{\bullet}OH$) generated by reaction of POM with H_2O seem to play a key role in the process [51]. Oxygen oxidizes (regenerates) the catalyst and through reductive activation may or may not participate further in the process, depending on the substrate [52]. Due to their photocatalytic performance, POM can be recognized as an AOP [42–44]. They have also been recognized as building blocks for efficient photocatalysts by hybridizing with photofunctional semiconductor nanostructures [53]. POM are almost as effective as the widely published TiO_2 [51], presenting similar behaviour with the semi-contacting oxide [51]. $^{\bullet}OH$ radicals have been used to explain similarities of POM and TiO_2, although in some cases the nature of substrate and the mode of investigation seem to play an important role in the process [54].

The purpose of this work was to study and compare the photocatalytic degradation and mineralization of GSM and MIB in water using a representative POM ($SiW_{12}O_{40}{}^{4-}$) and TiO_2. The comparative study of processes included also the identification of intermediate products formed as well as the effect of hydroxyl radical scavengers. To the best of our knowledge (a) the photocatalytic degradation of both GSM and MIB with POM and (b) the mineralization and the complete degradation pathways in the presence of POM or TiO_2 is reported here for the first time.

2. Experimental

2.1. Chemicals and reagents

GSM and MIB were purchased by Wako Pure Chemical Industries Ltd. GSM's standard is a colourless slightly yellow, clear liquid with min. 98.0% purity. MIB is white crystal solid with 99.8% purity.

Pottasium bromide was obtained from Fluka (Buchs, Switzerland) and tertiary butyl alcohol (TBA) (≥99.0%) was purchased from Sigma Aldrich (St. Louis, USA).

Silica tungstate ($SiW_{12}O_{40}{}^{4-}$) was obtained by Sigma Aldrich and titanium dioxide commercial Degussa P25 TiO_2 (Degussa AG, Germany) was used.

Extra pure oxygen and nitrogen were used for oxygenation and evaporation of the solutions. Water was purified with a Millipore Milli-Q Plus System.

2.2. Instrumentation

Irradiation in UV-A (315–400 nm) was performed with a laboratory constructed "illumination box" equipped with four F15W/T8 black light tubes (Sylvania GTE, USA). The maximum emission of these tubes is around 365 nm, emitting 71.7 mW cm^{-2} at a distance of 25 cm.

The GC–MS system used through was an Agilent 6890 Series gas chromatograph equipped with an HP-5 MS capillary column (30 m × 0.25 mm × 0.25 μm film thickness), interfaced to an Agilent 5973 mass selective detector.

Total organic carbon (TOC) measurements were carried out using a Shimadzu TOC-5000A which was calibrated with potassium hydrogen phthalate standards.

2.3. Photocatalysis experiments

In a typical experiment for GSM/MIB degradation, aqueous solution (20 mL) containing the photocatalyst $SiW_{12}O_{40}{}^{4-}$ (7×10^{-4} M, 200 mg L^{-1}) or commercial available TiO_2 Degussa P25 (200 mg L^{-1}) was added to a cylindrical pyrex cell, oxygenated for 20 min, spiked with GSM or MIB solution giving a total concentration of 1 mg L^{-1} and covered air tightly with a serum cap. Photocatalysts loadings were selected according to previous studies for comparison reasons [43,54]. Illumination was performed at ambient temperature in the photolysis apparatus. The solutions were magnetically stirred throughout the experiment. In experiments with $^{\bullet}OH$ radical trapping reagents (scavengers) KBr (10^{-2} M) and tertiary butyl alcohol (10^{-2} M) were used.

Analysis of the photolysed solutions was performed after filtration with Millex PVDF Durapore-GF 13 mm 0.22 μm, low protein binding filters. Degradation experiments performed in triplicate and the error bars on Figures represent the mean ± SD of the three separate measurements. The initial rates of substrates degradation were calculated from the slope of the curve obtained for the first 30% of the substrates destruction.

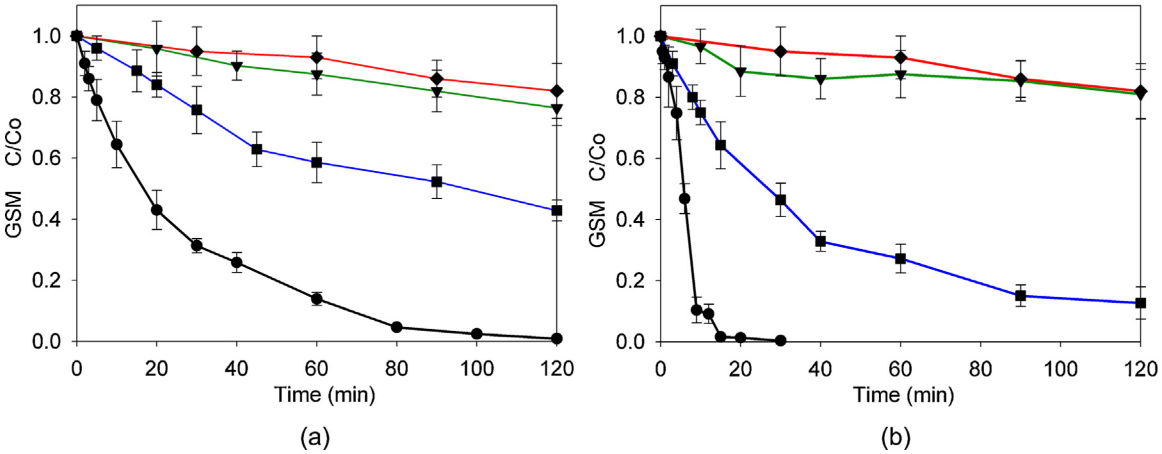


Fig. 1. Photocatalytic degradation of GSM (1 mg L^{-1}) under UV-A (λ_{max} = 365 nm) irradiation with (a) $SiW_{12}O_{40}^{4-}$ (7 × 10^{-4} M, 200 mg L^{-1}) and (b) TiO_2 (200 mg L^{-1}) in the presence and absence of scavengers. Conditions (♦) Photolysis, (●) No scavenger, (▼) KBr and (■) TBA.

2.4. Analytical determination

The determination of GSM and MIB in the water samples was performed by a headspace solid phase microextraction (HS-SPME)/gas chromatography–mass spectrometry (GC–MS) method [55]. Samples (2 mL) were placed in screw-capped, straight-sided headspace vials with PTFE-lined silicone septa. Sodium chloride (0.75 g) and a stirrer were added to the sealed vial and placed in 70 °C for 30 min. A GC temperature gradient program from 50 °C (held for 1 min) to 250 °C (held for 6 min), using a temperature ramp (12 °C min^{-1}) under constant flow (1 mL min^{-1}) was used. Extraction of analytes by HS-SPME was achieved using a Supelco fibre coated with Divinylbenzene/Carboxen/Polydimethylsiloxane (DVB/CAR/PDMS), Stableflex, 50/30 μm. Detection was performed in selected ion monitoring (SIM) mode at m/z: 112 (GSM) and 95 (MIB), respectively. Method linear range was 0–500 ng L^{-1}. Limit of Detection (LOD) at a signal to noise ratio greater than 3 (S/N > 3) was found to be 1 ppt for both compounds. For intermediates identification experiments, higher concentration was used for GSM/MIB (20 mg L^{-1}). Total volume (20 mL) was extracted in dichloromethane and evaporated to 0.5 mL, using low nitrogen flow at 35 °C.

Identification of intermediates was performed using the same instrument apparatus. The temperature programme applied in GC–MS was the same as above, in scan mode. Scanning was monitored at a m/z range from 20 to 300 amu. The injection was carried out splitless at 250 °C and the injection volume was 2.0 μl. The electron energy was set at 70 eV, the ion source temperature was maintained at 230 °C and the quadrapole temperature at 150 °C. Data acquisition, processing and instrument control were performed by the Agilent MSD Chem-Station software.

3. Results and discussion

3.1. Photocatalytic degradation of GSM and MIB in the presence of $SiW_{12}O_{40}^{4-}$ and TiO_2

Illumination of aqueous, oxygen saturated solutions of GSM (1 mg L^{-1}) and MIB (1 mg L^{-1}) under UV-A irradiation (λ_{max} = 365 nm) in the presence of $SiW_{12}O_{40}^{4-}$ (7 × 10^{-4} M, 200 mg L^{-1}) or commercially available TiO_2 Degussa P25 (200 mg L^{-1}) results in the degradation of both substrates. In Fig. 1, the disappearance of GSM at various illumination intervals in the presence of (a) $SiW_{12}O_{40}^{4-}$ and (b) TiO_2 is presented. Under the experimental conditions used, GSM disappeared after 30 min of illumination in the presence of TiO_2, while in the presence of POM required longer time reaching complete degradation at 120 min. Experiments were also performed in the absence of photocatalysts. A destruction of ~15% for GSM in UV-A was observed after 120 min of illumination (Fig. 1), indicating photolytic cleavage. Pemu et al. [40], in a study using TiO_2 photocatalysis for degradation of GSM, observed remarkable destruction in the absence of photocatalyst, under experimental conditions used. This was attributed to the energy of UV light emitted being of the same order of magnitude with those of bonds in GSM, causing cleavage of C—O and C—C bonds.

The photodegradation of oxygenated aqueous solution of MIB with and without photocatalysts is presented in Fig. 2, in the presence of (a) $SiW_{12}O_{40}^{4-}$ and (b) TiO_2. When photocatalysis performed in the presence of TiO_2, MIB was completely removed in the first 25 min. In the case of $SiW_{12}O_{40}^{4-}$, the destruction of MIB was complete after 100 min of illumination. Similar to GSM, photodecomposition of MIB also took place in the absence of photocatalysts reaching ~20% in 120 min of illumination.

Results also showed that degradation of GSM was slightly slower than MIB in the presence of both photocatalysts. This was also observed by Lawton et al. using TiO_2 photocatalysis [36]. In the frame of this study, the observed rate constants of the photocatalytic degradation of the substrates were found to be 0.349 and 0.639 × 10^{-1} min^{-1} using POM, and 0.613 and 1.23 × 10^{-1} min^{-1} using TiO_2, for GSM and MIB, respectively. Previous studies using TiO_2 gave similar results with the above. For GSM removal observed rate constants were 0.633 × 10^{-1} min^{-1} [36], 0.27 × 10^{-1} min^{-1} [56], 0.90 × 10^{-1} min^{-1} [40] and 0.21–0.55 × 10^{-1} min^{-1} [57]. Also, for MIB removal using TiO_2 observed rate constants were 1.979 × 10^{-1} min^{-1} [36] and 0.24 × 10^{-1} min^{-1} [58].

3.2. Photocatalytic degradation of GSM and MIB in the presence of •OH radicals scavengers

Experiments were also performed in the presence of •OH radicals scavengers, i.e. KBr and TBA.

KBr and TBA are •OH radical trapping reagents (scavengers) from which Br^- is stronger [59,60]. Experiments with both photocatalysts (POM, TiO_2), substrates (GSM, MIB) and scavengers were conducted side by side, under exactly the same conditions. Results are presented in Figs. 1 and 2, for GSM and MIB respectively.

In Table 1 the observed rate constants of the photodegradation of the substrates and how these are modified in the presence of •OH radical scavengers are given. Numbers in parentheses indicate, percentage-wise, the effect of scavengers on the observed rate constants. The observed rate constants of substrates degradation

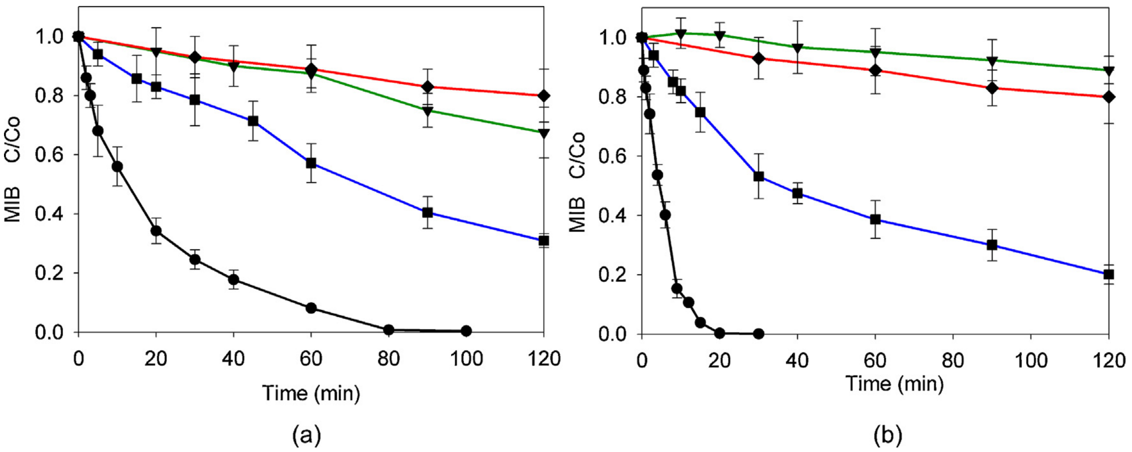


Fig. 2. Photocatalytic degradation of MIB (1 mg L^{-1}) under UV-A (λ_{max} = 365 nm) irradiation with (a) $SiW_{12}O_{40}^{4-}$(7 × 10^{-4} M, 200 mg L^{-1}) and (b) TiO_2 (200 mg L^{-1}) in the presence and absence of scavengers. Conditions (♦) Photolysis, (●) No scavenger, (▾) KBr and (■) TBA.

were calculated from the slope of the curve obtained for the first 30% of the substrates destruction upon illumination time.

Figs. 1 and 2 and Table 1, show that both scavengers retard the photodegradation of GSM and MIB, in accordance with their ability to scavenge $^{\bullet}$OH radicals. The second order rate constants (M^{-1} s^{-1}) of the scavengers used with $^{\bullet}$OH radicals are: 1.1 × 10^{10} for Br^- [59] and 3.1 × 10^8 for TBA [60]. The retardation of the photodegradation of GSM and MIB, in the presence of scavengers, denotes that $^{\bullet}$OH radicals should be the main oxidant for both photocatalysts. It was also appeared that both scavengers have the same influence on both of the substrates. The similarity on mode of operation of the two photocatalysts on GSM and MIB can be attributed on the similar structure of the substrates. These results come in agreement with previous study on atrazine, fenitrothion, chlorophenols and 2,4-DCP [54], where it was stated that the photooxidizing mode of POM and TiO_2 (i.e. $^{\bullet}$OH radicals versus h^+) is circumstantial depending on the nature of the substrate and the mode of investigation.

3.3. Photocatalytic mineralization of GSM and MIB in the presence of $SiW_{12}O_{40}^{4-}$ and TiO_2

To the best of our knowledge, degradation process of GSM and MIB has been studied only under limited time of illumination [36,37,40]. Even though mineralization of the total organic carbon in the solution might not be necessary for the elimination of the undesirable taste and odour characteristics of GSM and MIB in water, it can provide useful information on the mechanistic aspects of the photocatalytic process of the two materials. Prolonged illumination of aqueous solutions of GSM and MIB leads to the mineralization through the elimination of the organic carbon in the solutions, in the presence of both photocatalysts. As can be seen in Fig. 3, after 5 h of irradiation in the presence of TiO_2 65% and 80% of organic carbon has been recovered for GSM and MIB, while their degradation has been almost completed in ~30 and 25 min, respectively (Figs. 1 and 2). In the case of $SiW_{12}O_{40}^{4-}$ after 5 h of irradiation 50% and 65% mineralization of organic carbon was observed for GSM and MIB, respectively (Fig. 3). The shorter time needed for degradation than for mineralization is due to formation of organic intermediates that also react with the photocatalysts. Reduction of TOC is evidenced only after a small induction period indicating also that the mineralization proceeds through several intermediate steps. The incomplete removal of TOC (~80–85%) can be assigned to the formation of small partially oxidized molecules that are mineralized slowly.

Table 1
Observed rate constants from the initial rates of photodegradation of GSM and MIB in the presence of POM or TiO_2 and scavengers, calculated from Figs. 1 and 2 respectively.

Scavenger catalyst $k \times 10^{-3}$ min^{-1}; % ($k_{scavenger}$)/(k_{none})	None	KBr	TBA
GSM			
No catalyst	1.5		
POM	34.9 (100)	1.9 (5.6)	8.1 (23.1)
TiO_2	61.3 (100)	3.6 (5.9)	23.6 (38.4)
MIB			
No catalyst	1.7		
POM	63.9 (100)	2.6 (4.2)	6.1 (9.6)
TiO_2	123 (100)	1.0 (0.8)	16.9 (15.3)

3.4. Identification of intermediates and degradation pathway of GSM

GSM is photodegraded slowly in the absence of catalysts (Fig. 1). A small number of intermediates were produced three of which were identified (Table S1, Fig. S1) by comparison using Wiley mass spectra data base.

When illumination of GSM was performed in the presence of POM, the formation of numerous intermediate products took place (Scheme 1). In Table 2 all identified intermediates with matching greater than 80% are presented with their chromatographic

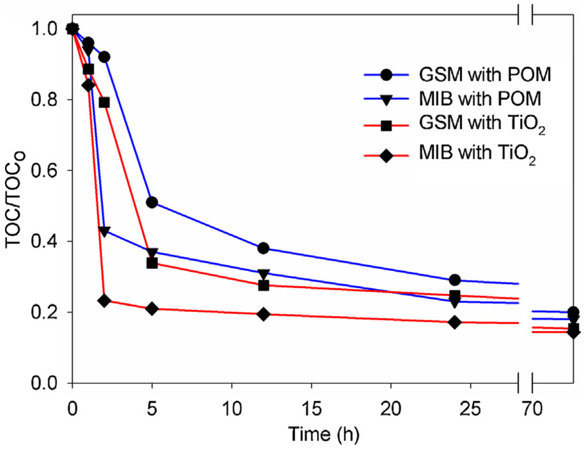
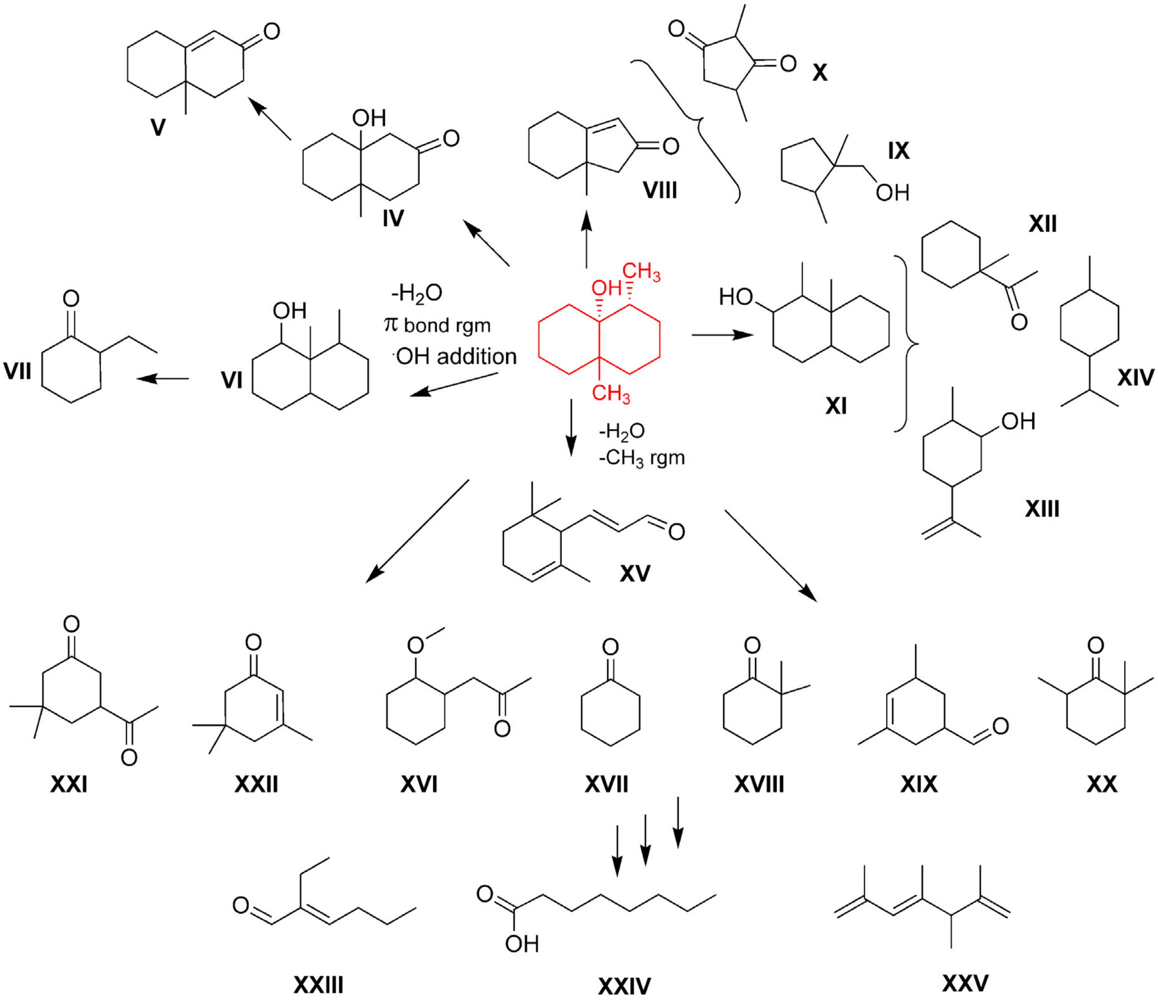


Fig. 3. Photocatalytic mineralization of GSM (10 mg L^{-1}) and MIB GSM (10 mg L^{-1}) under UV-A (λ_{max} = 365 nm) irradiation using $SiW_{12}O_{40}^{4-}$ (7 × 10^{-4} M, 200 mg L^{-1}) or TiO_2 (200 mg L^{-1}) catalyst.



Scheme 1. Intermediates formed during photocatalytic degradation of GSM by $SiW_{12}O_{40}^{4-}$ or TiO_2.

Table 2
Intermediates identified during the photocatalytic degradation of GSM with their retention time (t_R) and their spectral characteristics (M^+, m/z), in Scheme 1.

Name	Symbol	t_R (min)	M^+	m/z	$SiW_{12}O_{40}^{4-}$	TiO_2
GEOSMIN		10.89	182	112, 43, 55		
8a-Hydroxy-4a-methyl-octahydro-naphthalen-2-one	IV	13.28	182	112, 55, 97, 82	√	√
4a-Methyl-4,4a,5,6,7,8-hexahydro-3H-naphthalen-2-one	V	12.44	178	121, 136, 93	√	√
8,8a-Dimethyl-decahydro-naphthalen-1-ol	VI	13.34	182	112, 43, 55, 97, 126	√	√
2-Ethyl-cyclohexanone	VII	12.11	126	98, 55, 126	√	√
7a-Methyl-1,4,5,6,7,7a-hexahydro-inden-2-one	VIII	12.61	150	150, 135, 79, 93		√
2,4-Dimethyl-cyclopentane-1,3-dione	IX	7.48	126	126, 56, 111, 43	√	√
(1,2-Dimethyl-cyclopentyl)-methanol	X	11.83	128	97, 55		√
1,8a-Dimethyl-decahydro-naphthalen-2-ol	XI	12.86	182	112, 55, 41	√	√
1-(1-Methyl-cyclohexyl)-ethanone	XII	11.41	140	55, 97	√	√
5-Isopropenyl-2-methyl-cyclohexanol	XIII	12.44	154	136, 107, 121, 79	√	√
1-Isopropyl-4-methyl-cyclohexane	XIV	11.82	140	97, 55, 140, 41	√	√
3-(2,6,6-Trimethyl-cyclohex-2-enyl)-propenal	XV	12.86	182	112, 55, 41	√	√
1-(2-Methoxy-cyclohexyl)-propan-2-one	XVI	12.55	170	112, 43, 94	√	√
Cyclohexanone	XVII	5.27	112	68, 84, 112	√	
2,2-Dimethyl-cyclohexanone	XVIII	12.20	126	126	√	
3,5-Dimethyl-cyclohex-3-enecarbaldehyde	XIX	11.37	138	107, 95, 67	√	
2,2,6-Trimethyl-cyclohexanone	XX	6.37	140	82, 56, 69, 140	√	
5-Acetyl-3,3-dimethyl-cyclohexanone	XXI	7.73	152	68, 96, 152		√
3,5,5-Trimethyl-cyclohex-2-enone	XXII	7.48	138	82, 138, 39, 54		√
2-Ethyl-hex-2-enal	XXIII	11.96	126	55, 97, 126	√	√
Octanoic acid	XXIV	7.98	144	60, 73, 41, 101		√
2,4,5,6-Tetramethyl-hepta-1,3,6-triene	XXV	11.26	136	93, 79, 121, 108	√	√

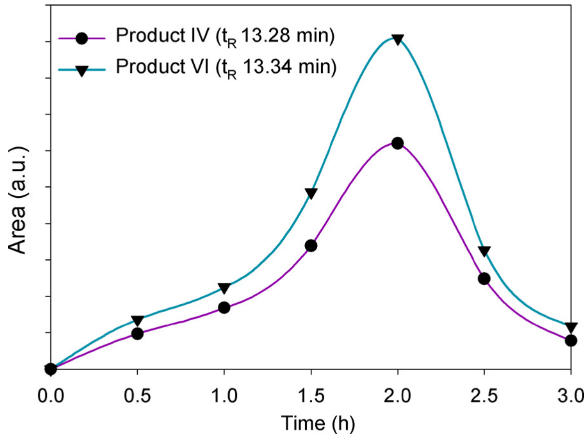


Fig. 4. Evolution and decay of main intermediate products (product IV: 8a-hydroxy-4a-methyl-octahydro-naphthalen-2-one and product VI: 8,8a-dimethyl-decahydro-naphthalen-1-ol), upon photocatalytic degradation of GSM (20 mg L^{-1}), using $SiW_{12}O_{40}{}^{4-}$ (7×10^{-4} M, 200 mg L^{-1}) under UV-A irradiation.

retention time (t_R) and their spectral characteristics (M^+ and m/z of major ions). Identification of the species detected was performed on the basis of comparison with Wiley mass spectra library, literature data and EI fragmentation patterns. The majority of the identified intermediates were cyclic ketones which upon ring opening lead to formation of linear saturated and unsaturated products (Scheme 1). The formation of all intermediates is followed by their decay during the photocatalytic process, coming finally to total photodecomposition to CO_2.

Identification of intermediates was also carried out upon photocatalysis in the presence of TiO_2. As it can be noticed from the chromatograms of the extracted photolysed solutions (Fig. S2) at various illumination intervals, the chromatographic patterns were mostly the same between POM and TiO_2, supporting the fact that the majority of intermediates reported in Table 3 are present during the photocatalytic degradation using either of the two photocatalysts.

Product IV (8,8a-dimethyl-decahydro-naphthalen-1-ol) and product VI (8,8a-dimethyl-decahydro-naphthalen-1-ol), due to their high abundance could be considered as the main intermediates produced during the photocatalytic degradation of GSM under UV-A irradiation in the presence of POM or TiO_2. In Fig. 4, the formation and decay of products IV and VI during the photocaralytic procedure is presented, with a peak on their concentrations at ~2 h of irradiation. A possible mechanism followed for the formation of product IV could be α-hydrogen abstraction from the tertiary carbon of GSM, β-scission abstraction, followed by hydroxylation from $^{\bullet}OH$ radical attack and finally ketone formation (Fig. S4) [61]. The second main intermediate product VI could be formed by dehydration of GSM and $^{\bullet}OH$ addition followed π-bond rearrangement (rgm) (Fig. S5) [61].

The presence of majority of oxygenated degradation products suggests that the mechanism involved in most identified intermediates is indeed $^{\bullet}OH$ oxidation, driven by electrophilic substitution reactions. Subsequent bond cleavage at multiple sites produces mainly cyclic ketones that upon further bond cleavage form open chain saturated and unsaturated compounds, i.e. alkenes, aldehydes and acids.

A few studies concerning the identification of degradation products of GSM under various processes have been reported in the literature. In 1999 Saito et al. [62] were the first to study a microbiological degradation pathway for GSM. In total, three products were identified; two of them were dehydration products of GSM and the third resulted from dehydration followed by enolation. Another study employing bacteria was performed by Eaton [63]. Two main intermediates were identified, i.e. 2- and 7-ketogeosmin. Song et al. [34] studied the ultrasonically induced degradation of GSM. Dehydrations, subsequent dehydrogenations and a ring opening reaction were observed due to pyrolytic bond scissions taking place.

Prior to our work, Pemu et al. [58] studied GSM degradation using photocatalysis with TiO_2. Only a small number of intermediates were identified (3,5-dimethylhex-1-ene, 2,4-dimethylpentan-3-one, 2-methylethylpropanoate and 2-heptanal) showing that GSM undergoes rapid ring opening producing aliphatic saturated and unsaturated compounds, including some alkanones and esters.

The intermediates detected in this study were similar in the presence of $SiW_{12}O_{40}{}^{4-}$ and TiO_2 (Scheme 1). This is in good agreement with previous studies where it has been demonstrated that the photocatalytic performance of POM and TiO_2 is similar in terms of the overall mechanism of photodecomposition of organic compounds, the intermediate species involved and the final photodegradation products (i.e., CO_2, H_2O and inorganic anions) [51]. This also tends to suggest, despite the recent arguments that exist [54], that the photodegradation mechanism in the case of GSM, by both catalysts ought to take place mainly via a common reagent, i.e. $^{\bullet}OH$ radicals. On the contrary direct photolysis, that causes degradation via direct absorption of light by GSM proceeds slowly via different intermediates (Table S1, Fig. S1).

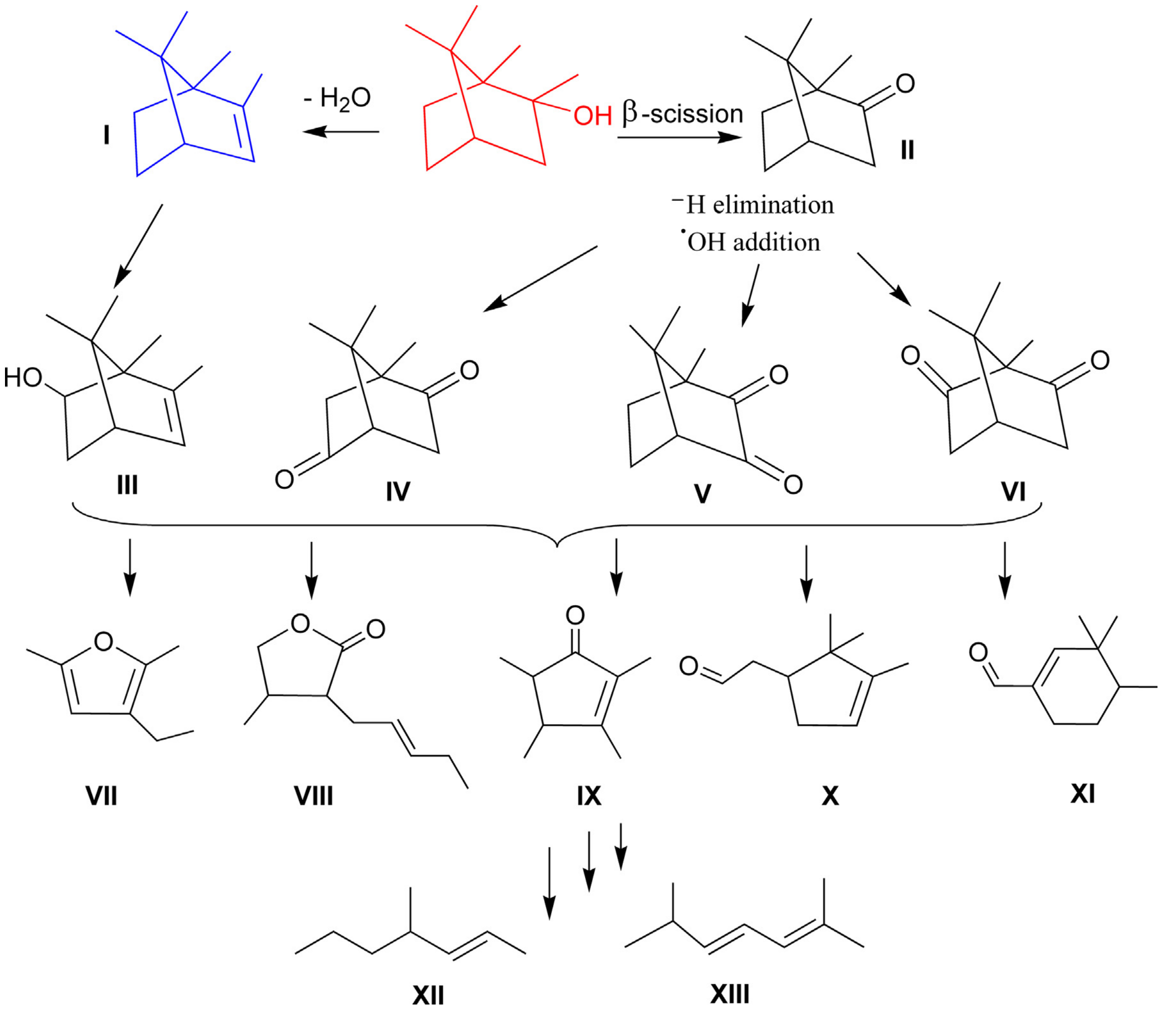
3.5. *Identification of intermediates and degradation pathway of MIB*

During photolysis of MIB in the absence of catalyst, a few peaks were detected in the chromatogram of the photolysed solution indicating photolytic cleavage. One of them was identified as 1,2,7,7-tetramethyl-bicyclo[2.2.1]hept-2-ene (I) (Scheme 2), that is

Table 3

Intermediates identified during photolysis and the photocatalytic degradation of MIB with their spectral characteristics (M^+, m/z), in Scheme 2.

Name	Symbol	t_R (min)	M^+	m/z	$SiW_{12}O_{40}{}^{4-}$	TiO_2
2-Methylisoborneol		8.28	168	95, 108		
1,2,7,7-Tetramethyl-bicyclo[2.2.1]hept-2-ene	I	6.08	150	107, 79, 93, 135		
1,7,7-Trimethyl-bicyclo[2.2.1]heptan-2-one (d-camphor)	II	7.80	152	95, 81, 41, 55, 108	√	√
1,6,7,7-Tetramethyl-bicyclo[2.2.1]hept-5-en-2-ol	III	7.48	166	108, 93	√	
1,7,7-Trimethyl-bicyclo[2.2.1]heptane-2,5-dione	IV	9.21	166	166, 69, 109, 83, 123	√	√
1,7,7-Trimethyl-bicyclo[2.2.1]heptane-2,3-dione	V	9.64	166	95, 83, 69, 55	√	√
1,7,7-Trimethyl-bicyclo[2.2.1]heptane-2,6-dione	VI	9.73	166	166, 41, 67, 97, 83	√	√
3-Ethyl-2,5-dimethyl-furan	VII	10.85	124	109, 124	√	√
4-Methyl-3-pent-2-enyl-dihydro-furan-2-one	VIII	10.74	168	99, 43	√	√
2,3,4,5-Tetramethyl-cyclopent-2-enone	IX	8.77	138	123, 95, 138, 67	√	√
(2,2,3-Trimethyl-cyclopent-3-enyl)-acetaldehyde	X	11.34	152	108, 93, 67	√	√
3,3,4-Trimethyl-cyclohex-1-enecarbaldehyde	XI	9.03	152	95, 81, 123, 67	√	
2,6-Dimethyl-hepta-2,4-diene	XII	10.81	124	109, 124	√	√
4-Methyl-hept-2-ene	XIII	8.09	112	69, 41, 55, 112	√	√



Scheme 2. Intermediates formed during photolysis and photocatalytic degradation of MIB by $SiW_{12}O_{40}^{4-}$ or TiO_2.

possibly formed by dehydration of MIB. Its retention time (t_R) and spectral characteristics are given in Table 3.

A detailed study of the photodegradation of MIB (Scheme 2) with $SiW_{12}O_{40}^{4-}$ revealed the formation and decay of several products prior to the final decomposition to CO_2. Many chromatographic peaks appeared in the photolyzed solution in the presence of $SiW_{12}O_{40}^{4-}$ which were not present without photocatalyst. The intermediates identified together with their retention times (t_R) and spectral characteristics are given in Table 3. They are compiled as follows: alcohol-(III), ketone-(II) and diketone-(IV, V, VI) derivatives of MIB, oxygen containing cyclic compounds (VII, VIII, IX, X, XI) and open chain aliphatic compounds (XII, XIII).

Similar photocatalytic experiments were also performed in the presence of TiO_2. The intermediates detected were identical with those found in the presence of $SiW_{12}O_{40}^{4-}$ (Table 3, Fig. S3). We propose here (Scheme 2) a possible photodegradation mechanism for MIB, that applies to both POM and TiO_2, which provides a reasonable explanation for the similar intermediates formed in both processes.

Product III (1,6,7,7-Tetramethyl-bicyclo[2.2.1]hept-5-en-2-ol) is formed with hydroxylation of product I suggesting the presence of •OH radicals. Product II (*d*-camphor) is proposed to be the primary intermediate produced during photocatalysis of MIB formed with a β-scission reaction mechanism on the methyl group of MIB that generates a ketone. Products IV, V and VI are possibly formed by hydrogen elimination followed by •OH addition and oxidation of secondary alcohol, leading to the formation of ketone, starting from product II. As far as concerning the other identified saturated and unsaturated oxygen containing cyclic intermediates, mechanisms involved are hydroxyl radical oxidation of compounds, driven by electrophilic substitution. The majority of those are five-membered rings revealing ring opening on MIB molecule. Linear aliphatic compounds were identified during the later stages of photo-oxidation similar to previous studies of Hiskia et al. [64].

Sumimoto [65] was the first to study MIB's degradation pathway using biodegradation by gravel sand filtration. Tanaka [66] using biodegradation identified some of the products formed which were camphor and two dehydration products, one of them also found in current study (product I in Scheme 2). Song et al. [34] carried out ultrasonically induced degradation of MIB and defined the pathway due to pyrolytic transformations taking place. Qi et al. [58] and later Li et al. [67] applying ozonation processes investigated the degradation of MIB and proposed a pathway of ozonation of MIB. The majority of the intermediates identified in those two studies were identical. According to these studies, *d*-camphor was likely to be the primary degradation product that it is further degraded into other byproducts, including aldehydes. Qi et al. [58] also investigated the effect of •OH using scavengers on the ozonation of MIB, with results suggesting that the presence of •OH was the predominant oxidant. The full agreement of our results with those of ozonation of MIB [58,67] is a further evidence that the main oxidant is •OH in all cases, i.e. photocatalysis with $SiW_{12}O_{40}^{4-}$ or TiO_2 and ozonation.

3.6. Photocatalytic degradation mechanisms of GSM/MIB in the presence of $SiW_{12}O_{40}^{4-}$ and TiO_2: a comparison study

An objective of this study was the comparison of photodegradation mechanisms followed by POM and TiO_2 in the cases of GSM and MIB, via degradation, mineralization and identification of intermediate products, under UV-A irradiation.

Several examples, from both photocatalysts, have been reported to demonstrate that their performance is similar in terms of the overall mechanism of photodecomposition of organic compounds, the intermediate species involved and the final photodegradation products (i.e., CO_2, H_2O and inorganic anions) [51]. However, parallel experiments under similar conditions, using various substrates (atrazine, fenitrothion, 4-chlorophenol and 2,4-dichlorophenoxyacetic acid) and $^{\bullet}OH$ radical scavengers, have shown that the photooxidizing mode of POM and TiO_2, i.e., $^{\bullet}OH$ radicals and/or holes (h^+), depends on the nature of substrate and the mode of investigation [54,68]. Atrazine showed that both POM and TiO_2 mainly operate through $^{\bullet}OH$ radicals and with a lower extent with h^+, whereas fenitrothion suggested the almost exclusive operation of both photocatalysts via $^{\bullet}OH$ radicals. On the other hand, differences between the two photocatalysts have been proposed with 4-chlorophenol and 2,4-dichlorophenoxyacetic acid, with POM operating via $^{\bullet}OH$ radicals and TiO_2 mainly via h^+. Overall, the action of $^{\bullet}OH$ radicals relative to h^+ appears to be more pronounced with POM than TiO_2 [54]. An example against the above mechanism for POM has been reported for the degradation of dichlorobenzene in the presence of $^{\bullet}OH$ radicals scavengers suggesting that POM act via h^+ rather than $^{\bullet}OH$ mediated oxidations [69]. As a conclusion, whether an $^{\bullet}OH$ or h^+ mediated mechanism is followed depends on various parameters (e.g., the kind of substrates, the substrate-photocatalyst interaction) and should be considered on a case by case basis [68].

In accordance with the results given in this study on degradation and mineralization (TOC measurements and identification of formed intermediates) of GSM and MIB, it has been concluded that the same photodegradation mechanism is followed when POM and TiO_2 are used as photocatalysts. The similarities of the intermediates identified (presence of the same oxidized derivatives) and results from experiments with $^{\bullet}OH$ radical scavengers, as well tend to suggest that $^{\bullet}OH$ is the common oxidant, as has been also mentioned for other organic compounds[43].

4. Conclusions

This work focused on the removal of taste and odour compounds (GSM/MIB) from water using photocatalysis with POM and TiO_2. Both photocatalysts found to be effective in degradation of target analytes. Experiments were also performed in the presence of $^{\bullet}OH$ radicals scavengers showing retardation of the photodegradation of GSM and MIB, which indicates that $^{\bullet}OH$ radicals should be the main oxidant for both photocatalysts. The photocatalytic degradation of GSM and MIB in the presence of both photocatalysts leads to the formation of a plethora of intermediates prior to mineralization. In the case of GSM the majority of the identified intermediates were cyclic ketones which upon ring opening lead to formation of linear saturated and unsaturated products. For MIB degradation identified intermediates are consisted by alcohol-, ketone- and diketone-derivatives of MIB, oxygen containing cyclic compounds and open chain aliphatic compounds. A complete degradation pathway is proposed for target compounds during their photocatalytic degradation with common intermediates identified, using either POM or TiO_2 with $^{\bullet}OH$ radical attack to be mainly responsible for the mechanism. These results suggest that photocatalysis using either POM or TiO_2 demonstrates significant potential for the complete removal of taste and odour compounds that taint water. Although scaling up is necessary for application, the elucidation of degradation pathways provides us with a better understanding of the photocatalytic process. However, this initial study is promising presenting a novel approach for water purification from compounds resistant in standard water treatments.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jphotochem.2014.04.013.

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