Effect of activated carbon, oxidation and UV treatment on 2-methylisoborneol and geosmin removal from treated water

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ABSTRACT

Geosmin and 2-methylisoborneol (MIB) are two contributors to taste and odour in water, and originate from cyanobacteria and other microorganisms in surface water. This thesis examined the use of activated carbon, hydrogen peroxide and UV treatment on removal of these two compounds from water.

Geosmin and MIB were analysed using headspace solid phase micro-extraction (SPME) and gas chromatography coupled with mass spectrometry and flame ionization detection. Method development examined the effect of salt addition, sample heating time, and extraction time on GC peak area. Salt addition gave up to 40% lower GC peak areas for MIB and geosmin compared to samples without salt, while increasing sample heating time and extraction time increased GC peak area, increasing the lower detection limits. Two minutes extraction time gave peak areas 75% of that for 10 minutes extraction time. Both GC-MS and GC-FID were reliable methods for analysis with standard deviations being less than 5% of the average peak area obtained from the GC.

Activated carbon was effective at removing geosmin and MIB, with 500 mg GAC per L removing 90% of the geosmin and MIB. Geosmin absorption showed a type II isotherm suggesting monolayer followed by multilayer absorption, while MIB absorption was almost linear. Langmuir-Freundlich and Freundlich isotherms fitted the MIB data well but not as well for geosmin. Oxidative treatment using H_2O_2 removed 84 % of geosmin and 49 % of MIB. UV degradation of geosmin and MIB using the Steriflo system removed up to 31 % of MIB and 76 % of geosmin after 4 hours. After 18 hours, geosmin had 84 % removal while MIB was only 66 %. Addition of H_2O_2 increased removal for MIB and geosmin up to 89 and 90 % respectively after 18 hours. Experimental results were simulated using a model that accounted for UV and hydrogen peroxide degradation, using one set of parameters over a range of conditions for each of MIB and geosmin.

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

1 INTRODUCTION

Water constitutes most parts of liquid substances on the earth. Among the water in the earth, there is only 3% fresh water while the other 97% is saline. Even in the fresh water, only 0.3% of it are found in lakes, swamps and rivers, known as surface water (Figure 1-1), while the other 99.7% are found in icecaps and glaciers or ground water (John, 1997). So the available fraction of water is lacking.

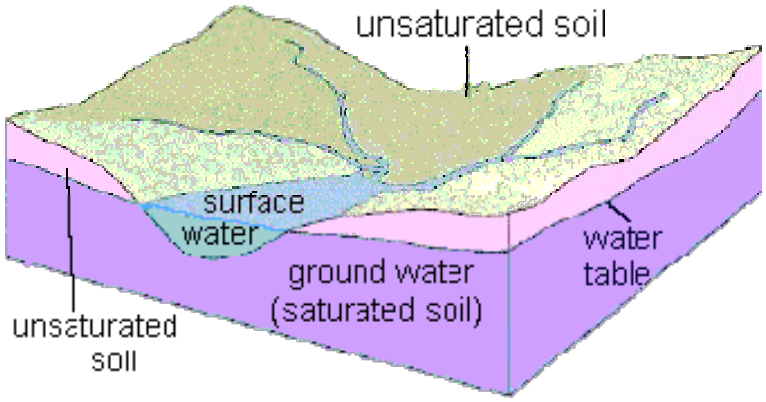

Figure 1-1-the areas of ground water and water table saturated (John, 1997).

1.1 THE MAIN COMPOUNDS EFFECT WATER ODOUR

The quality of treated water is one of the big concerns of daily life. While there are many factors influencing the quality of treated water, one of the main elements is taste and odour caused by compounds in water produced by microbes (Richardson, 2008). Geosmin and 2-methylisoborneol (MIB) are two organic compounds mainly produced by blue-green algae and actinobacteria with an obvious earthy flavour and odour. The threshold concentration of these compounds in water producing a musty odour that a human can discern is generally around 0.004-0.20 µg/L (Suarez et al, 2008). In treated water, human can detect geosmin between 1 -10 ng/L, and 5-10 ng/L for MIB. The two compounds were first found in the early 1960s, and since then scientists started researching methods to minimize their concentration in water. Japan is the first country that list geosmin and MIB in their drinking water standards, followed by China, and the U.S. After national standards

for specific odour chemicals have been adopted, Australia and New Zealand have set limits for geosmin and MIB to 10 ng/L (Jefferson et al, 2000).

Geosmin and MIB can be found all over the world. Lake Kasumigaura in Japan, Lake Mathews in USA, Lake Maritoba in Canada and East Lake in China have a serious problem of taste and odour. The concentration of MIB and geosmin can be up to 560 ng/L and 90 ng/L in Lake Kasumigaura (Izaguirre et al, 1982). It was found that the main source of MIB are streptomyces (actinomycetes) and Lyngbya, Phprmidium (cyanobacteria). The main source of geosmin are Streptomyces (actinomycetes) and Anabaena (cyanobacteria) (Young et al, 1996).

1.2 DEVELOPMENT OF REMOVAL OF GEOSMIN AND MIB

1.2.1 Monitoring of geosmin and MIB

Typical methods for monitoring geosmin and 2-methylisoborneol concentration include liquid phase extraction and solid phase extraction. Liquid phase extraction is based on the relative solubility of the compound in two different immiscible liquids. It involves a substance moving from one liquid into another liquid phase in which it is more soluble (Khiari et al, 1995). Since headspace solid phase micro-extraction (SPME) been introduced, it has been widely used for measuring volatile compounds. The method has advantages such as short time needed, low cost, and easy sampling. It involves absorbing the volatile components present in the headspace of the sample vial onto a microfiber, transferring the microfiber to a gas chromatography system, heating the fibre to desorb the volatile components and analysing them using a flame ionization detector or mass spectrometry (Lloyd et al, 1998).

1.2.2 Effective ways to remove geosmin and MIB

At the moment, most water treatment industries use traditional methods include coagulation, sedimentation, and filtration and disinfection. Many researchers have analysed traditional methods on removing taste and odour compounds (Ma et al, 2007)and they also have done some research on activated carbon adsorption,

advanced oxidation, chemical oxidation and biological methods (Hyun Jo et al, 2008).

1) Traditional water treatment technology

Coagulation, sedimentation and filtration are typical traditional water treatment methods. They are effective at removing taste and odour compounds while decreasing water turbidity and concentration of other organic compounds. According to previous research, the removal rate of geosmin and MIB can reach to around 70% and 60% respectively (Palmentier et al, 1998). Many other factors may affect the remove rate of these compounds as well, such as water source and original concentration of geosmin and MIB influence the removal result. While traditional methods are easy to apply and cheap, the final concentration of geosmin and MIB are still higher than detection threshold, so simply relying on traditional water treatment is not enough to achieve the required water quality standard.

2) Advanced oxidation technology

Advanced oxidation technology removes target compounds by using an oxidizer to force them to decompose. Most water treatment industries apply chlorine as an oxidizer. In order to enhance removal, more chlorine is needed for pre-treatment, which can result in disinfection by-products that may be carcinogens. As alternative oxidizers, ozone and hydrogen peroxide can also be used, however, the new by-products and remaining oxidizer result in some smells and taste compounds as well. According to previous research, it is known that ozone has a great potential in drinking water treatment due to its high adsorption capacity to activated carbon and UV. Combining treatments can reduce the remaining oxidizer present in the treated water (Howell et al, 2008).

3) Activated carbon adsorption technology

There is plenty of research about using activated carbon adsorption to remove taste and odour compounds in water. Some research illustrated that other compounds that exist in raw water may take the place of geosmin and MIB to be

adsorbed by activated carbon. Also the shape of activated carbon is another factor that influences the removal rate. Particularly powdered activated carbon is more effective in removing organic compounds compared to granular activated carbon due to the increased contact surface area between the carbon and organic compounds (Llompart et al, 1998). Activated carbon can remove up to 70% of geosmin and MIB from clean water, but when applied to raw water, the removal rate will decrease depending on the different water sources. Scientists have not found more functional methods to remove taste and odour compounds apart from activated carbon and oxidation due to financial considerations and the environmental impact (Kang et al, 1999).

4) Biological method

Because taste and odour compounds exist in natural water sources at very low concentrations, most chemical reactions cannot remove some of those compounds due to the reactions being reversible (Froelich et al, 1979). Biological methods can be an effective way to decrease the concentration of these compounds. Microorganisms can decompose and use organic compounds as part of their metabolism. However, it takes a long time to develop a biological approach due to the long time it takes to get microorganisms to adapt (Campos et al, 2002).

1.3 KNOWLEDGE GAPS

Previous literature used activated carbon, oxidation and UV treatment to remove taste and odour compounds. In activated carbon treatment, powdered activated carbon has been applied for most research and was shown to be a good method to remove odour compounds from water. Powdered activated carbon showed a higher efficiency in removing odour compounds (Watson et al, 1999), while only a few papers applied granular activated carbon in water treatment due to its variety of efficiencies from being available in different shapes and types. Further research on using granular activated carbon for removing MIB and geosmin is needed. In addition, different oxidation treatment has been analysed by many researchers and most have suggested using ozone rather than other oxidizers. It has been

shown that ozone and ozone/peroxide combined with UV can remove odour compounds effectively (Esplugas et al, 2002). Since hydrogen peroxide is a widely used oxidizer, research about applying hydrogen peroxide to remove taste and odour compounds is needed, most paper report use of hydrogen peroxide with other oxidative technologies. UV treatment is mostly associated with oxidizers in previous research, individual UV treatment to remove odour compounds could also be explored (Pera-Titus et al, 2004).

1.4 RESEARCH OBJECTIVES

This research will explore the ability of coconut shell granular activated carbon, hydrogen peroxide and UV treatment to remove MIB and geosmin from water. As a major part of the work is in the analysis, this work will first explore the effect of parameters such as headspace extraction time, presence of salt in the sample vial, temperature and holding time in the GC on MIB and geosmin analysis using GC-MS and GC-FID to determine an optimal analytical technique.

1.5 THESIS STRUCTURE

Chapter 2 will cover related literature to this research, and provide a general overview of water treatment, including water source, water treatment, New Zealand water usage problems, water contaminants and some effective methods to remove contaminants. Chapter 3 covers the methods, materials and equipment used in this research. Results and discussion are presented in Chapter 4 along with comparisons to model data. Conclusions and suggestions for future research are listed in Chapter 5.

2 LITERATURE REVIEW

2.1 WATER SOURCE AND PROBLEM IN NEW ZEALAND

New Zealand water resources are typically high quality due to the low level of contaminants and low population (Crittenden Trussell et al, 2012). However more than 97% of New Zealand's surface water flows to the sea, and only 2% of the freshwater resource is used. The main sources of water in New Zealand are rivers and aquifers where every year, nearly 27,000 x 10^6 m^3 of water were abstracted from rivers and aquifers (Dewandel et al, 2003). 16,000 x 10^6 m^3 of water is for the Manapouri hydropower scheme that takes water from the Waiau River and discharges it directly to the sea. The rest, 11,000 x 10^6 m^3 of water is used for irrigation, drinking and daily consumption (Bremere et al, 2011).

Water is used in many different ways from supporting life, entertainment, and environmental development to hydroelectricity generation (Rong et al, 1999). The different uses of water requires different water quality standards.

In the early days of New Zealand's history, when forest land were being converted to pasture, lands started to suffer from soil erosion, sending large quantities of sand, silt and clay into the rivers. Since the mid-20^{th} century, eroded soil was the main contaminant affecting rivers and lakes (Carr, 2006). Natural erosion contributed sand, salt and clay to rivers, lakes and coasts. In addition, organic wastes from dairy industries were not treated before being discharged into the waterways, including heavy metals, nutrients, pathogens, nitrates and phosphates which can cause ill health, and can promote the growth of water organisms such as algae which is the main source of MIB and geosmin. Other pollution is caused by farming, where large quantities of cattle and sheep contribute to the raised levels of dairy waste and sediment in the waterways (Figure 2-1) (Westerhoff, 2005).

Figure 2-1-Contaminants released to water source (Bremere et al, 2011).

Other sources of water pollution may come from point sources such as waste water and storm water discharges (including suspended solids, organic matter, nitrates, phosphates, fecal coliforms, and other microorganisms), geothermal waters (which include arsenic, heavy metals, and silica), accidental spills, dairy farm runoff, and livestock directly contaminating waterways (Cortada, 2011). Other sources include microbial growth such as Didymo, cyanbacteria (which widely exist in New Zealand lakes such as Lake Rotorua and Taupo), or pollution from recreational activities such as boating (petroleum spills).

Efforts to improve water quality focused on reducing pollution of various water sources rather water reticulation (Legrini et al, 1993). One of the reasons is that a number of New Zealand's lakes have been damaged by different kinds of pollution

from human activities and other natural sources. The resource management act was carried out to protect water sources by setting up sustainable water programme, water allocation and improving irrigation (Crittenden, Trussell et al, 2012).

2.2 CONTAMINANTS

Contaminants in untreated water include biological contaminants (bacteria, algae, and other microscopic organisms), most of which exist in surface water. Inorganic contaminants consist of metals, salts, fluoride, nitrate, heavy metals (arsenic, cadmium, copper and other radionuclides or toxic compounds) (Mezyk et al, 2006; Richardson, 2007; Satchwill et al, 2007; Makogon et al, 1997; Persson, 1980; Sathyan, 2006; Serpone et al, 1995), and trace hormones, endocrine disruptors and other carcinogens. The contaminants in untreated water contribute to turbidity, colour, odour and taste as well as being detrimental to human health (Ou, 2004).

Safety of drinking water is one of the biggest societal concerns due to the potential health impacts from drinking untreated water (Khiari, 1995). Approximately 780 million people in the world do not have access to treated drinking water (Peter and Von Gunten, 2007).

Drinking water standards follow international guidelines. Drinking water quality standards describes the quality parameters set for drinking water by the World Health Organization (WHO). WHO provide guidelines that are used as the basis for regulation and standard setting in developing and developed countries world-wide (Richardson, Plewa et al, 2007).

Over 90% of the contaminants can be moved by general water treatment, however there are still contaminants contained in water which can be a problem (Rosenfeldt et al, 2005). These include microbial, organic contaminants, inorganic contaminants and disinfection by-products. Some typical contaminants are shown in Table 2-1.

Table 2-1-Typical contaminants after general water treatment.

THMs	Trichloromethane
	Bromodichloromethane
	Chlorodibromomethane
	Tribromomethane
HAAs	Chloroacetic acid (MCAA)
	Dichloroacetic acid (DCAA)
	Trichloroacetic acid (TCAA)
Odorants	Geosmin
	MIB
	Nonadienal

2.2.1 Microbes

Coliform bacteria (Figure 2-2) is one of the most common microbes in the environment, it causes no disease but the presence of the bacteria indicate that there will be other pathogens present such as Protozoa Giardia and Cryptosporidium (Korich et al, 1990).

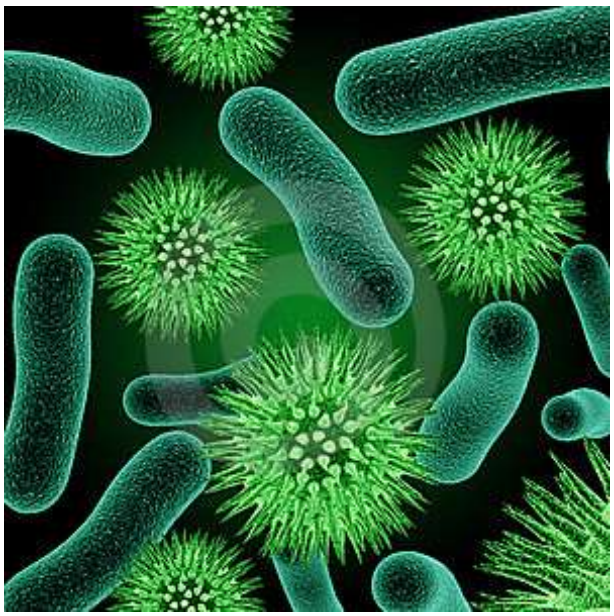

Figure 2-2-Coliform bacteria micro structure (Izaguirre et al, 1982).

Cryptosporidium and Giardia are commonly present in surface water that has been contaminated by sewage and animal waste. They are not easily removed due to their ability to survive outside the body and are tolerant to chlorine

disinfectants (Peter and Von Gunten, 2007). Both these parasites produce cysts that can survive in very harsh environmental conditions. Not all of the cysts can cause illness but some of them are still harmful to human health, although Cryptosporidium and Giardia can be cleared by healthy people without any treatment within about one month (Glaze et al, 1995). Drinking water treatment can efficiently remove these parasites by using UV combined with chlorine. Boiling water is another way to inactive them while also destroying other microorganisms (Westerhoff et al, 2005).

Water turbidity can interfere with disinfection because the suspended particles can provide surfaces for bacteria to grow, so suspended particles should be removed first.

2.2.2 Volatile organic contaminants

Volatile organic compounds are identified as gases present under ambient temperature that contain organic carbon, some of which may affect health. Normally the concentration of volatile organic contaminants inside home is higher than outside, from plastics, paints, donated products, craft materials and photographic solutions (Lesser et al, 2004). Products such as white waste and housekeeping stuff that contain high levels of volatile organic compounds can cause serious pollution problems if they enter the soil and reach groundwater. Other VOCs such as dichloromethane (methylene chloride), tetrachloroethylene (perchloroethylene) are normally found in surface water and groundwater, and not all of them stay in treated water as they tend to evaporate into the air. Over 20 different types of contaminants are regulated as VOCs in drinking water (Table 2-2) and quite a few of them are recognised as a health concern for human body (Milano et al, 1992).

Some of the compounds such as naphthalene and chloroform result in serious health problems, especially with the liver and kidneys. The effects depend on the toxicity, concentration and exposure time. A few of the volatile organic contaminants such as methylene chloride has been found to cause cancer in animals. Now many treatment industries carry out activated carbon adsorption to

remove VOCs from drinking water so the drinking water reaches the minimum safe standards (Besarab et al, 1998).

Table 2-2-Typical VOCs in drinking water.

Chlorinated solvents	**carbon tetrachloride**
	1.2-dichloroethane
	1,1-dichloroethylene
	cis-1,2-dichloroethylene
	trans-1,2-dichloroethylene
	methylene chloride
	tetrachloroethane
	1,1,1-trichloroethane
	trichloroethylene
	vinyl chloride
Fuel components	benzene
	methyl tert-butyl ether
	toluene
	xylenes

2.3 GEOSMIN AND 2-METHYLISOBORNEOL

Geosmin (GSM) and 2-methylisoborneol (MIB) are organic compounds that smell like the earth after rain. They are released by certain soil bacteria called actinomycetes and falling rain causes them to be released into the air. MIB and geosmin in surface water is mainly produced by certain types of cyanobacteria, and are two of the main compounds causing a musty taste and odour in drinking water, although they have not been determined to cause any health problems. The threshold detection concentration for MIB and geosmin for humans is only up to 20 µg/L (Conte et al, 1996).

The name geosmin (also known as trans-1, 10-dimethyl-trans-9-decalol) comes from Egypt. “Ge” means earth and “osmin” means smell, so in this way geosmin means earthy odour. In 1967, $C_{12}H_{22}O$ and $C_{11}H_{20}O$ was identified as geosmin and 2-methylisoborneol’s chemical structure (Figure 2-3 and Figure 2-4) (Gaya and Abdullah, 2008).

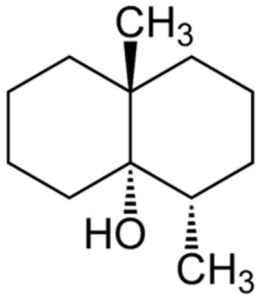

Figure 2-3-Chemical structure of geosmin (Kim et al, 2014).

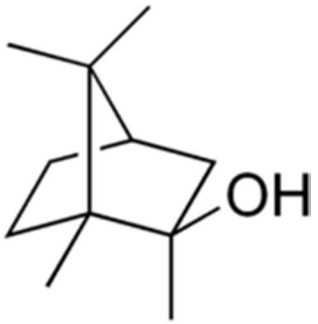

Figure 2-4-Chemical structure of 2-methylisoborneol (Kim et al, 2014).

Geosmin and 2-methylisoborneol are tertiary alcohols. According to their boiling points and Henry's law they are semi-vaporable organic compounds. The solubility of these two compounds in water is not high, however, they can easily dissolve in methanol and other organic solutions. Volatilization occurs at room temperature and humans are very sensitive to their smell. In pure water, people can detect GSM from 1~10 μg/L and MIB from 5~10 μg/L (Yoon et al, 2006). Other animals are also sensitive to their smell, for example, in the desert, camels find water sources by their sensitivity to those special odors. The threshold of detection is based on temperature and other environmental factors, which is why many papers have different detection thresholds for geosmin and MIB (Elhadi et al, 2004). There are some other odorous compounds as well as geosmin and MIB listed in Table 2-3 which illustrate how temperature affect the detection threshold.

Table 2-3- Detection threshold of several kinds of odour and taste compounds (Young et al. 1999).

Name	25 ℃		40 ℃	
	Average threshold (μg/L)	Minimum threshold (μg/L)	Average threshold (μg/L)	Minimum threshold (μg/L)
4-Chloroanisole	10	6.2	20	<2.0
2-Chlorophenol	0.97	0.14	0.36	0.088
2,4-Dichloroanisole	0.4	0.08	0.5	0.21
2,6-Dichlorophenol	0.02	0.0062	22	5.9
2,4,6-Trichloroanisole	0.05	0.025	0.0009	0.00008
Geosmin	0.016	0.0075	0.0038	0.0013
2-Isobutyl-3-methoxypyrazine	0.003	0.0004	0.001	<0.00005
2-Isopropyl-3-methoxypyrazine	0.02	0.0099	0.0002	<0.00003
2-Methylisoborneol	0.018	0.0025	0.015	0.0063

Since geosmin and MIB have been recorded, there has been no reported case about these compounds causing bad health (probably due to the very low concentrations in the water) (Young et al. 1996).

2.4 ACTINOMYCETES

Geosmin and MIB widely exist in Japan, USA, Canada and China, where they contribute to different extents to the taste and odor present in the water. Research found that the main organism responsible for the taste and odor compounds are actinomycetes (Figure 2-6 and Figure 2-7). In New Zealand, blue-green algae (Figure 2-5) is the main cause of the taste and odor compounds.

Figure 2-5-Blue-green algae in Lake Waihola.

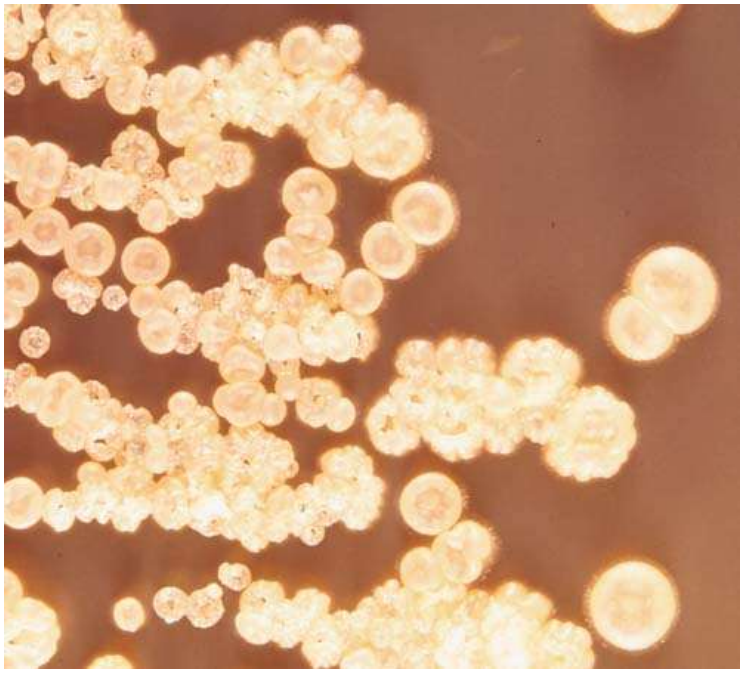

Figure 2-6-Streptomyces griseous. The bacterium Streptomyces griseous is an example of an actinomycete (Asseng et al, 2004).

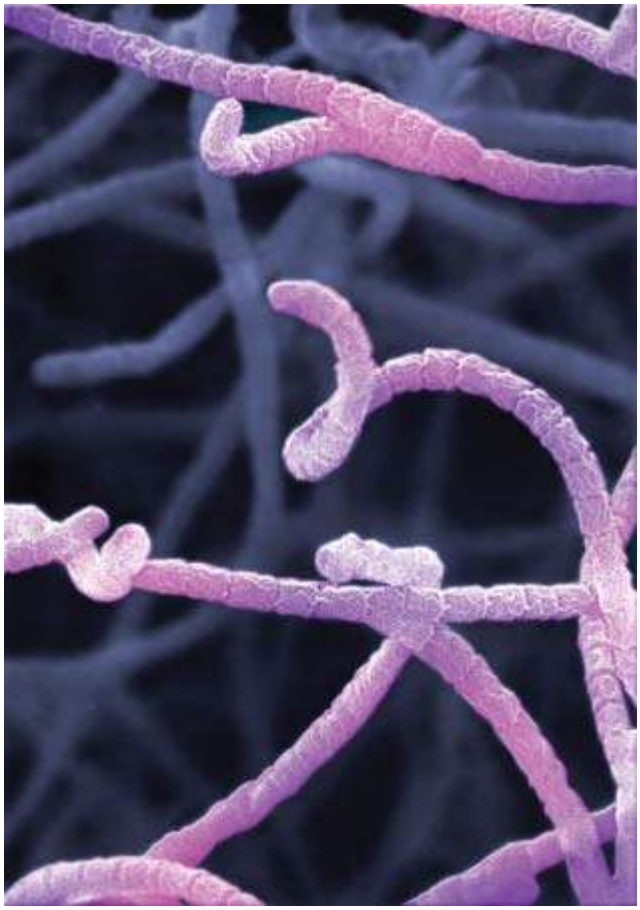

Figure 2-7-Streptomyces virginiae, a type of actinomycete, produces antibiotics that are commonly used in livestock (Lifongo et al, 2004).

Ma (2007) tracked the concentration of MIB in water at a water treatment plant named Yangshupu Waterworks for one year (Table 2-4 and Figure 2-8). MIB and geosmin concentration increased from July and reached a peak in August then decreased gradually. The cause of the increase was growth in algae in the sedimentation tubes due to the high temperature in the summer season, resulting in MIB increasing in the treated water.

Table 2-4-Concentration of MIB and geosmin in Yangshupu Waterworks industry (Ma, 2007).

	Odour compounds (μg/L)	
Month	MIB	Geosmin
1	5.46	2.78
2	5.72	2.87
3	4.41	4.82
4	6.2	3.62
5	14.56	6.89
6	10.52	7.24
7	35.08	3.61
8	97.94	5.42
9	36.38	5.54
10	19.02	3.65
11	9.9	3.9
12	7.36	4.35

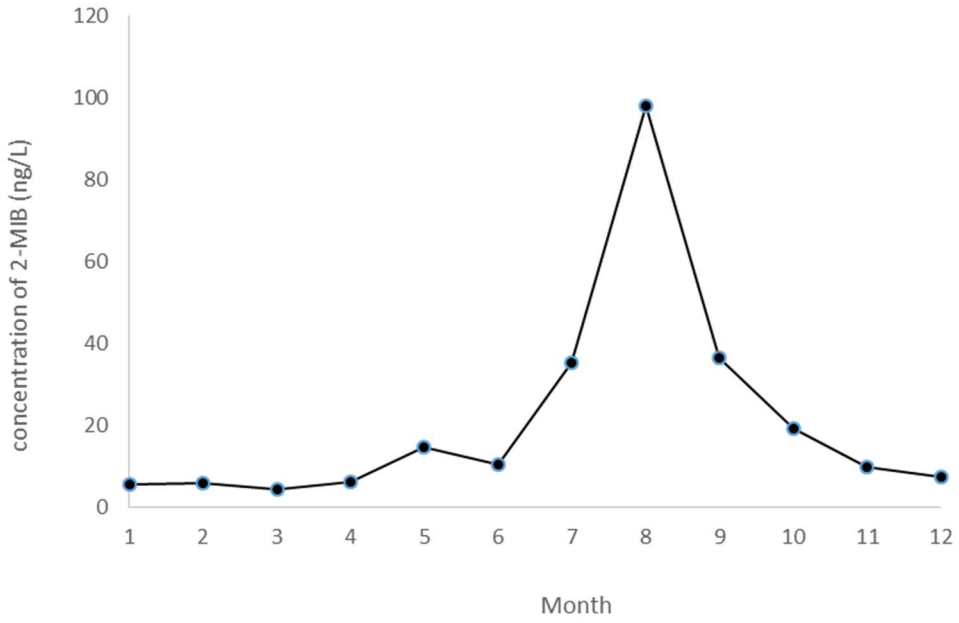

Figure 2-8-Concentration of MIB in general water treatment plant of Yangshupu Waterworks (Ma, 2002).

Concentrations of MIB at Phoenix's water treatment plants normally remain at concentration less than 20 ng/L except during the summer season. The data from Phoenix's water treatment plants show the concentration of MIB over three years from 1999 to 2001 (Figure 2-9). It was shown that MIB has a high concentration during summer season because high temperature promoted algal growth, not only in the water source and canals, but also in the water treatment plant.

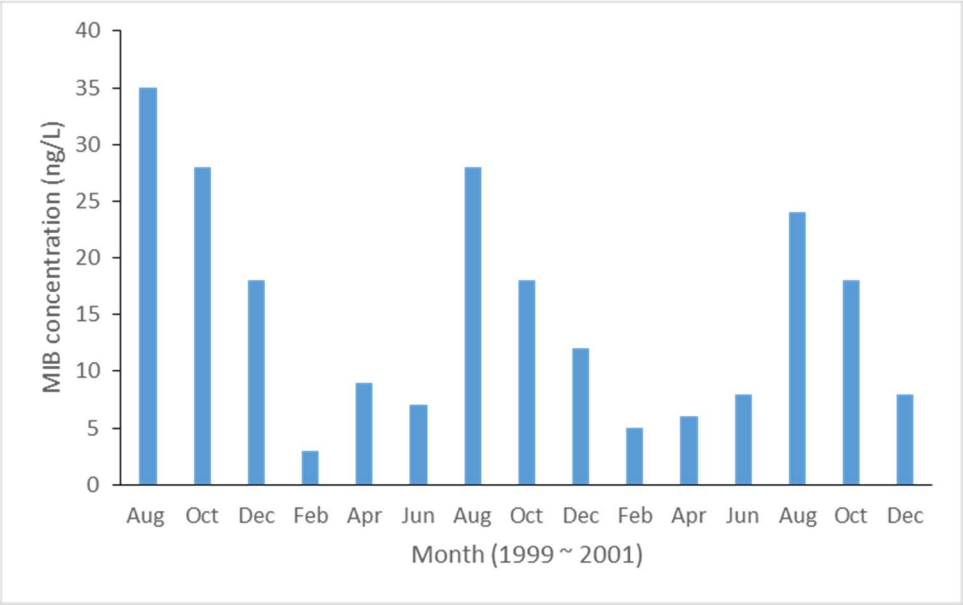

Figure 2-9-Concentration of MIB in MIB in Phoenix's water treatment plants for 3 years from 1999 to 2001 (Larry Baker, 2002).

Several methods were implemented to control taste and odour (Larry Baker, 2002).

1. Reservoir management: Blending of water from the river and the lake outlet reduced the concentration of MIB and geosmin.
2. Canal treatment: Removing algae growing on the sides of canal, therefore reducing the production of MIB.
3. Powdered activated carbon (PAC): PAC treatment in the water treatment plants were used to remove MIB from water source, although PAC treatment could effectively remove MIB, there are were still limits

including the PAC loading capacity, pumping systems and hydraulic short circuiting. Individual PAC treatment was not the most effective way compared to a multi-barrier strategy.

2.5 METHODS OF ANALYSIS FOR GEOSMIN AND 2-METHYLISOBORNEOL

Gas chromatography coupled with a mass spectrophotometer or flame ionization detector is the most widely used method to detect taste and odour compounds (Barnett, 2005). Typical methods of taste and odour compound extraction include liquid phase extraction of the compounds into a solvent such as methanol or solid phase extraction from liquid onto a solid surface that will absorb the compounds.

Headspace solid phase micro-extraction (SPME) involves inserting a microfiber that absorbs the compounds in the air space in a vial containing the sample (Watson et al, 1999). Extraction is relatively quick and simple, and the fibre can be reused.

The extract is then injected into the GC, volatilised off the fibre or with the solvent by heating, and passed through a chromatography column using an inert gas (nitrogen, argon, helium or hydrogen) as the mobile phase, where the different compounds separate out based on their affinity to the column (the stationary phase), and elute separately (Bucchetti et al, 2011) (Figure 2-11). If the elution points of each compound are known, FID can be used to quantify the compounds, based on detector response and comparison to calibration standards. If there are multiple compounds where the elution points are uncertain, mass spec can be used to identify and quantify the compounds.

Detector response in FID will depend on the compound of interest, so ideally a calibration curve for each compound being analysed is needed (Watson et al, 1999).

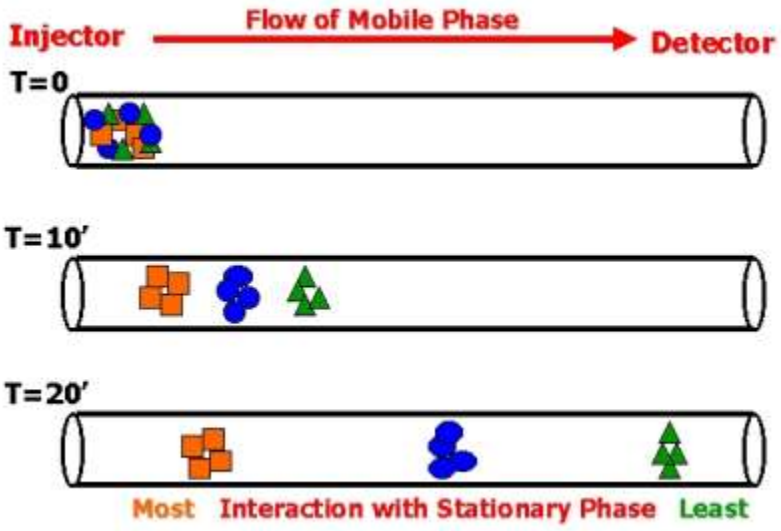

Figure 2-10-Mobile phase flow illustration (Suffet et al, 1999).

The equipment used for gas chromatography generally consists of an injection port at one end of a column filled with substrate material and a detector at the other end of the metal column (Vöhringer et al, 2007). Normally, the sample is injected into the injection port with a needle and a syringe capable of delivering a known volume. The injection port contains a septum made from neoprene rubber or silicone to prevent the sample gases from escaping. The injection port is maintained at a temperature at which the sample is vaporized immediately. Ideally for good separation the sample is uniformly spread across the cross section of the column, forming a plug (Van et al, 2012). A carrier gas (argon, helium, hydrogen, nitrogen, or hydrogen) drives the sample down the column at a constant flowrate. Many analysts use helium as it does not react. Hydrogen is normally a good carrier gas, but may react with the sample. The best choice for a carrier gas will also depend on the type of detector used.

The column is a metal tube, often filled, or the inside coated, with polysiloxane coated with for example, methyl, cyanopropyl, trifluoropropyl or phenyl side groups that interact with the solutes in the gas (Figure 2-11). Alternatively polyethylene glycols, styrenes, or aluminium oxides may be used, and may involve separation of the solutes of interest on the basis of size and/or shape. As the

sample moves through the column, the different molecular characteristics determine how each substance in the sample interacts with the surface of the column and packing. Substances that do not adhere to the column packing, or do not diffuse into the packing pores, move through the column rapidly (Ma et al, 2011).

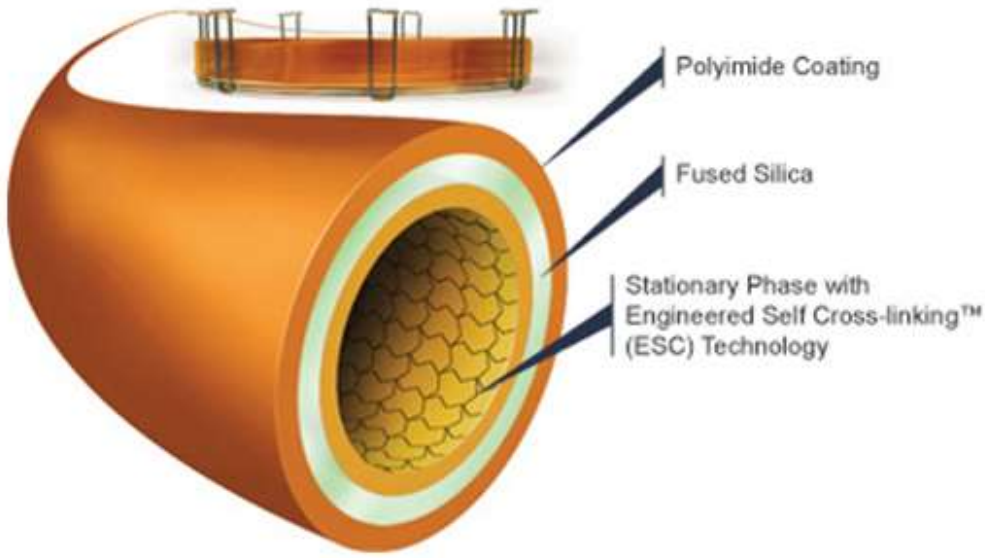

Figure 2-11-Structure of GC column (Ma et al, 2011).

The GC instrument uses a detector to measure the different compounds as they emerge from the column. Among the available detectors are argon ionization detector, flame ionization detector, flame emission detector, detector cross section, thermal conductivity detector, and the electron capture detector. Choosing the right sensor depends on usage (Ma et al, 2011). Some considerations are that flame detectors will destroy the sample, the thermal conductivity detector is universally sensitive, and argon ionization detector requires an argon carrier gas. The spectral output usually electronically stored and displayed on a monitor.

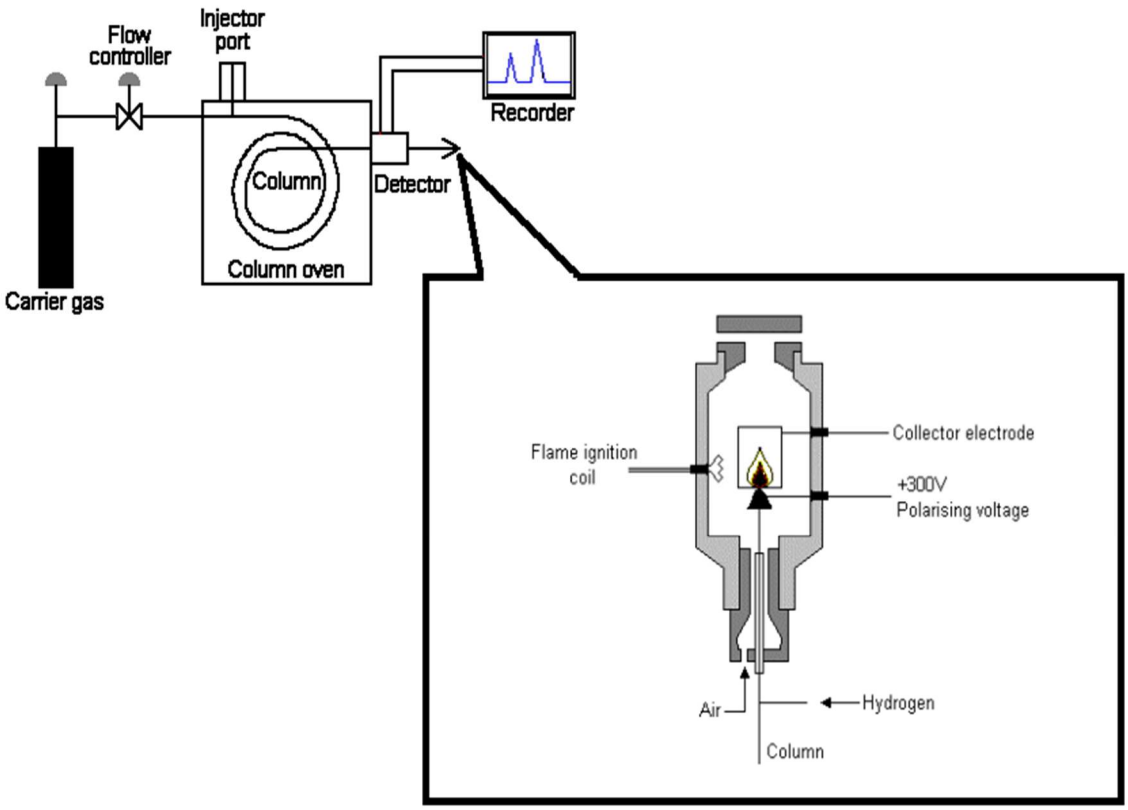

Figure 2-12-GC-FID set up and flame ionization detector (Benitez et al, 1996).

An example of FID is shown in Figure 2-12. The carrier gas from the column is mixed with hydrogen and air, and they are ignited when arriving at the flame ionization detector. Organic compounds in the fire are conductive and will carry a charge from the polarizing voltage electrode to the collector electrode (Serpone et al, 1995). FIDs are more sensitive to mass instead of concentration. So this gives the advantage that the changes in mobile phase flow rate would not influence the detector's reaction. FID is sensitive, has a linear response range, exhibits low noise, and is easy to use.

GC-MS uses a mass spectrometer for its detector (Figure 2-13). The sample inlet is maintained at a high temperature, 400°C (752°F), to ensure that the sample remains a gas (Benitez et al, 1996). Next the sample enters the ionization chamber. An electron beam is accelerated by a high voltage. The molecules break into well-defined fragments on collision with the electrons. Each fragment is loaded and shifted to a single particle accelerator where they are accelerated along a curved

path until they reach the detector. When an individual charged particle hits the detector surface, several electrons (charged particles) also output from the detector surface. Next, these electrons are accelerated toward a second surface, generating more electrons bombarding other surface (Guttman, 2012). The result is amplification of the original charge through a cascade of electrons that reach the collector. At this point, the instrument measures the load and records the fragment mass as the mass is proportional to the detected load (Kim et al, 2007). The MS instrument produces the output drawing a series of peaks on a graph, the mass spectrum. Each peak represents a value for a mass of fragments. A peak height increases with the number of fragments detected with a particular single mass. As with GC detectors, a peak height may differ in detector sensitivity used.

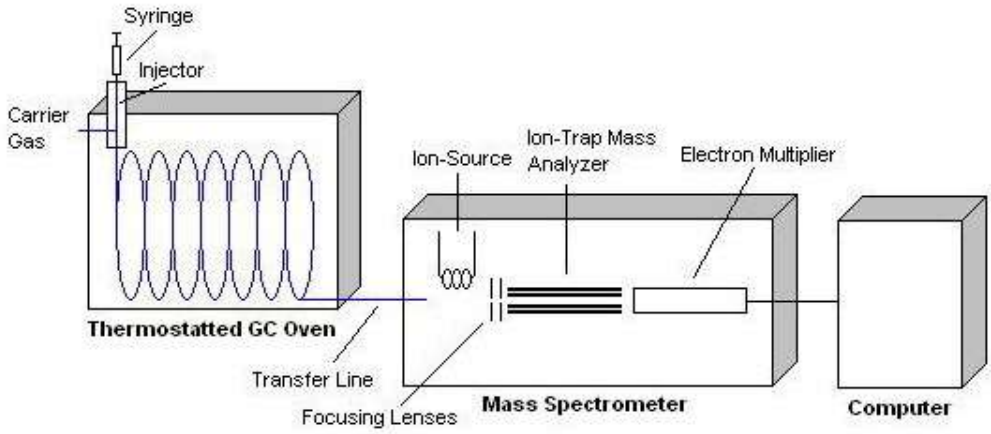

Figure 2-13-Gas chromatography mass spectrometry structure (Mullet, 2002).

2.5.1 Liquid – liquid extraction (LLE)

Liquid – liquid extraction involves adding a solvent that is immiscible with the bulk liquid to extract the solute of interest, assuming the solute is soluble in the solvent. It is the most widely used water pre-treatment method. It extracts the solute by mixing a small volume of extraction solvent along with a certain volume of dispersive solvents into the bulk liquid, ensuring it is well mixed resulting in a cloudy suspension, during which the solute migrates into extraction solvent (Figure 2-14) (Holt et al, 2005). The solvent is then allowed to separate by either centrifugation or other means, and the solvent then analyzed using GC. This

method has the disadvantage that the solute takes time to migrate between sample and the extraction solvent, the need for a dispersant, that extraction solvent then needs to be recovered and it cannot be automated (De Angelis F, 2003). Examples of research using LLE include Cortada (2011), Ma (2007). In all cases GC-MS was used.

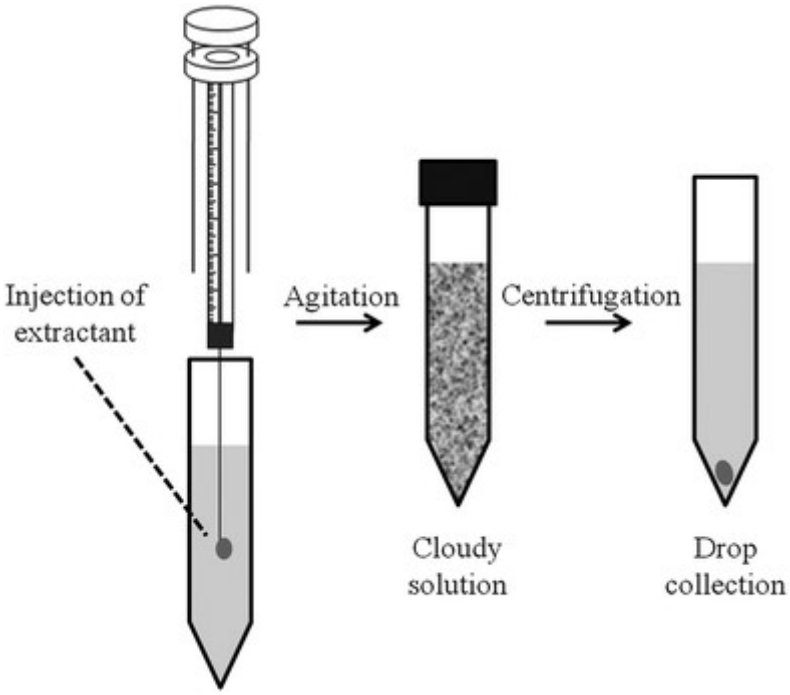

Figure 2-14-General scheme of dispersive liquid–liquid micro-extraction (LLME). (Ma, 2011).

2.5.2 Stir bar sorptive extraction (SBSE)

This method involves placing the sample in a vial with a magnetic stirrer, which keeps the sample well mixed. A polydimethylsiloxane (PDMS) fibre is dipped in the sample, and the solute of interest absorbs onto the fibre (Richardson, 2003). Extraction takes about 30-60 minutes. Then the fibre is removed from the vial and inserted into the GC injection port, where the solute is volatised off the fibre (Figure 2-15). This method is used for screening of drugs and pharmaceuticals since the process is simpler and less labour intensive than traditional methods and

is solvent free. Examples of research using SBSE include Lambert and Mullett (2005), Baltussen (1999).

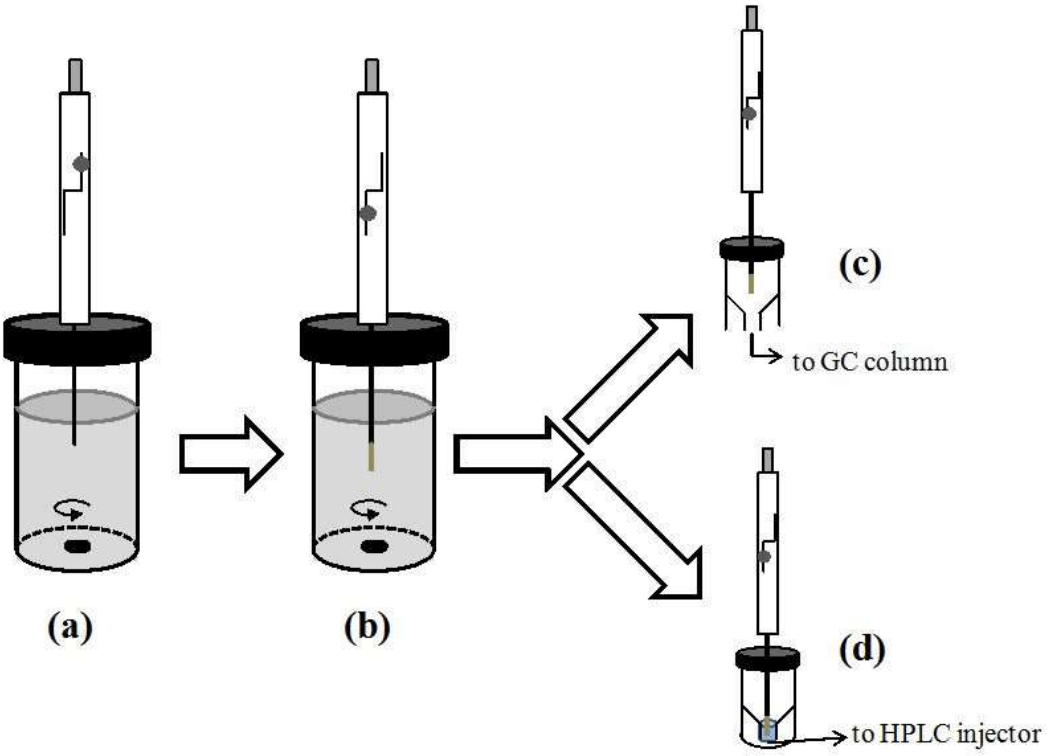

Figure 2-15-General scheme of stir bar sorptive extraction (Lambert and Mullett, 2005)

2.5.3 Solid phase micro-extraction (SPME)

As was stated previously, solid phase micro-extraction (SPME) involves inserting a microfiber into the airspace of a heated vial that contains the sample. The compounds of interest in the airspace absorb onto the fibre, reducing the vapour pressure of the compound in the air space, resulting in more of it vaporising from the liquid, effectively concentrating the compound on the fibre (Chen et al, 2011). Finally, the needle is introduced to the GC injector, then GC will desorb the sample from fibre and deliver it to GC column (Figure 2-16). Extraction is relatively quick and simple, and the fibre can be reused. From the 1990's solid phase micro-extraction techniques became a common technique and is widely used for drinking water odour and taste detection (Chary, 2012). Because the compound is

concentrated on the fibre, and is rapidly delivered to the GC, minimum detection limits are improved and resolution is maintained (Baltussen et al, 1999).

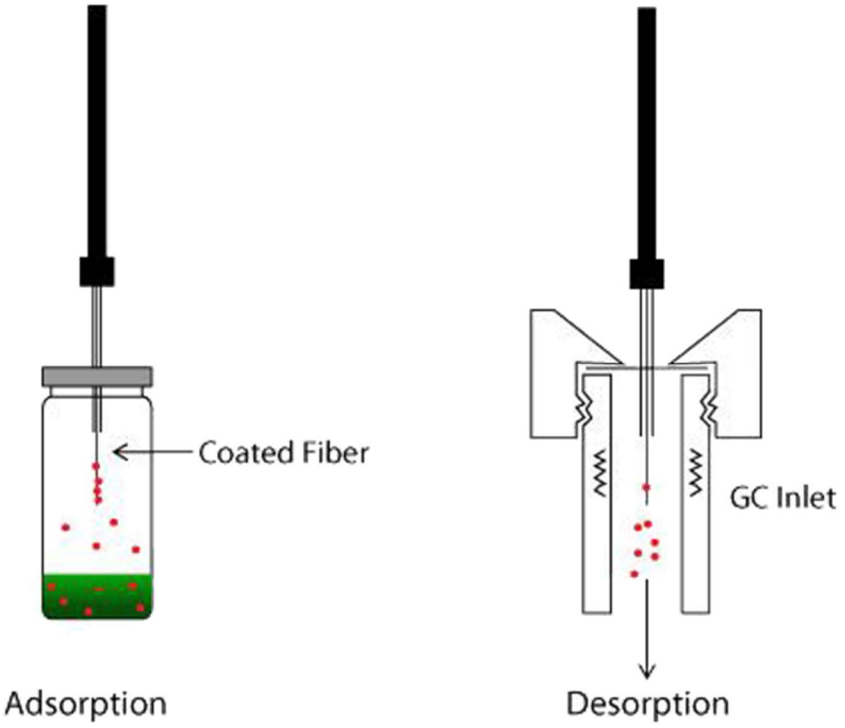

Figure 2-16-Schematic representation of the headspace solid-phase micro extraction adsorption/desorption (Gbatu et al, 1999).

The fibre that is used for SPME is Divinylbenzene/Carboxen/Polydimethylsiloxane (DVB/CAR/PDMS) (Figure 2-17).

Figure 2-17-DVB/CAR/PDMS fibre.

Examples of research using SPME are shown in Table 2-5.

Table 2-5-Examples of research that has used SPME.

Detector	Method	Author	Date
GC-MS	SPME	Watson	2000
GC-MS	SPME	Lloyd	1998
GC-MS	SPE	Ma	2007
GC-FID	SPME	Gnatu	1999
GC-FID	SPME	Lloyd	1997

2.6 METHODS OF REMOVING MIB AND GEOSMIN

MIB and geosmin are typically concentrated within algae (Ma, 2007). Conventional water treatment methods including coagulation, flocculation, clarification and filtration will remove 60-70% of these compounds.

2.6.1 Coagulation and flocculation

Coagulation/flocculation is a chemical technique in water treatment to encourage suspended and dissolved solids present to agglomerate prior to sedimentation and filtration (Figure 2-18). Most solids suspended in water have a negative charge so they repel each other and remain suspended. Aluminium sulphate or ferric chloride is added to neutralise the negative charges on the solids so they can agglomerate (E.R. Sholkovitz, 1976). Metal coagulants fall into two general classifications: aluminium or iron containing coagulants. The aluminium coagulants incorporate aluminium sulphate, aluminium chloride and sodium aluminate. The iron coagulants incorporate ferric sulphate, ferrous sulphate, ferric chloride and ferric chloride sulphate. Other chemicals utilized as coagulants include hydrated lime and magnesium carbonate (Matilainen et al, 2010). When metal coagulants are added to water the Al and Fe hydrolyse quickly to form large structures with the suspended solids.

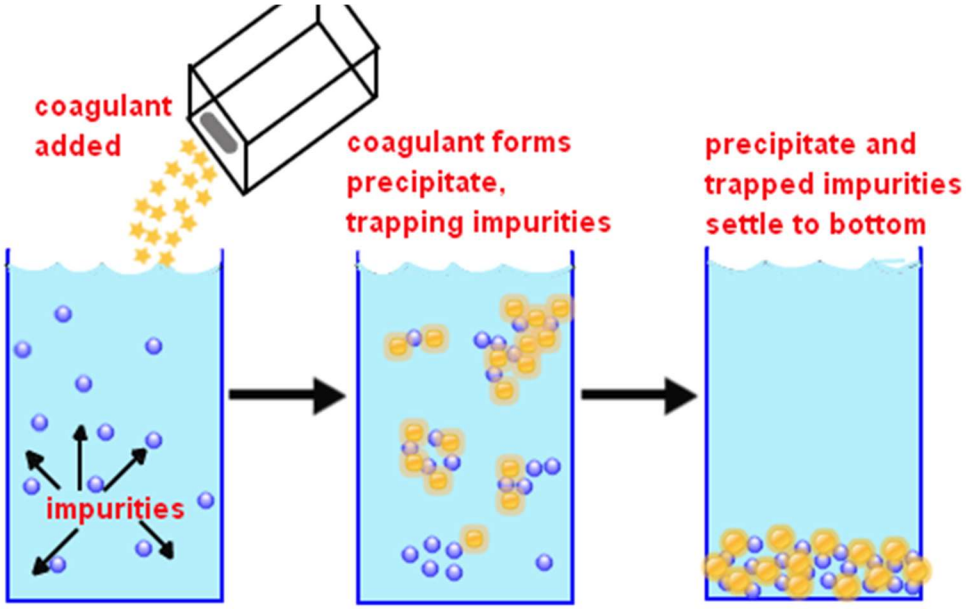

Figure 2-18-coagulants principle and processing (Matilainen et al, 2010).

There has been extensive improvement of pre-hydrolysed inorganic coagulants. These incorporate aluminium chlorohydrate, polyaluminum chloride, polyaluminum sulphate chloride, polyaluminum silicate chloride and types of polyaluminum chloride with natural polymers (Kuo et al, 1982). Iron structures incorporate polyferric sulphate and ferric salts with polymers. There are additionally polymerized aluminium-iron mixes. They work effectively over a wide range of pH and water temperatures, require lower amounts to achieve the same reduction in suspended solids, with lower dissolved solids. As the coagulants all behave differently and have different properties, jar testing is carried out to determine which one works best for a particular raw water.

Flocculation is sometimes carried out following coagulation using an anionic polymer to increase the particle size (Figure 2-19). Naturally available polymers have long been utilized as flocculants. For instance, Sanskrit writing from around 2000 BC mention the use of pulverized nuts from the Nirmali tree (Strychnos potatorum) for clearing up water – a practice still alive today in parts of Tamil Nadu, where the plant is known as Therran and grown for its restorative properties (Muellner et al, 2007). The utilization of manufactured polymers is more common due to their greater reliability and ease of manufacture (Zeng et al, 2008).

Polymers are available as powders, oil or water-based emulsions and need to be rapidly mixed with the water to ensure good dispersion and flocculation properties.

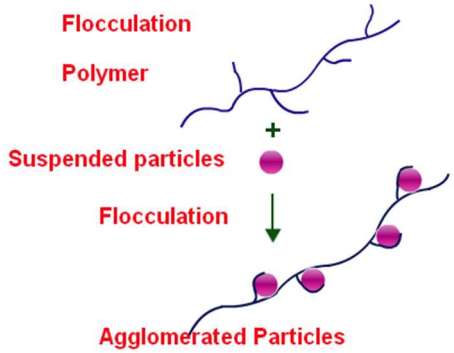

Figure 2-19-Flocculation system (Zeng et al, 2008).

There are different approaches to ensure good mixing between the coagulant, flocculant and the suspended solids including chambers, granular media beds, diffused air, winding stream chambers, responding cutting edges and pivoting sharp edges (Al-Halbouni, 2008). Once the floc has formed it is then separated out, either by settling, flotation or filtration.

2.6.2 Sedimentation

Sedimentation is a physical treatment of water where suspended solids are allowed to settle out under gravity. It is a low cost and widely used process which can remove suspended materials by letting the water settle for some time ranging from a few hours to days, although natural bacteria die off if left to settle for too long, which in the case of cyanbacteria, can result in increased geosmin and MIB in the treated water. Sedimentation is not significantly effective in removing viruses and bacteria without coagulation and flocculation (Ndabigenesere et al, 1995).

The particles that settle out form a layer which thickens as it continues to settle, a process known as solidification. This layer can be mechanically thickened.

Sedimentation may be used before coagulation to decrease the amount of the coagulating chemicals required, or after coagulation and flocculation (Brandhuber, 1998).

2.6.3 Filtration

Filtration uses screens, packed beds of granular material, fabric or membranes to remove suspended solids, particles and large debris from water. Screens are commonly utilized at the start of water treatment to remove large objects such as leaves, fish, and coarse rubbish (Oyler et al, 1982). The spacing between the bars ranges from 1 to 10 cm. Micro-strainers consist of a fine metal fabric and are used to remove fine sediment and leaf litter (Figure 2-20) (Zularisam et al, 2006).

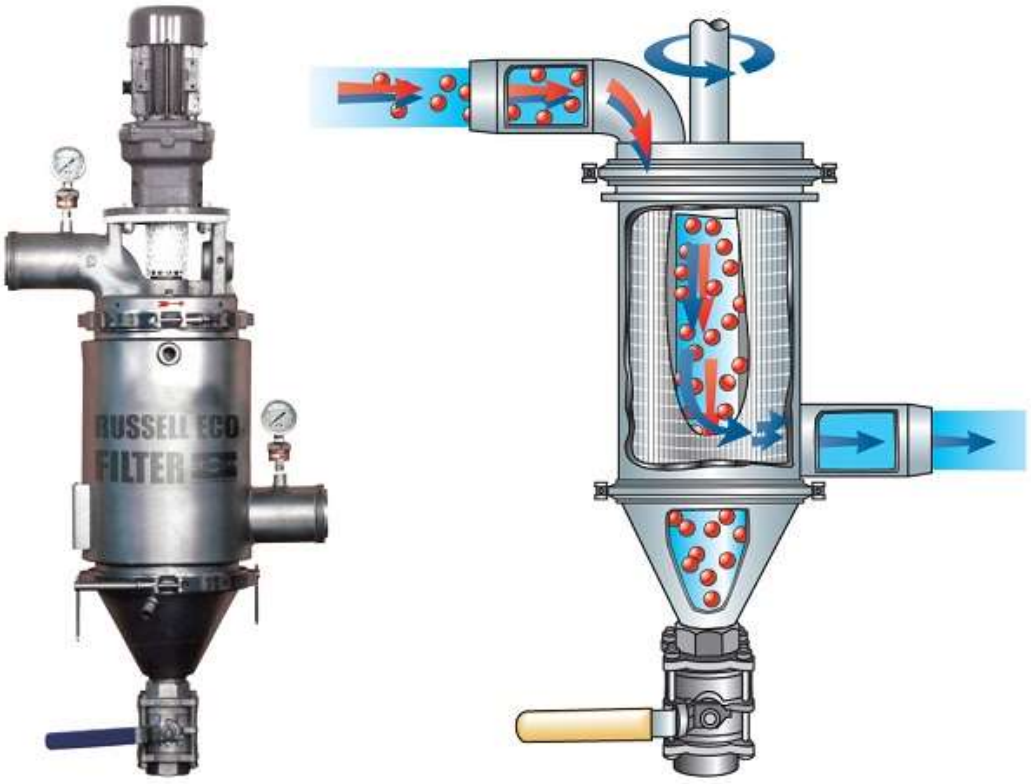

Figure 2-20-Self-cleaning strainer filter process (Zularisam et al, 2006).

Filters consist of a medium such as sand or fabric which trap suspended solids. These may be disposable cartridge filters for household and small scale applications, or large cartridge filters which can be cleaned by back flushing. Some

filters are coated with diatomaceous earth to improve filtration properties every time the filter has been cleaned (Betancourt et al, 2004).

Sand filters contain sand or other granular material, e.g. anthracite or smashed glass, as the filter medium that is porous enough to allow water to flow through the bed under gravity. Suspended solids accumulate on the surface of the filter bed forming a 'schmutzdecke' (Betancourt et al, 2004) resulting in slower water movement through the bed. The beds can be cleaned by back washing and air scouring.

Granular activated carbon filters absorb trace organic substances for removal of inorganic and natural particles. This is covered in more detail later on. There are also filters that absorb iron, manganese and arsenic (Salánki, et al, 2002).

Membrane separation techniques have been widely used in water treatment in recent years in many industries because of their good environmental sustainability and economics. It has low energy consumption because it operates at room temperature, and different kinds of membrane can be used that provide high selectivity (Crittenden, 2012). Membrane separation can operate in dead-end flow mode for treating water with low levels of contaminants (e.g. filter socks) and cross flow mode (e.g. spiral wound tangential flow membranes or hollow fibre membranes for water with higher levels of contaminants (Figure 2-21) (Tansel et al, 2006).

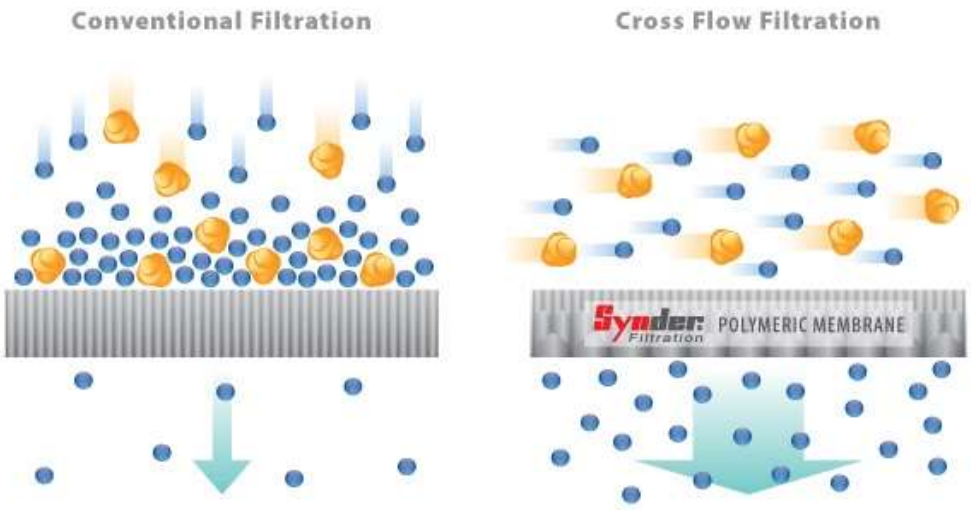

Figure 2-21-Dead-end flow and cross flow filtration (Tansel et al, 2006).

2.6.4 Activated carbon

After flocculation, coagulation, clarification and filtration, there may still be trace organics present that contribute to water taste and odour or may be toxic. Activated carbon is a common method employed to remove these organics (Li et al, 2008).

Activated carbon is produced by pyrolysing carbonaceous raw material, e.g. wood, peat, coal, coconut husk, at temperatures between 450-900^{o}C in atmospheres containing low oxygen. The material may be activated by pretreating the raw material with a strong acid, alkali or salt prior to pyrolysis, or after pyrolysis in an oxidising atmosphere containing oxygen or steam at temperatures between 600-1200^{o}C. This results in highly porous material with a large surface area (Gaya et al. 2008).

Different organic compounds will have different affinities for activated carbon, which means that some compounds will bind while other will not (Kim et al. 2007). Activated carbon has a limited life time depending on the adsorption capacity of

the carbon, mass and type of activated carbon, the concentration of trace organics in the water, and the flow rate of the water. Once it becomes saturated, or reached capacity, the organics start to exit the filter, and the activated carbon will need to be replaced, or regenerated. Many industries use two or more activated carbon filters to avoid breakthrough occurring (Melchers, 2005).

Examples of granular activated carbon (GAC) used to remove MIB include: coal-based GAC (Figure 2-22), coconut shell GAC (Figure 2-23), and jujube seed GAC (Figure 2-24). The amount of organics (Q) absorbed by activated carbon can be calculated using the difference in input and exit organic concentrations ($C_0 - C$), solution volume (V) and activated carbon weight (W) (Ma, 2007):

$$Q = \frac{(C_o - C)V}{W}$$

The adsorption isotherms for MIB differ for the different kinds of granular activated carbon, coal-based GAC and coconut shell GAC are more effective at removing MIB compared to jujube seed GAC because they have higher affinities for MIB, and are able to absorb more MIB at lower solution concentrations than jujube seed GAC.

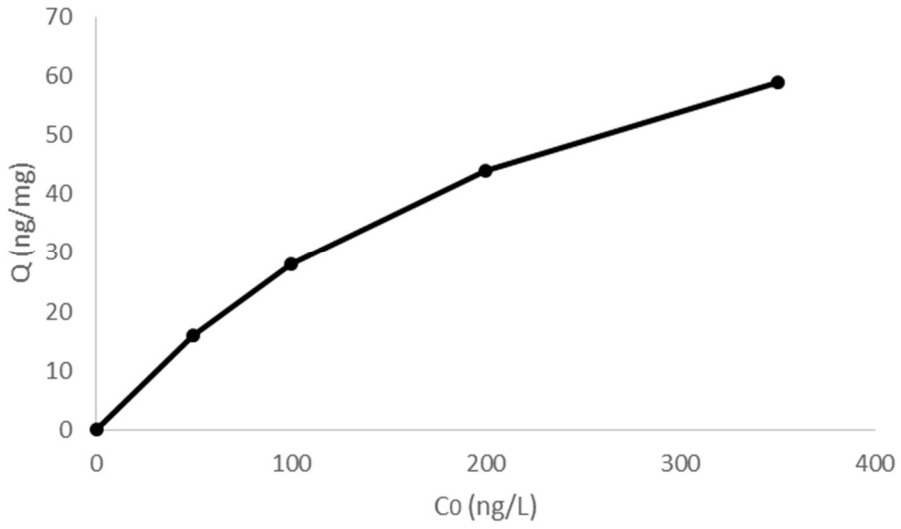

Figure 2-22-Isothermal of coal-based GAC adsorption of MIB.

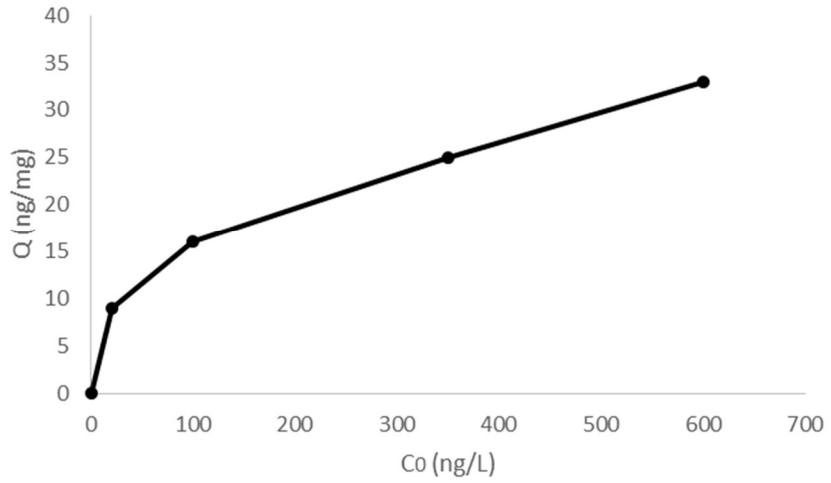

Figure 2-23-Isothermal of coconut shell GAC adsorption of MIB.

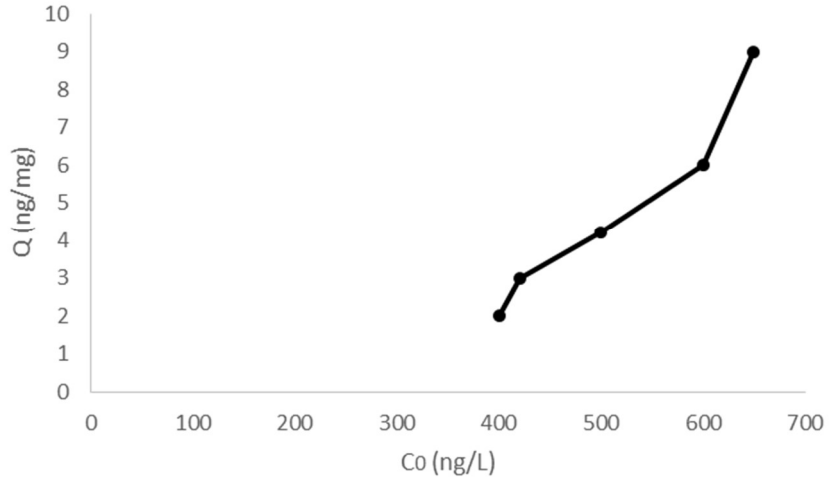

Figure 2-24-Isothermal of jujube seed GAC for adsorption of MIB.

Other research by Kim (2014) about removal of geosmin and MIB by powdered activated carbon looked at the effect of using distilled water or raw water on removal (Figure 2-25). Removal of geosmin and MIB was lower in raw water than

distilled water because of competition with other compounds for binding sites on powdered activated carbon.

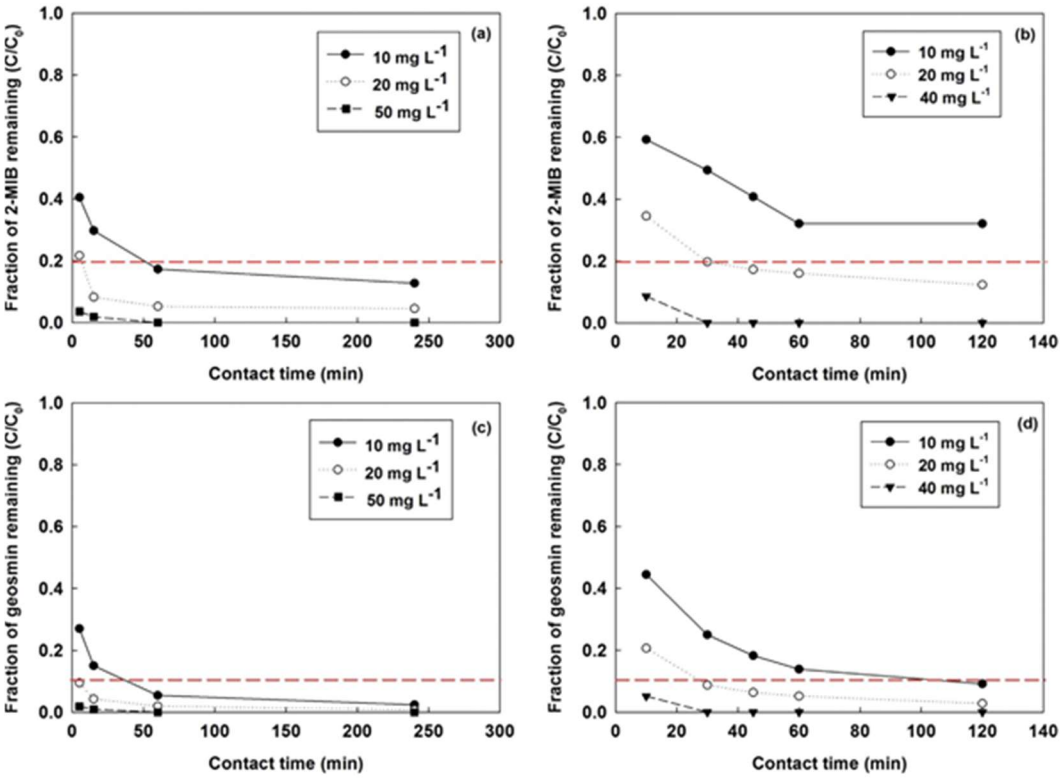

Figure 2-25-Removal of geosmin and MIB by powdered activated carbon distilled water and raw water source. Left is distilled water and right is raw water, top is MIB and bottom is geosmin (Kim et al, 2014).

Many methods to remove contaminants from water using activated carbon have been combined with other methods such as oxidation, and UV treatment (Ma, 2007).

2.6.5 Hydrogen peroxide and ozone

Hydrogen peroxide (H_2O_2) is widely used as a bleach and sanitiser. It decomposes into hydroxyl radicals (groups with unpaired electrons), which will scavenge electrons by oxidising carbon-carbon double bonds in organic compounds, reducing the colour in coloured compounds, and damaging organic matter in living organisms.

Aleksey (Hyun Jo, 2011) compared the effectiveness of ozone and hydrogen peroxide on removing odour compounds in water, when combined with UV light. Ozone has a much greater oxidising potential at lower concentrations compared to hydrogen peroxide (Figure 2-26).

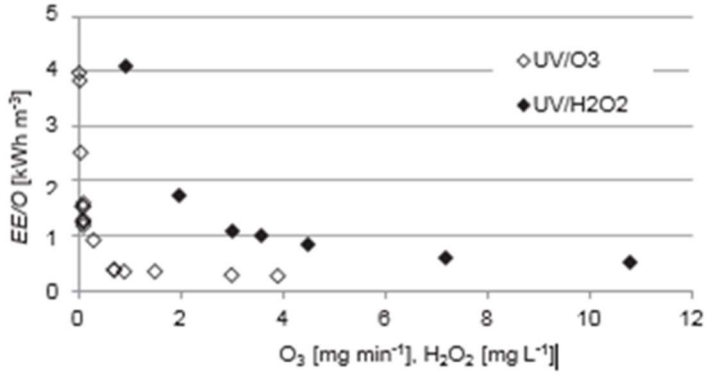

Figure 2-26-Comparison of UV/O_3 and UV/H_2O_2 efficiency (Hyun Jo, 2011).

Hydrogen peroxide sold for medicinal purposes is normally diluted into 3% - 10% solution. Adding hydrogen peroxide to water is considered a safer way to treat water than chlorine, as it does not produce disinfection products such as halogenated organic compounds. Most water treatment industries which use hydrogen peroxide will combine it with UV light due to the increased effectiveness in removing contaminants (Young et al, 1996).

Ozone can partially remove geosmin and MIB, but can also produce other compounds that are more susceptible to biodegradation. Elhadi (2004) used ozone followed by granular activated carbon to remove MIB and geosmin. Initial removal rate was 76-100% for geosmin and 47 to 100% for MIB, this decreased as the activated carbon became exhausted, but began to increase again over time due to growth of micro-organisms on the activated carbon. A combination of oxidation and biofiltration is a possible approach for MIB and geosmin removal.

2.6.6 Ultraviolet Light

Ultraviolet (UV) light is a product of sunlight with a wavelength in the region between visible light and X-Rays or between 100 nm to 400 nm. UV lamps contain

a small amount of mercury which emits UV light when an electric current is applied (Figure 2-27) (Johnsen, 2011).

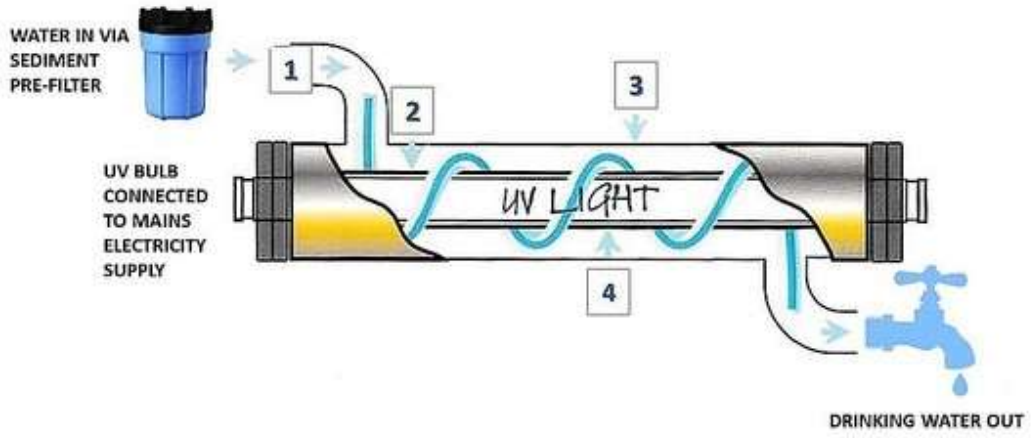

Figure 2-27-Structure of ultraviolet light and UV treatment process (Zhao Lin et al. 2005).

UV light will attack DNA in microorganisms. The UV light initiates a reaction between two molecules of thymine found in DNA, resulting in kinked DNA that inhibits normal cellular function (Duguet et al, 1987) killing microorganisms or preventing them from reproducing.

Research from Hyun-Jo (2008) analysed the effect of UV and UV/H_2O_2 on removing odour and other organic compounds in water. He used a batch UV reactor at 253.7 nm wavelength and 7.2 mW/cm^2 total UV intensity. Solutions were mixed with H_2O_2 at 6 mg/L. Geosmin and MIB have molar absorption coefficients of 540 and 780 $M^{-1}.cm^{-1}$ (Figure 2-28). Geosmin and MIB results showed 40% and 20% removal with UV treatment alone and 90% and 65% removal respectively with a UV dose of 1200 mJ/cm^2 and 6 mg/L H_2O_2. Hyun-Jo (2008) suggested that geosmin and MIB concentrations are mainly reduced by reaction with the hydroxyl radical produced by UV light rather than by direct photolysis of these compounds.

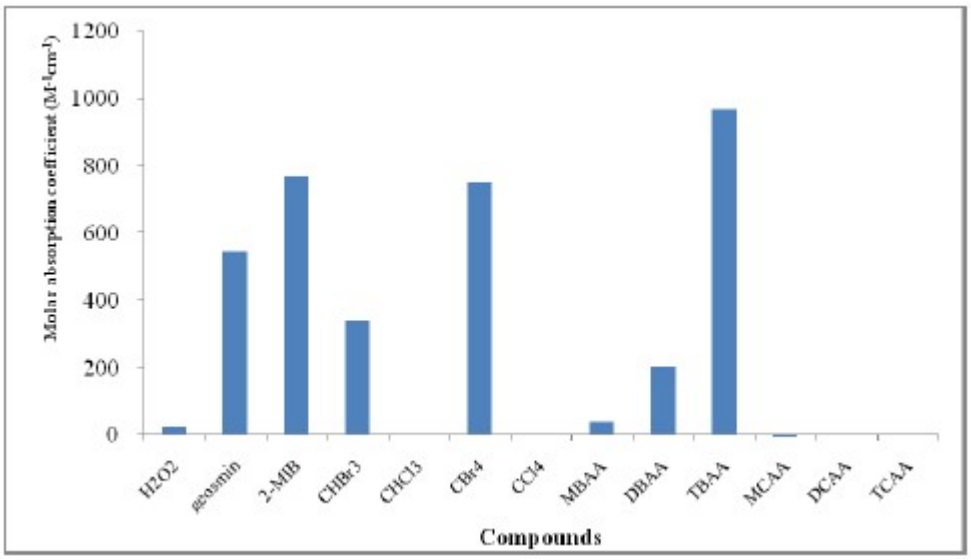

Figure 2-28-Acceptability of geosmin and MIB by UV wavelength at 254 nm (Hyun-Jo, 2008).

2.6.7 Disinfection and disinfection by-products

In order to prevent microbial growth and disinfect water, most water treatment suppliers use chlorine as a disinfectant. However certain pathogens such as cryptosporidium are able to resist disinfection (Barnett et al, 2005). The disinfectant can react with organic matter in the water and create by-products which can also cause problems to human health (Zaitlin, 2006). It is hard to control the concentration of the by-products when using chlorine for disinfection without removing the organic matter first.

Most general disinfection by-products are trihalomethanes and haloacetic acids (Figure 2-29) which can be carcinogenic (Zhang et al, 1998).

Trihalomethanes are chemical compounds where three of the four hydrogen atoms of methane are replaced by halogen atoms. Common trihalomethanes found in water as disinfection by-products are chloroform and bromodichloromethane, the maximum concentration for those two compounds are 0 and 0.07mg/L respectively (Richardson, 2003).

Haloacetic acids are carboxylic acids where a single halogen atom takes the place of a hydrogen atom in acetic acid, and are known as a common undesirable

disinfection by-product of drinking water chlorination. Compared to trihalomethanes, haloacetic acids are not affected by storage or boiling, but can be removed by filtration.

Apart from chlorine by-products, hundreds of disinfection by-products such as Ozonation by-products have been reported from using other disinfectants such as ozone, chlorine dioxide, chloramines and their combinations as well, while only a small number of them such as chloroform and bromodichloromethane have been demonstrated to have health risks.

(a) (b)

Figure 2-29-Structure of trihalomethanes (a) and haloacetic acids (b) (Rosenfeldt et al. 2005).

Many water treatment factories have started to use chloramine as disinfectant, which will also cause disinfection by-products (Melcher et al, 2005). Chloramine is a combination of chlorine and ammonia – a colourless gas with a characteristic pungent smell. With more industries using chloramine in water treatment plants, more than twenty percent of household water supplies have been shown to have chloramine present (Li et al, 2008). Compared to chlorine, chloramine is more difficult to remove and has a longer life time water. Furthermore it cannot be removed by boiling, distilling, settling or other physical processes. In addition, chloramine can also evaporate into indoor air and concentrate in the closed areas (Young, 1999).

Even if there are potential risks from other disinfection by-products, trihalomethanes are still the main concern (Li et al. 2005). General water treatment processes do not effectively reduce trihalomethane formation (Orozco et al, 2008), however household chlorination of turbid or non-turbid waters was shown not to create high concentrations of trihalomethanes. Therefore this was considered a generally safe practice. Reducing water turbidity by letting the water settle followed by filtration before chlorination (Zander, 1997) would reduce disinfection by-product formation. The potential health risk from disinfection by-products are still important issues for recent piped water systems for example, disinfection by-product may damage various systems of the body including the nervous and reproductive systems and the kidneys, and it can cause high blood pressure and anemia. So the world health organization are looking for an effective method to reduce its prevalence (Kim et al, 2007). At the moment, household water filtration can remove chlorine and by-products from drinking water and is also inexpensive (Zhang et al, 1995).

2.7 CONCLUSION

MIB and geosmin in water can be removed by activated carbon, UV and oxidation. Conventional water treatment processes will remove up to 60-70% as these compounds are found in algae in raw water, which can be removed coagulation, filtration and sedimentation. UV by itself is not very effective at removing MIB and geosmin because of their low susceptibility to UV light. A combination of UV and oxidation is much more effective, and a combination of oxidative and biofilters has been suggested.

This thesis will explore the effect of activated carbon, UV light and hydrogen peroxide on removal of MIB and geosmin. As part of the research, method development for GC analysis of these two compounds will also be carried out.

3 MATERIALS AND METHODS

3.1 OVERVIEW

This chapter presents the analytical materials and methods used in this research. The materials include samples, detection equipment, characterise products for treatment and gas chromatography. The detection methods include solid phase micro-extraction (SPME) and process of gas chromatography mass spectrometry (GC-MS) and gas chromatography flame ionization detector (GC-FID). Treatment methods include application of granular activated carbon, hydrogen peroxide and UV.

3.2 REAGENTS

The following reagents were used:

- Geosmin - 1 ml of 2 mg/ml geosmin (>97%) in methanol (Sigma Aldrich), diluted to $2x10^7$ ng/L in a 100 ml grade A volumetric flask with 10% methanol and remainder distilled water.
- MIB - 5 mg 2-methylisoborneol (>98%) as a powder (Sigma Aldrich), diluted to $5x10^7$ ng/L in a 100 ml grade A volumetric flask with 10% methanol and remainder distilled water.
- Napthalene D8 (Sigma Aldrich), dissolved in methanol and diluted to 200 ng/L in a 100 ml grade A volumetric flask.
- Methanol, analytical grade (Scharlab S.L.)
- Distilled water (Lab supply)
- NaCl (Lab supply, University of Waikato science stores)
- Hydrogen peroxide (33% v/v, Ajax Finechem)
- Granular activated carbon (Spherical, Seachem)

3.3 EQUIPMENT

3.3.1 Geosmin and MIB Extraction

- Divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS) fibres (Sigma Aldrich) and manual fibre holder (Sigma Aldrich) (Figure 3-1)
- 20 ml sample vials with caps with rubber septums (Duran glass tube, silicone rubber seals, plastic screw caps)
- Block heater (Grant Instruments)

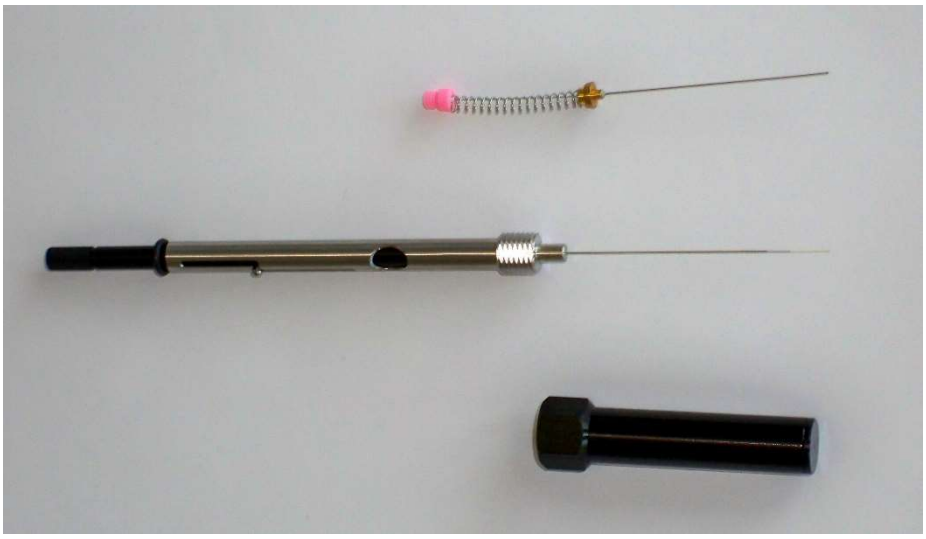

Figure 3-1-SPME manual holder and PDMS fibre.

3.3.2 Standard method of extraction

15 ml of sample contained geosmin and/or MIB was autopipetted into 20 ml sample vials using a 5 ml autopipette and sealed with a cap with a rubber septum. This was heated at 80^{o}C for 30 minutes in the block heater or in the GC oven. The DVB/CAR/PDMS fibre (Figure 3-1) was injected into the headspace of vial, and given 2 minutes for the geosmin and MIB to absorb onto the fibre. The fibre was removed and injected into the manual injection port of the GC (FID or MS) (Figure 3-2 and Figure 3-3) and the method shown in 3.3.2 was used for analysis. This was carried out in triplicate for each set of samples.

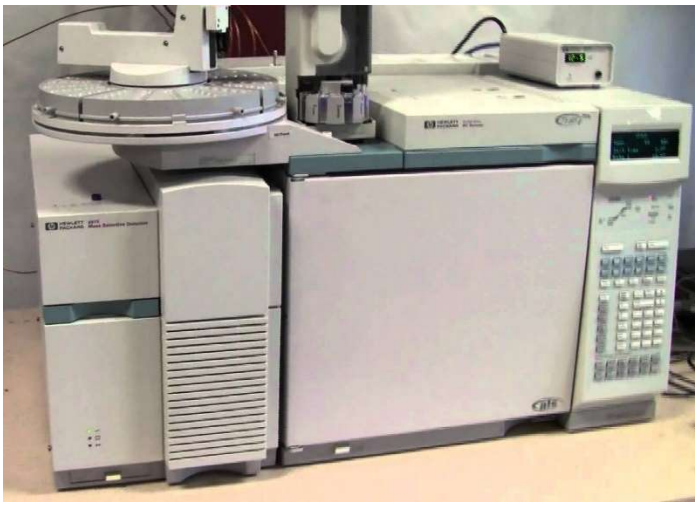

Figure 3-2-Gas chromatography 5973 mass selective detector.

Figure 3-3-Gas chromatography flame ionization detector 2010 plus.

3.3.3 Effect of MIB and geosmin concentration

MIB was diluted to 5, 10, 25, 35, 50 ng/mL and geosmin diluted to 2, 10, 20, 36, 50 ng/mL using a 5 ml autopipette. These were extracted using the standard method and high concentrations were analysed using GC-MS to determine retention time.

MIB and geosmin were also diluted to 200, 400, 600, 800, 1000 ng/L using a 5 ml autopipette and analysed using GC-FID using the retention time found in the GC-MS as a guide.

3.3.4 Effect of salt

Geosmin and MIB solutions were diluted to 10, 20, 30 ng/mL concentratons using a 5 ml autopipette. The effect of salt on geosmin and MIB extraction was then investigated by adding 5 mg of NaCl to 15 ml of sample in the sample vial for each of the dilutions and sealed. These were left overnight at 4^{o}C, before using the standard method of extraction. Samples were analysed using GC-MS.

3.3.5 Effect of heating time

Geosmin and MIB solutions were diluted to 10, 20, 30 ng/mL concentrations using a 5 ml autopipette. These were then extracted using the standard method of extraction, but were heated to 80^{o}C for 30 and 60 minutes. Samples were analysed using GC-MS.

3.3.6 Effect of absorption time

Geosmin and MIB solutions were diluted to 10, 20, 30 ng/mL concentrations using a 5 ml autopipette. These were then extracted using the standard method of extraction, but the fibre was exposed to the headspace for 2 and 5 minutes. Samples were analysed using GC-MS.

3.3.7 Effect of using naphthalene D8 as an internal standard

Geosmin and MIB solutions were diluted to 10, 20, 30 ng/mL concentrations using a 5 ml autopipette. 1 ml of 200 ng/L naphthalene was added to each solution and then left overnight at room temperature before using the standard method of extraction. Samples were analysed using GC-MS.

3.3.8 Geosmin and MIB Analysis

Two GC systems were used:

- GC-MS - HP Hewlett Packard GC system 5973 Plus Mass selective detector with a Zebron ZB – 5 column and manual sample injection (Figure 3-2). Helium (BOC analytical gas) was used for the running gas.
- GC-FID - 2010 Plus Shimadzu FID with a Zebron ZB – 5HT column and manual sample injection (Figure 3-3). Nitrogen (BOC analytical gas) was used as the running gas.

Initial experimental work was carried out on the GC-MS. Both the ZB-5 and ZB-5HT columns were readily available in the lab, have a 5% phenyl 95% methylpolysiloxane phase, column dimensions are 30 m x 0.25 mm x 0.25 µm, and the ZB-5 is rated to 360^{o}C, while the ZB-5HT is rated to 400^{o}C.

The parameters of the GC-MS and GC-FID are shown in Table 3.1 and Table 3.2. A typical run time for GC-MS was 16 minutes per analysis, the oven and injection port allowed to cool before a blank run was run to ensure the fibre was clean, the oven and injection port allowed to cool again before another sample was analysed. Nine samples could be analysed per day. Cooling took longer for GC-FID so only eight samples could be analysed per day.

GC peaks representing geosmin, MIB and naphthalene D8 were identified using mass spec, and the retention time used to identify peaks for GC-FID. Average peak area was determined for each set of results and concentrations were determined by comparing peak area to calibration curves for geosmin and MIB. GC data was also analysed for evidence of column and microfibre deterioration, which is represented by peaks other than those associated with geosmin, MIB or naphthalene. Blanks of “cleaned” microfibers were also run to ensure the fibres were clean.

Table 3-1-Parameters for GC-MS and oven.

Gas Chromatography:	Hewlett Packard GC Plus+
Analytical column:	ZB-5 (30m x 0.25mm x 025µm)
Injection temperature:	200°C
Injection type:	Splitless
Sampling time:	1 minute
Flow control mode:	Pressure 76.3 KPa
Carrier gas type:	Helium
Carrier gas flow rate:	1 mL/min

Gradient (°C/min)	Temperature (°C)	Hold Time (min)
0	50°C	3 min
20°C	180°C	0.5 min
10°C	250°C	0.5 min

Table 3-2 - Parameters for GC-FID and oven.

Gas Chromatography:	SHIMAZU GC-FID 2010PLUS
Analytical column:	ZB-5H (30m x 0.32mm x 025µm)
Injection temperature:	200°C
Injection type:	Splitless
Sampling time:	1 minute
Flow control mode:	Pressure 69.4 KPa
Carrier gas type:	Nitrogen
Carrier gas flow rate:	1 mL/min

Gradient (°C/min)	Temperature (°C)	Hold Time (min)
0	50°C	3 min
20°C	180°C	0.5 min
10°C	250°C	0.5 min

3.4 ACTIVATED CARBON TREATMENT

Different weights (50, 100, 200, 350, 600 mg) of activated carbon were added to 100 mL solutions containing 20 µg/L geosmin and 25 µg/L MIB in covered beakers and left for 3 hours. The solutions were mixed periodically. Three lots of 15 ml samples were taken from each solution, extracted using the standard extraction method and analysed using GC-MS.

This was repeated using 55, 100, 300, 550, 900 mg of activated carbon in 1000 mL of 200 ng/L geosmin and MIB in covered beakers and left for 3 hours. These were

mixed periodically. Three lots of 15 ml samples were taken from each solution, extracted using the standard extraction method and analysed using GC-FID.

3.5 HYDROGEN PEROXIDE TREATMENT

Different volumes of 33% v/v hydrogen peroxide (0.5, 2, 5, 10 mL) was added to 1000 mL of 200 ng/L geosmin and MIB and left to react for 5 hours. Three lots of 15 ml samples were taken from each solution, extracted using the standard extraction method and analysed using GC-FID.

3.6 UV TREATMENT

2L of 200 µg/L geosmin and MIB were prepared and passed through a Steriflo UV system (Contamination Control Ltd - now Davey Water Care Products) (Figure 3-4) at 5 L/min using a Johnson 800 GPH bilge pump (Figure 3-5) (Wholesale Industrial Supplies). Hold up volume in the system was 400 ml. Three lots of 15 ml samples were collected at 2, 3, 4, and 18 hours, extracted using the standard extraction method and analysed using GC-FID.

This experiment was repeated using different concentrations of hydrogen peroxide in bulk solution (0.5, 2, 5, 10 mL hydrogen peroxide to 2 L of solution). Again three lots of 15 ml samples were collected at 2, 3, 4, and 18 hours, extracted using the standard extraction method and analysed using GC-FID.

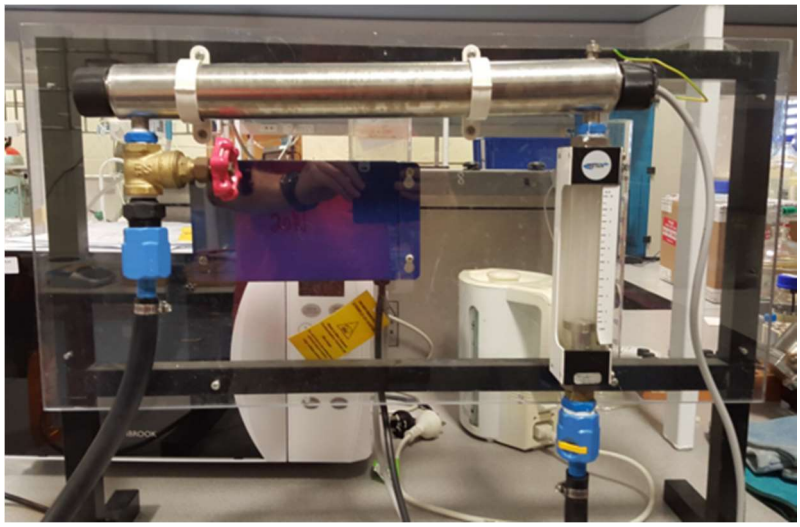

Figure 3-4-Steriflo UV system.

Figure 3-5-Johnson pump for UV system.

4 RESULTS AND DISCUSSION

4.1 MIB AND GEOSMIN RETENTION TIME

Two example GC spectra for MIB and geosmin are shown in Figure 4-1 and Figure 4-2. MIB has a retention time of 6.6 minutes (Figure 4-1) and geosmin has a retention time of 8.2 minutes (Figure 4-2). The peak at 4 minutes is methanol, which was used to dissolve the MIB and geosmin before dilution in the 100 ml volumetric flask.

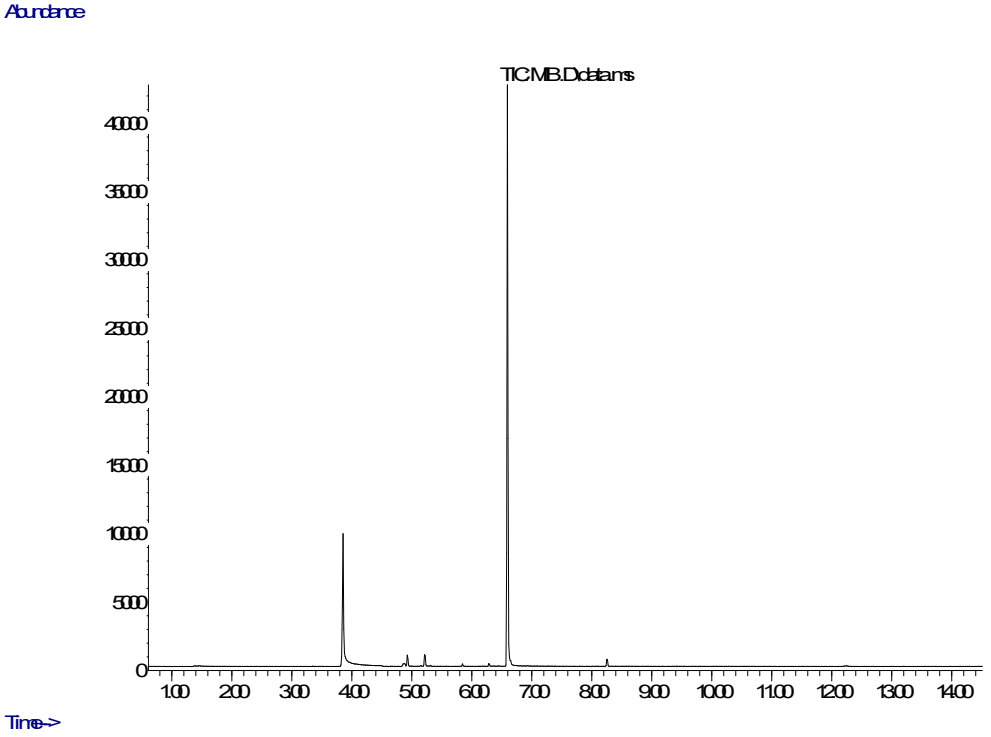

Figure 4-1-Example GC-MS spectrum for analytical grade MIB dissolved in methanol and water and extracted using SPME. The peak at 4 minutes is methanol and the peak at 6.6 minutes is MIB, minor peaks are contaminants.

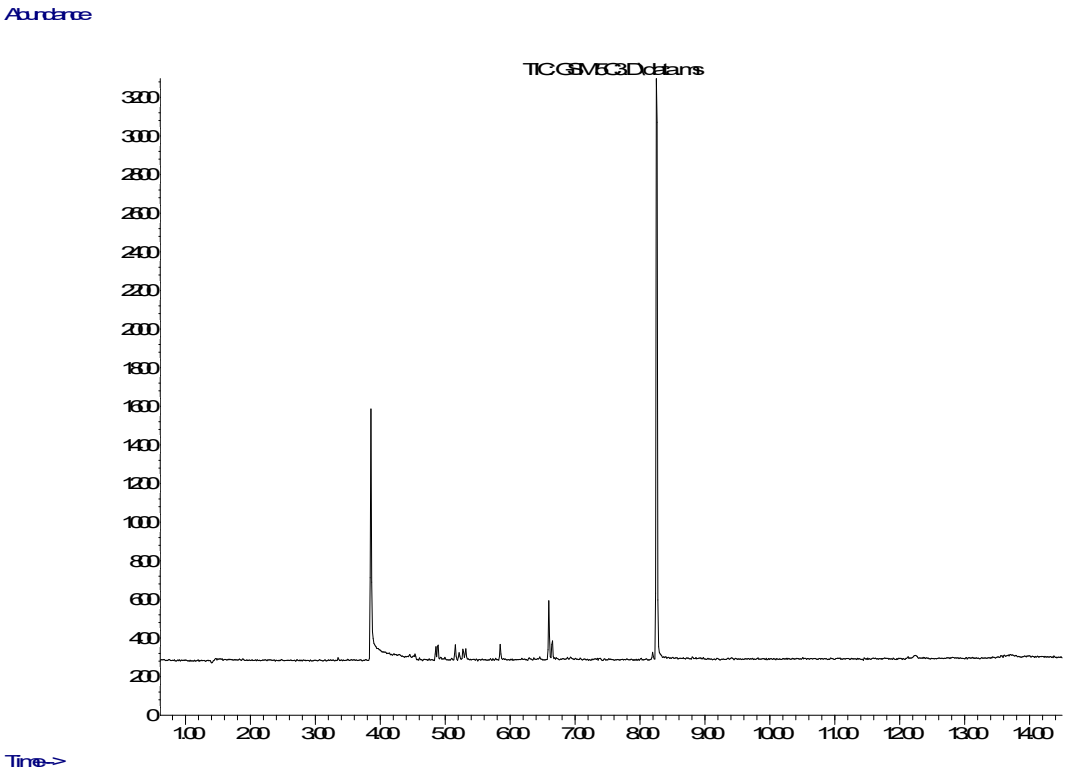

Figure 4-2-Example GC-MS spectrum for analytical grade geosmin dissolved in methanol and water and extracted using SPME. The peak at 4 minutes is methanol and the peak at 8.2 minutes is geosmin, minor peaks are contaminants, including MIB at 6.6 minutes.

4.2 METHOD REPRODUCIBILITY AND INTERNAL STANDARD

For each set of analysis, peak areas were averaged and standard deviations were calculated. These are shown as error bars in each of the subsequent graphs where peak area is on the Y axis of the graph. Standard deviations were typically small, less than 5% of the average value for most data, showing the method was highly reproducible. However, usually the first run of the day for GC-MS gave a large variation in results, so where a large variation was observed, extractions and GC runs were repeated and outliers omitted. GC-FID was very stable and gave more consistent results with standard deviations less than 3%.

Another effect noted was a general trend of GC-MS peak area decreasing for repeat analysis of samples. This could be due to the microfiber assembly heating up with repeated GC runs resulting in lower amounts of MIB or geosmin absorbing on to the microfiber. For example for a sample containing 25 µg/L MIB, resulting peak areas were 246239, 243976, and 233892 mAu.min. In this case the standard

deviation was only 2.7% of the average value. When the run was repeated the following day, the peak area had increased again, followed by a gradual trend down. It is also possible the decrease in GC-MS peak area could be due to the ionising filament responsible for bombarding molecules with electrons for MS gradually fouling, resulting in a loss of sensitivity. This has been reported by other users in online forums. This effect was not observed to the same degree with GC-FID, which was very stable and gave more consistent results with standard deviations less than 3%.

An internal standard was trialled for one set of extractions where naphthalene D8 (Watson et al, 1999) was used at the same concentration as geosmin and MIB. It was found that naphthalene absorbed in preference to geosmin and MIB, saturating the microfiber and appearing as a large peak exceeding the maximum detection limit for GC-MS. Geosmin and MIB could not be detected or appeared as very small peak. Furthermore, not all of the naphthalene D8 would be removed from the microfiber during the GC runs, with the naphthalene D8 peak appearing at slightly lower peak areas in the blank runs compared to the actual runs. Given that data obtained from extractions were highly reproducible, and using naphthalene D8 as an internal standard was not successful, attempts to use an internal standard were abandoned.

4.3 Effect of salt

Most research on taste, odour and VOC compounds from water sources add salt to the sample prior to headspace analysis, while other papers do not report whether or not salt was added. It was assumed that adding salt would act to drive the VOCs out of solution into the headspace. Therefore MIB and geosmin extractions were tried at different concentrations with and without salt to determine the effect of salt on extraction. Extractions with salt resulted in lower amounts of MIB and geosmin being absorbed onto the microfiber (Figure 4-3 and Figure 4-4), which was contradictory to what was expected. Therefore, this

experiment was repeated twice more to confirm the result, and the results showed the same trend each time.

MIB and geosmin can be associated with organic matter in raw water or trapped within microorganisms, so salt is normally added to reduce the interaction and lyse the microorganism cell walls, freeing the MIB and geosmin (e.g. Cortada and Canals, 2011). In addition, some enzymatic activity after cell lysis might also contribute to increases MIB and geosmin yields (e.g. Cortada and Canals, 2011). For the research in this thesis, pure MIB and geosmin was used, no other organic matter was present, therefore it is possible that instead of increasing MIB and geosmin recovery, salt was having a negative effect.

Upon further investigation of literature it was found that adding salt, which is non-volatile, to water increases the boiling point of water and reduces the vapour pressure of water and other volatile compounds present, because the chemical potential of those compounds is reduced by dilution with the non-volatile compound, which is known as boiling point elevation (Chary, 2012) hence a lower amount of MIB and geosmin in the headspace and being absorbed onto the microfiber. Another possibility is that the increased ionic strength of the water forces the geosmin and MIB molecules to clump together as micelles with the hydroxyl group facing outwards to reduce their interaction with water, which would also reduce the amount entering the headspace and absorbing onto the microfiber. In both cases, salt and without salt, two minutes of extraction time was used, so it is possible that allowing a longer extraction might have increased the amount of geosmin and MIB that was absorbed, particularly if salt was slowing the rate of geosmin and MIB entering the headspace and absorbing onto the fibre. Some authors report using 30 minutes extraction time (Ma, 2007), but in the case of this research, this would have resulted in the sample cooling down, unless it was left in the heating block.

For the remainder of the experiments in this research, salt was not added to the sample vials for MIB and geosmin extraction.

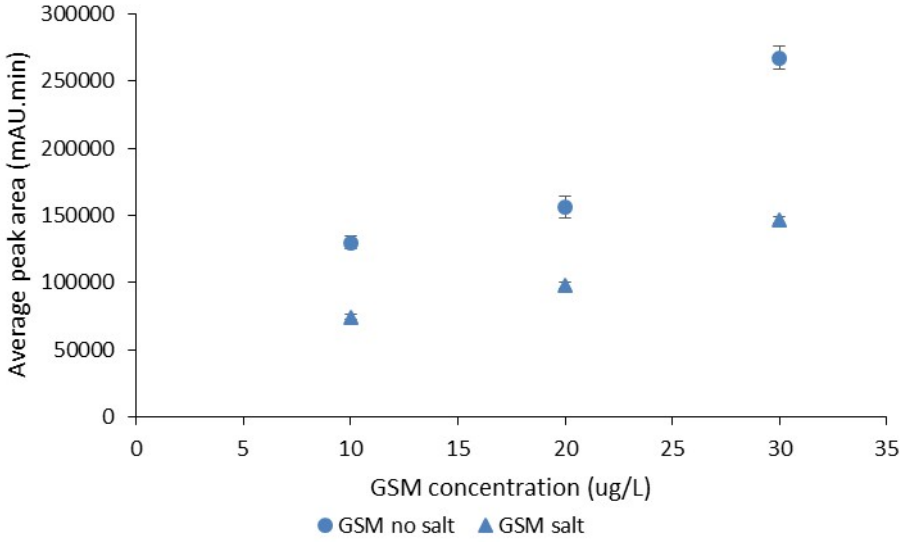

Figure 4-3-Comparison between peak area of extracted geosmin with salt and no salt.

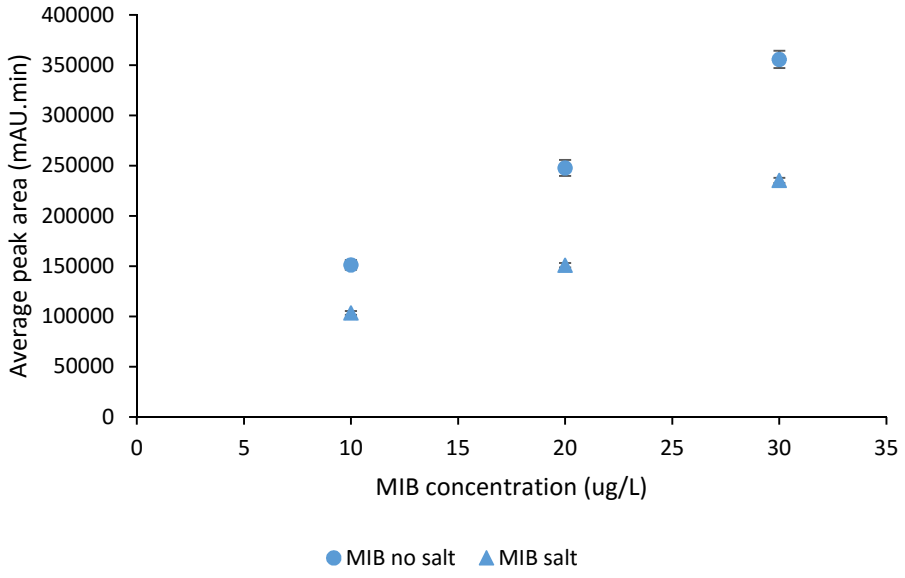

Figure 4-4-Comparison between peak area of extracted MIB with salt and no salt.

4.4 EFFECT OF HEATING TIME

The sample vials containing geosmin or MIB were pre-heated in the GC oven or heating block prior to carrying out microfiber extraction. The effect of heating time was explored by looking at the resulting GC peak area when 30 or 60 minutes heating time was used. In both cases, peak area increased, with geosmin showing

the greater increase, with the peak for 30 minutes heating time being 75% of the area as for 60 minutes heating time, while for MIB, the peak area was 90% (Figure 4-5). This is due to MIB diffusing through and volatising from solution at a greater rate than geosmin because MIB has a smaller molecular weight and greater vapour pressure (Table 4-1). MIB has a molecular weight of 168.28 g/mol and a vapour pressure of 6.68×10^{-5} atm while geosmin has a molecular weight of 182.3 g/mol and a vapour pressure of 5.49×10^{-5} atm. Some microfiber extraction methods use a stir-bar (Lambert and Mullett, 2005) to keep the solution agitated which would reduce the time it takes to reach equilibrium, but this was not possible for this work. Having the longer heating time would result in less samples being able to be processed in a day, so it was decided to use 30 minutes heating time.

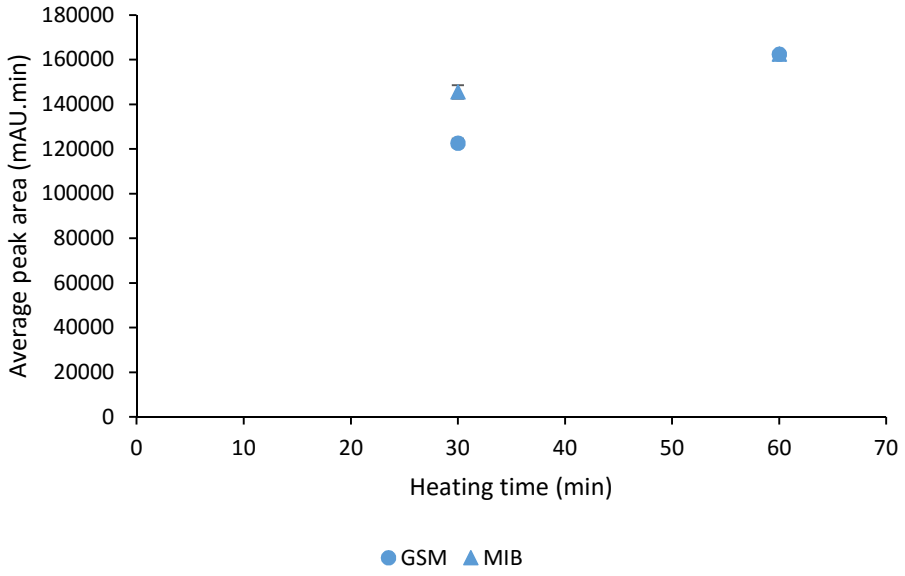

Figure 4-5-The relationship between peak area and heating time for MIB and geosmin extraction.

Table 4-1-MIB and geosmin properties.

	MIB	Geosmin
MW (g/mol)	168.3	182.3
Vapour pressure (atm)	6.68×10^{-5}	5.49×10^{-5}

4.5 EXTRACTION TIME

The effect of extraction time on GC peak area was investigated by leaving the microfiber in the headspace for 2, 5 and 10 minutes after the vial was pre-heated for 30 minutes. Peak area increased slightly with extraction time with geosmin reaching equilibration sooner than MIB (Figure 4-6), suggesting geosmin had a greater rate of absorption onto the microfiber than the rate of mass transfer from solution and appeared to plateau, while MIB was still increasing. Again, in the interest in reduced analysis time the 2 minute extraction time was used for subsequent MIB and geosmin analysis.

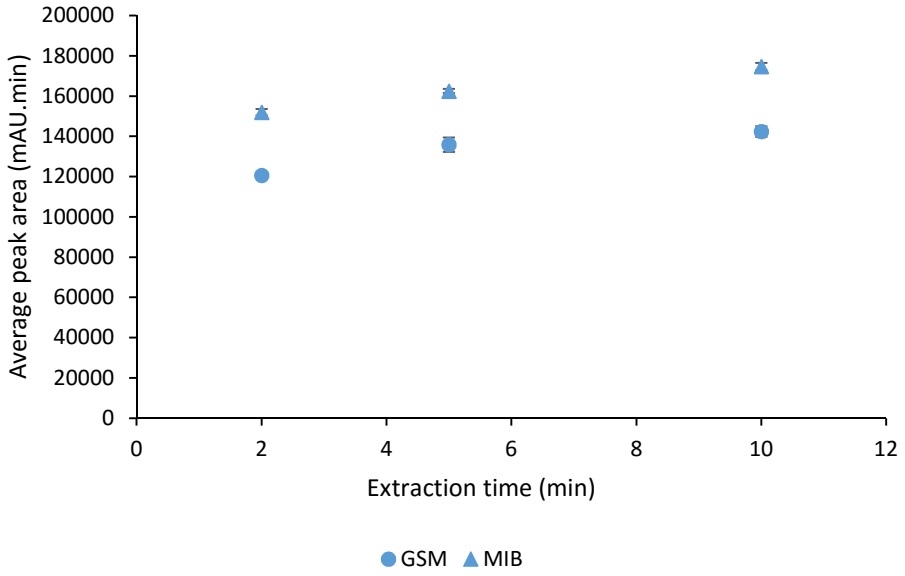

Figure 4-6-The effect of extraction time on average peak area for geosmin and MIB.

4.6 GC-MS CALIBRATION

After the initial method development, it was decided not to use salt in the microfiber extractions, set pre-heating to 30 minutes, and extraction time to 2 minutes. This was used for all subsequent analysis.

For quantifying the peak areas for MIB and geosmin, calibration curves were carried out, and equations fitted. Standard deviations for MIB were between 1.5 to 3.8 % of average and 1.7 to 7.6 % of average for geosmin. The geosmin curve did not trend towards zero, but flattened out at 110,000 mAu.min, suggesting

some background detection (Figure 4-7). Calibration curves for geosmin showed a good fit with an R^2 of 0.99. The MIB curve trended towards zero and R^2 was also 0.99 (Figure 4-8).

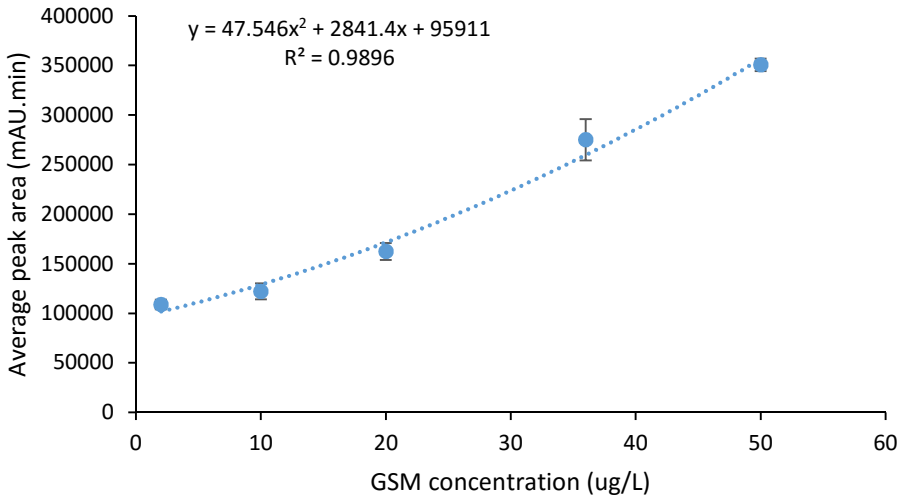

Figure 4-7-Relationship between concentration of geosmin and peak area in GC-MS.

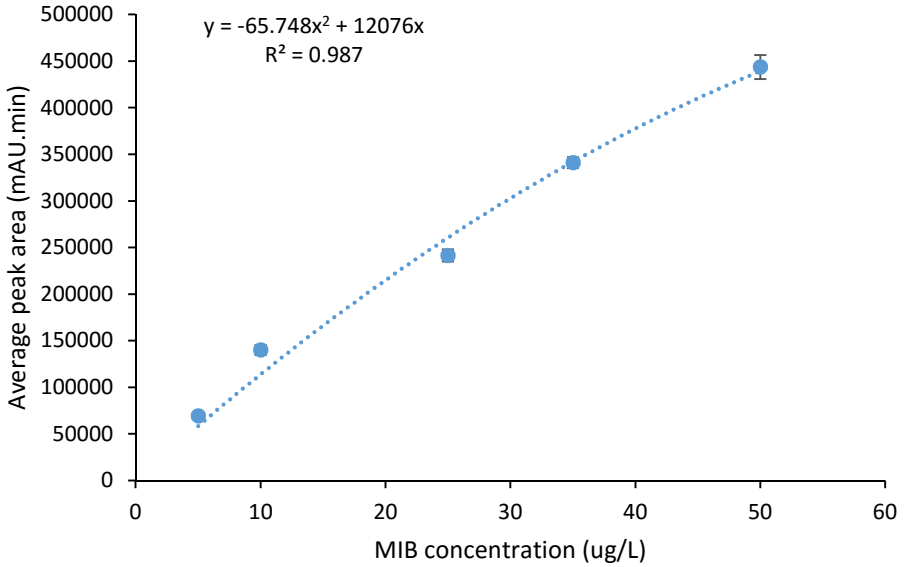

Figure 4-8-Relationship between concentration of MIB and peak area in GC-MS.

4.7 EFFECT OF GRANULAR ACTIVATED CARBON DETECTED BY GC-MS

After geosmin and MIB's calibration curves were completed, absorption of MIB and geosmin by activated carbon in 100 ml beakers were carried out to determine absorption parameters (Figure 4-9). The samples were analysed by GC-MS. Almost all of the geosmin was absorbed resulting in the peak areas not being able to be converted into concentrations because the calibration curve did not go below 100,000 at 2 µg/L (Figure 4-7). MIB was not as strongly absorbed, with around 80% of the MIB absorbed at 600 mg of activated carbon (Figure 4-9).

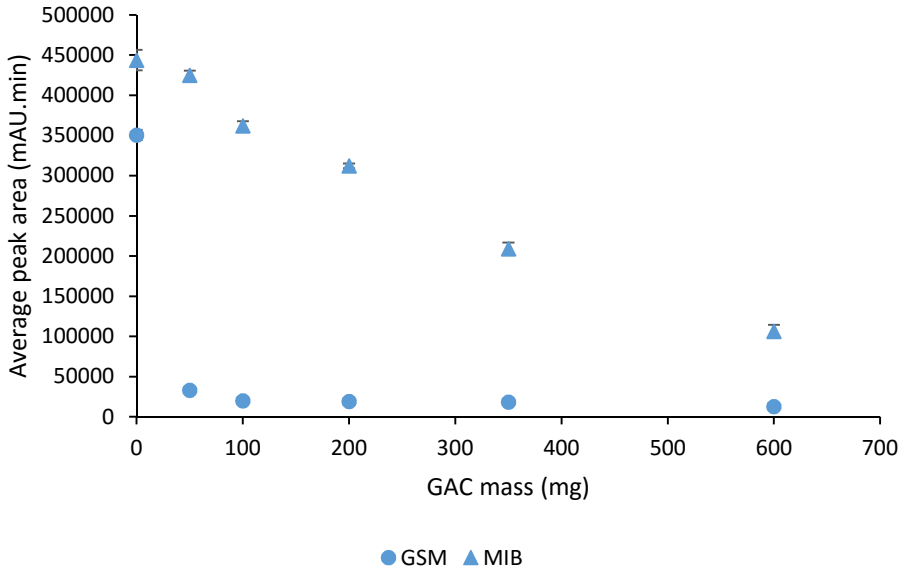

Figure 4-9-Effect of GAC on peak area of geosmin and MIB.

Given that the amount of geosmin was too low and the amount of activated carbon too high, to give data for isotherm curve fitting, it was decided to repeat this experiment with a greater volume of solution (1 L). In addition, due to the GC-MS not being stable, there being some issues with availability of equipment, but retention times being known for the column used, it was decided to change to GC-FID for analysis for the remainder of the experiments.

4.8 GC-FID CALIBRATION

For quantifying the peak areas from GC-FID for MIB and geosmin, calibration curves were carried out, and equations fitted (Figure 4-10, Figure 4-11). Standard

deviations for geosmin were between 0.4 to 2.7 % of average and 0.3 to 3.5 % of average for MIB, much more consistent than for GC-MS. Both curves trended towards zero and R^2 were slightly better than for GC-MS calibration curves.

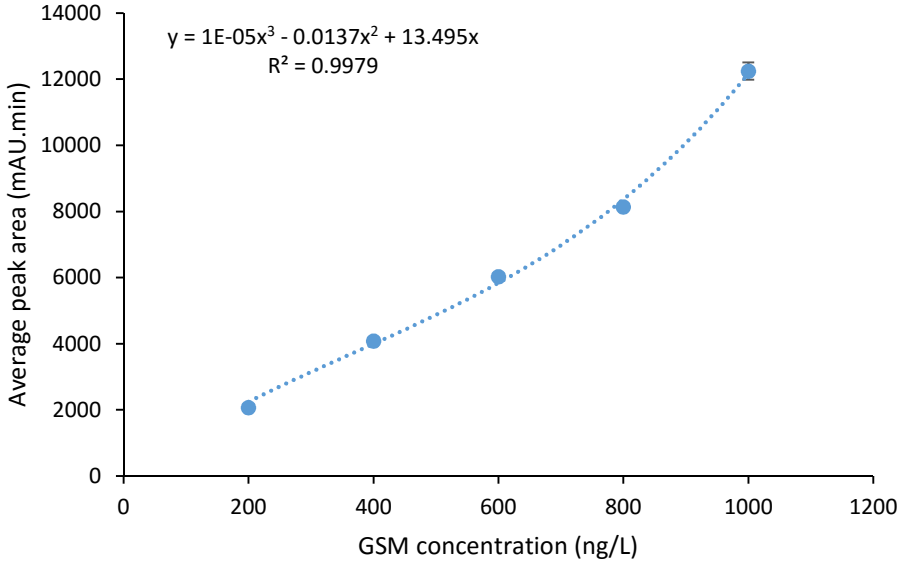

Figure 4-10-Calibration curve of geosmin in GC-FID.

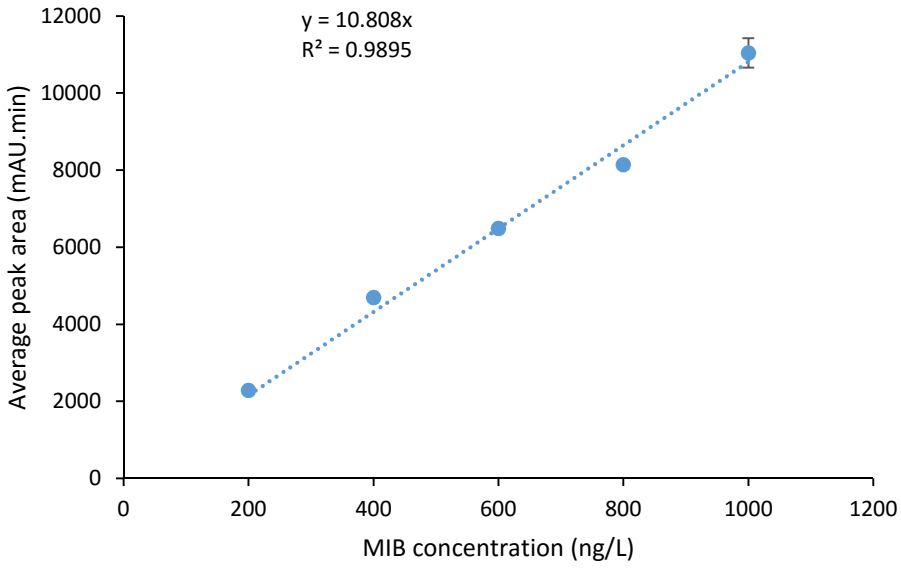

Figure 4-11-Calibration curve of MIB in GC-FID.

4.9 ACTIVATED CARBON ON GC-FID

The effect of activated carbon on geosmin and MIB concentrations and % removals are shown in Figure 4-12, Figure 4-13, and Figure 4-14. Standard deviations for peak area for geosmin were 1 to 7.3% of the peak area, the higher one for the very low geosmin concentrations, while for MIB, standard deviations were 1.2 to 5.4 % of average (Figure 4-12). In both cases, and as expected concentrations decreased and % removal increased with increasing activated carbon, with 96% removal for geosmin and 93% for MIB at 900 mg GAC in 1 L on solution.

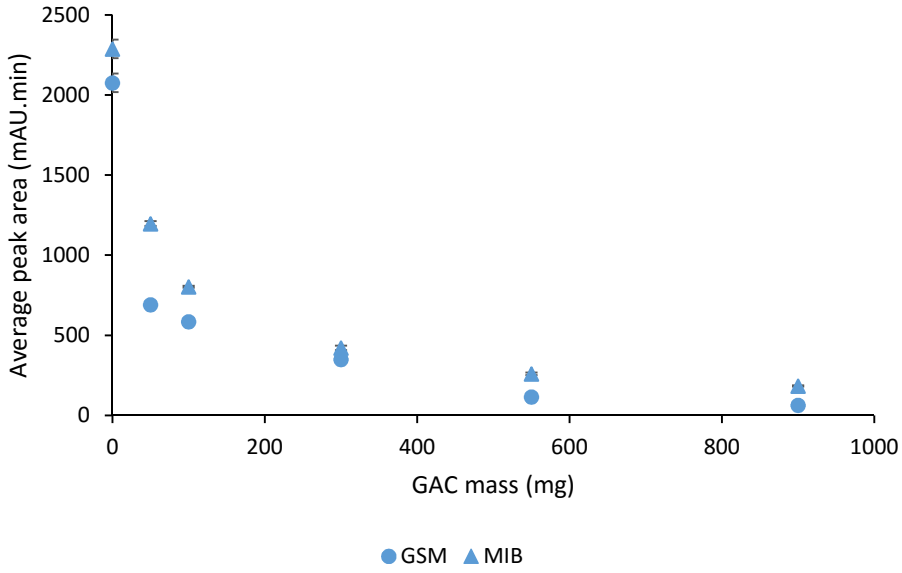

Figure 4-12-Effect of GAC on peak area.

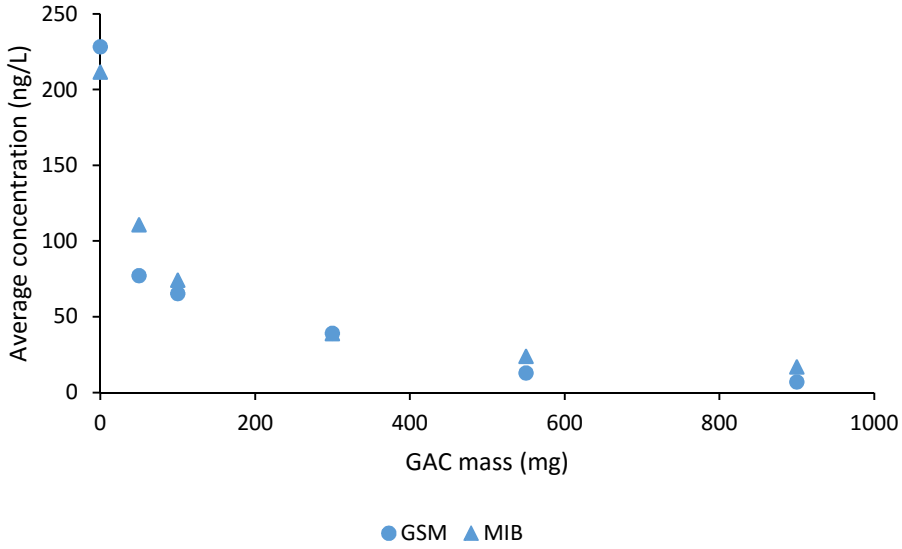

Figure 4-13-Effect of GAC on geosmin and MIB concentration.

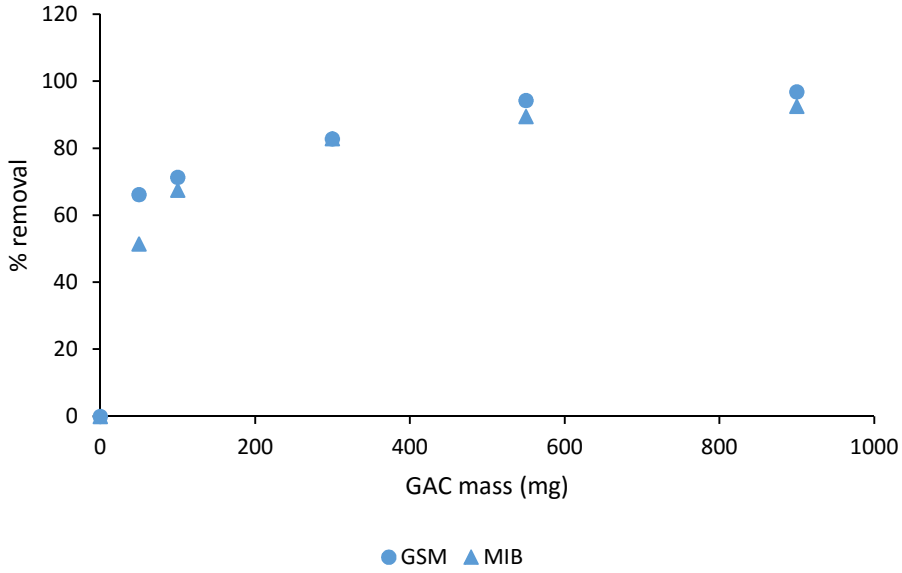

Figure 4-14-Effect of GAC on percentage removal for geosmin and MIB.

Based on final solution concentrations for MIB and geosmin, amount of these solutes absorbed onto the activated carbon were calculated based on mass difference. In both cases, absorbed concentration increased with increasing equilibrium concentration. Geosmin exhibits a type II isotherm suggesting monolayer absorption up to 30 ng/L followed by multilayer absorption (Figure 4-15). MIB shows an almost linear absorption isotherm. A similar response was

observed by Ma (2007) for MIB and powdered activated carbon, although the absorbed values were much lower at around 75 ng/mg at 100 ng/L.

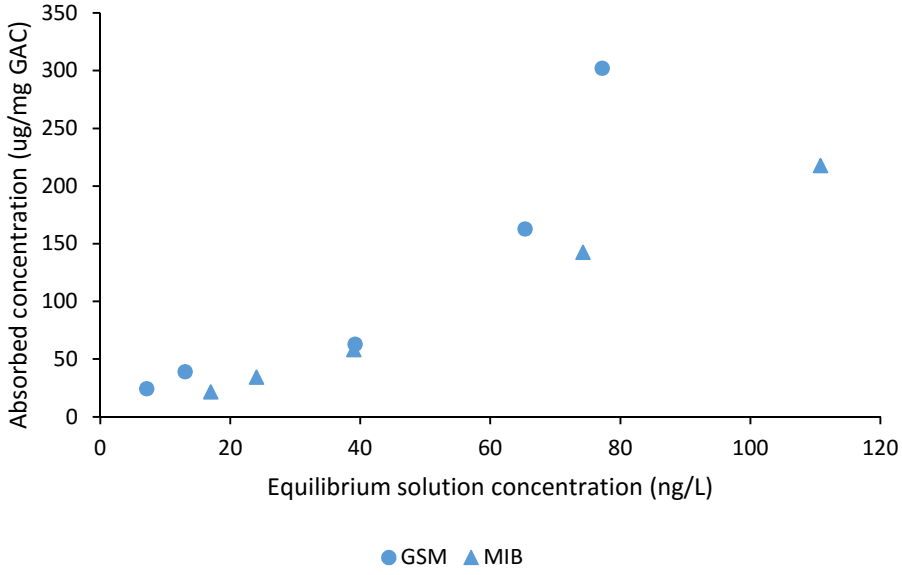

Figure 4-15-Absorption isotherm of GAC for geosmin and MIB.

The absorption isotherms were modelled using the Langmuir-Freundlich and Freundlich equations, given by

$$C_{GAC}^{*} = \frac{KC^{*n}GACmax}{1 + KC^{*n}}$$

$$C_{GAC}^{*} = KC^{*n}$$

Where C_{GAC}^{*} is the concentration of MIB or geosmin on the granular activated carbon at equilibrium, K is the equilibrium coefficient, $GACmax$ is the saturation concentration of MIB or geosmin, C^{*} is the solution concentration at equilibrium, and n is the Freundlich parameter. Units and fitted parameters are given in Table 4-2. Parameters were obtained by using Excel Solver to fit the model to the experimental data by reducing the sum of square errors (SSE). Comparison of model curves and experimental data are shown in Figure 4-16 and Figure 4-17. Both models fitted the MIB curves well, with low SSE's (Table 4-2), but the model fits for geosmin were not as good. Another isotherm model like the BET isotherm might be more appropriate because that can fit type II isotherms, but that is

commonly used for gas absorption onto absorbent surfaces. GACmax appears to be too high at 1.9 mg geosmin per mg GAC and 3.5 mg MIB per mg GAC, which suggests that fully saturated GAC would be 60-80% by weight or more MIB or geosmin. This is an artefact of model fitting without being able to take the GAC close to saturation. Other papers report 0.4 to 0.6 ug/mg GAC.

Table 4-2-Langmuir-Freundlich and Freundlich model parameters and goodness of fit (SSE).

Langmuir Freundlich			Freundich		
Parameters	Geosmin	MIB	Parameters	Geosmin	MIB
K (ml/ug)	0.000038	0.000189	K (ug.ml/ng.mg)	0.0026	0.7602
GACmax (ug/mg)	1866	3481	n (-)	2.67	1.20
n (-)	1.93	1.25			
SSE	4397	57	SSE	2841	71

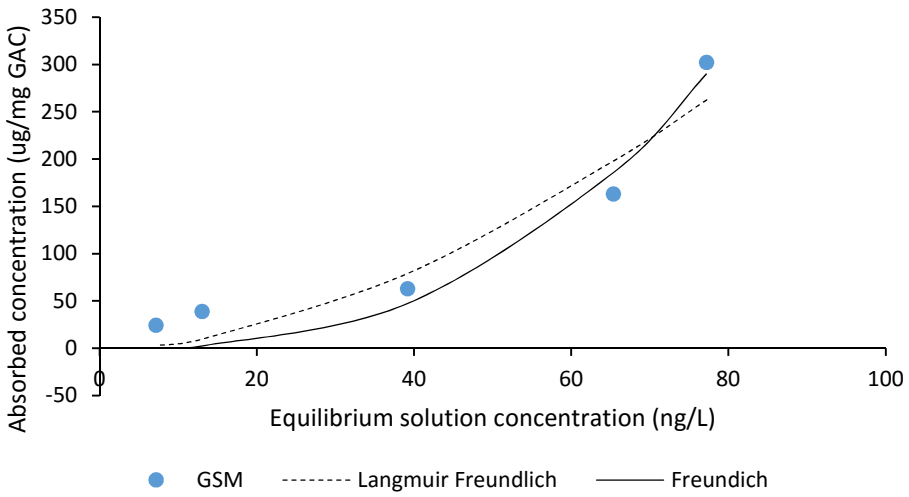

Figure 4-16-Isothermal of granular activated carbon for adsorption of geosmin.

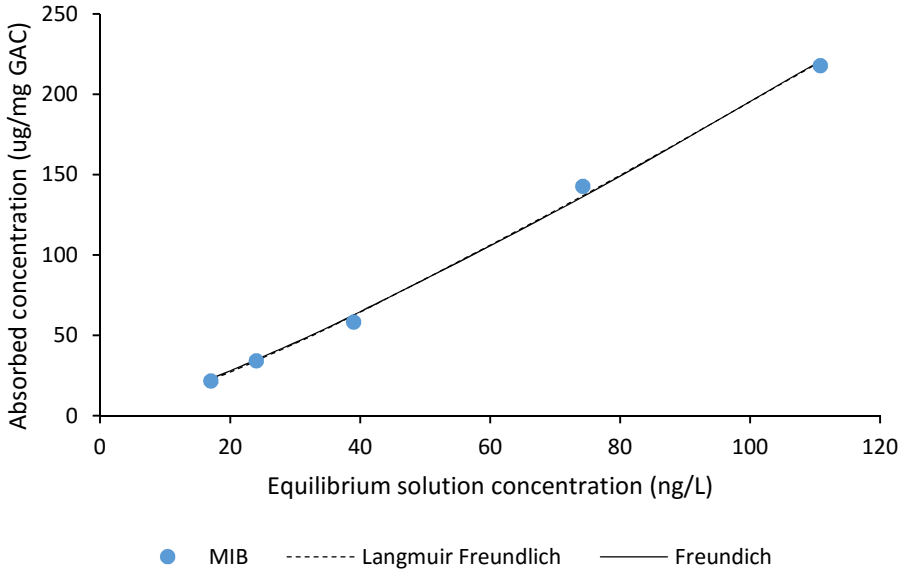

Figure 4-17-Isothermal of granular activated carbon for adsorption of MIB.

4.10 UV LIGHT TREATMENT

The effect of UV light on geosmin and MIB concentrations was explored by recirculating solutions containing geosmin and MIB through a Steriflo UV system and collecting samples. Peak area, concentration and % removal are shown in Figure 4-19, Figure 4-20 and Figure 4-21. Standard deviations for geosmin were 1.5 to 2.4 % of the average peak area, while for MIB, standard deviations were 0.4 to 3.2 % (Figure 4-12).

MIB was not as susceptible to UV light degradation compared to geosmin, with only 31 % removal at 4 hours while geosmin had 76 % removal. At 18 hours, geosmin had 84 % removal while MIB was only 66 %. From Figure 4-18, it can be seen that MIB and geosmin have very low molar absorption coefficients at 254 nm, but geosmin has a slightly higher coefficient than MIB.

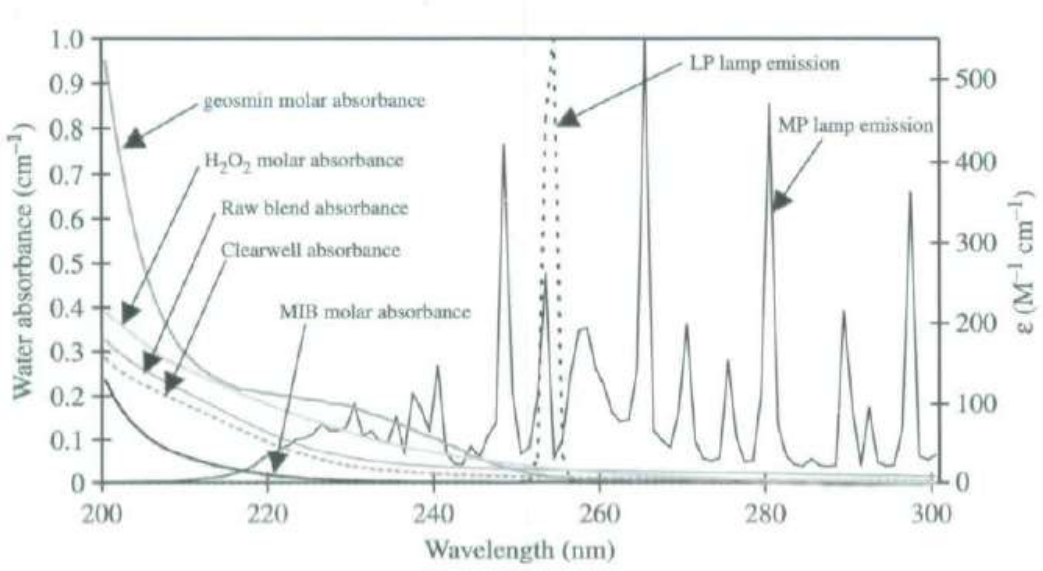

Figure 4-18-Geosmin and MIB absorbence at different wavelengths (Rosenfeldt et al 2005).

Hyun-Jo (2008) reported only 20% removal of MIB and geosmin with a UV dose of 1200 mJ/cm^2. Normally UV is calculated using an iodide/iodate actinometer (Hyun-Jo 2008), but this was not available for this research. Instead, UV dose from the Steriflo system was estimated based on the rated power (35 watts), efficiency (30% conversion to UV light) (Schalk, 2005), and transmittance of the quartz cyclinder (90%) (Schalk et al 2005), and surface area of the lamp (0.02 m^2), and exposure time of solution in the reactor (0.2 of the total running time because the UV reactor had an open volume of 400 ml and 1600 ml of solution was in the bucket). Distilled water was used, so 100% transmittance was assumed for water and there was no interfering solutes. For one hour exposure time, the UV dose was estimated to be 327 J/cm^2. To achieve the same dose as was applied by Hyun-Jo (2008), an exposure time of 13 seconds would have been required, the equivalent of 3 runs through UV reactor given a residence time of 4.8 seconds at 5 L/min. To confirm the actual UV dose from the Steriflo system, it is recommended that a iodide/iodate actinometer be used in the future.

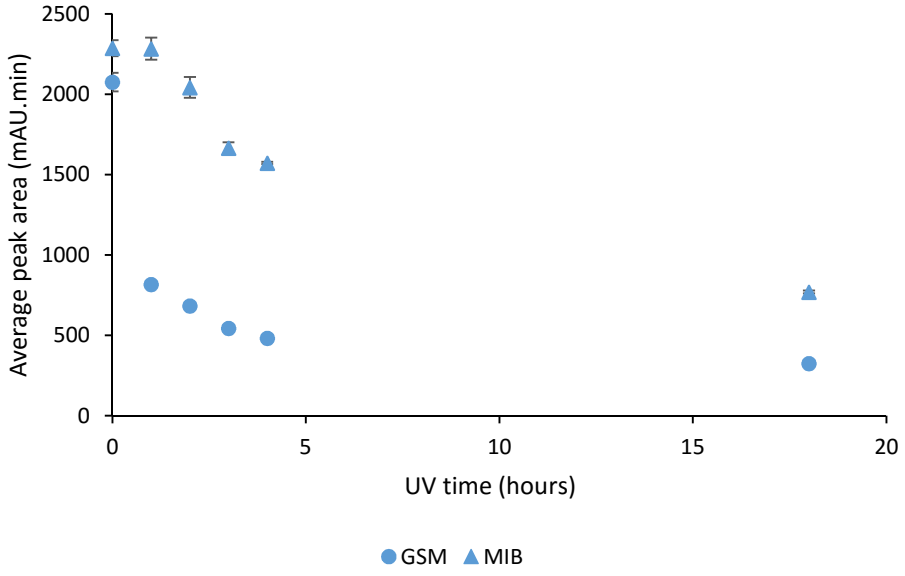

Figure 4-19-Relationship between UV light time and Peak area of geosmin and MIB.

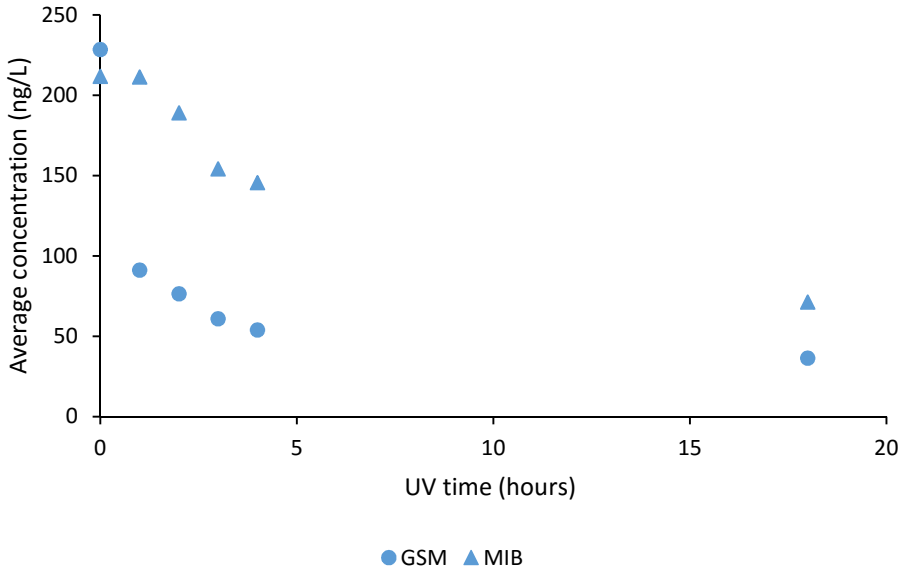

Figure 4-20-Relationship between UV light time and concentration of geosmin and MIB.

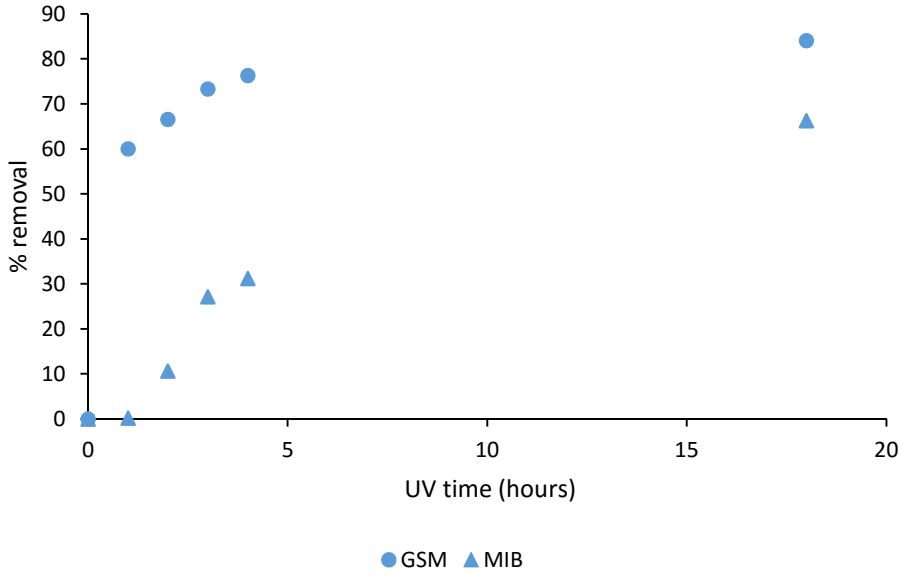

Figure 4-21-Relationship between UV light time and removal percentage of geosmin and MIB.

4.11 Effect of H_2O_2 on MIB and geosmin

The effect of H_2O_2 on geosmin and MIB concentrations was explored by adding H_2O_2 to solutions containing geosmin and MIB and leaving them to react over 3 hours, after which samples were collected. Peak area, concentration and % removal are shown in Figure 4-22, Figure 4-23, Figure 4-24. Standard deviations for geosmin were 1 to 3.2% of the average peak area, while for MIB, standard deviations were 1.2 to 3.3 % (Figure 4-22). Removal was 84 % for geosmin and 49 % for MIB at 10 ml of H_2O_2 in 1 L of solution.

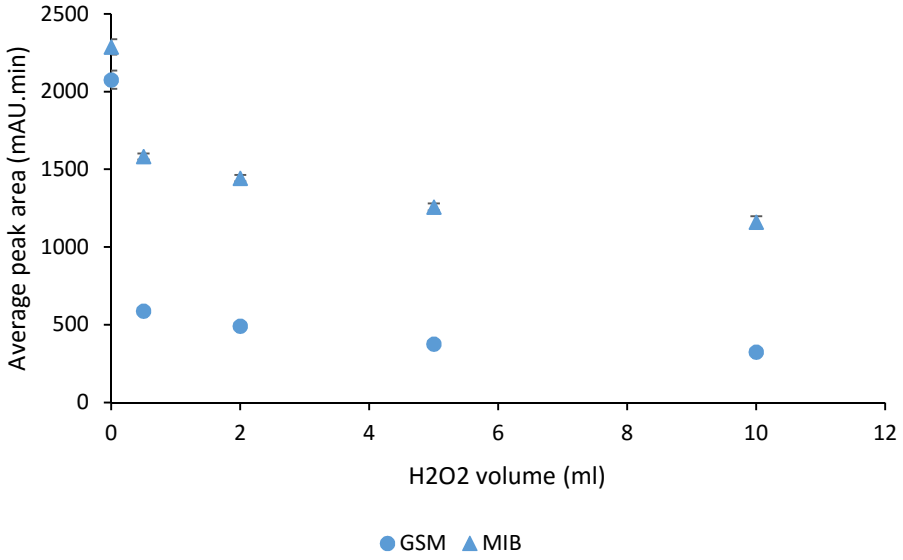

Figure 4-22-Relationship between H_2O_2 volume and peak area geosmin and MIB.

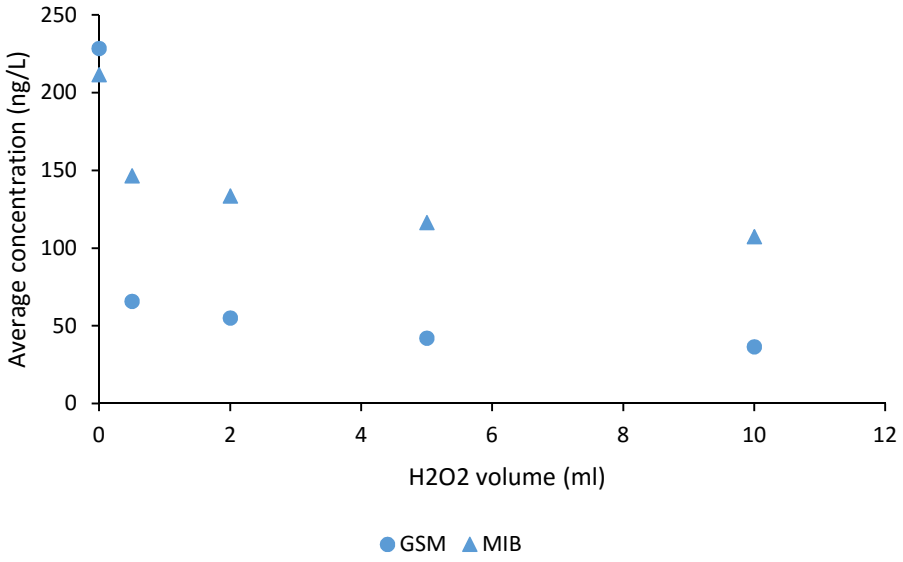

Figure 4-23-Relationship between H_2O_2 volume and concentration of geosmin and MIB.

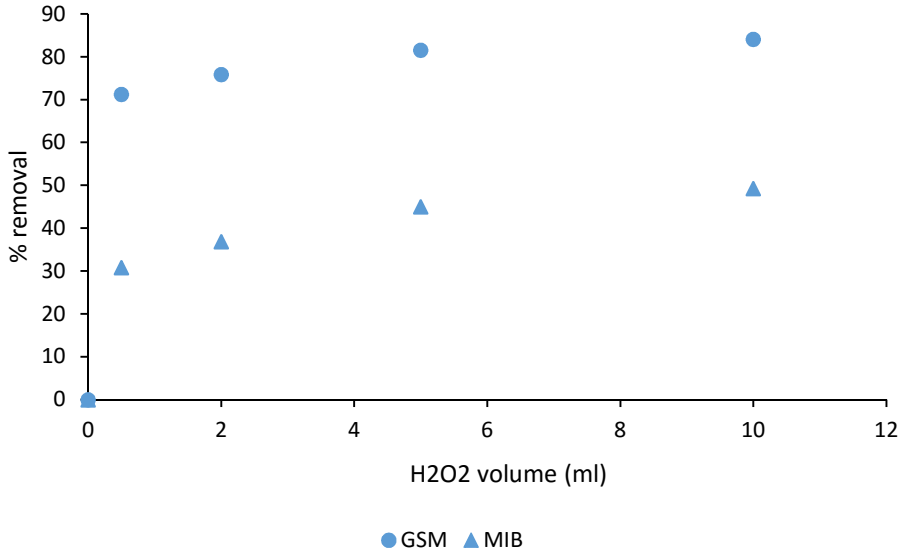

Figure 4-24-Relationship between H_2O_2 volume and removal percentage of geosmin and MIB

While it was not possible to find papers which had used hydrogen peroxide as an oxidant in isolation (most used hydrogen peroxide with ozone or UV in combination (Rosenfeldt, 2005; Hyun Jo, 2002), one patent did report 50% removal for geosmin and 72% removal for MIB using hydrogen peroxide (Table 4-3) (Robinson et al 2009). This was contradictory to the findings in this thesis, which found geosmin easier to remove. Current research is focusing on MIB removal because it is more difficult to remove than geosmin (Ma, 2007, Hyun Jo, 2008).

Table 4-3 - Effect of different treatment methods on removal of geosmin and MIB (Robinson et al, 2009).

Treatment	**Feed Rate (mg/L)**	**Removal (%)**	
		Geosmin	***MIB***
Powdered activated carbon	10	40	62
Powdered activated carbon	25	52	65
Potassium permanganate	0.8	42	28
Chlorine	2	45	33
Hydrogen peroxide	1	50	72
Ozone	2.5	94	77
Ozone and hydrogen peroxide	2.5	97	95

4.12 COMBINATION OF H_2O_2 AND UV

Seeing as either using H_2O_2 or UV was not very effective in removing geosmin and MIB, a series of experiments was carried out using a combination of H_2O_2 and UV. Peak area, concentration and % removal for geosmin are shown in Figure 4-25, Figure 4-26, Figure 4-24 and MIB in Figure 4-28, Figure 4-29 and Figure 4-30. Standard deviations for geosmin were 0.4 to 8 % of the average peak area, while for MIB, standard deviations were 0.3 to 3.1 % (Figure 4-22). Removal was more rapid with increasing H2O2 content from 60% after 1 hour to 73% with 10 ml of H_2O_2 in 1 L of solution for geosmin and for MIB it increased from 1% to 57% after 1 hour. In both cases 90% removal was achieved after 18 hours. Hyun-Jo (2008) achieved 90% removal for geosmin and 65% removal for MIB with a UV dose of 1200 mJ/cm^2 and 6 mg/L H_2O_2. In Hyun-Jo's research, a Rayonet RPR-100 photochemical batch reactor was used, but exposure time was not mentioned. For this research, to achieve the equivalent radiation dose, 15 seconds in the Steriflo would have been needed, but it is clear from the data that it would have taken much longer using the Steriflo to achieve a similar removal. In addition, this research used 1.9 g/L H_2O_2 which was much higher than that used in Hyun-Jo's research. Further work would be needed to examine why the Steriflo was not as effective as batch systems.

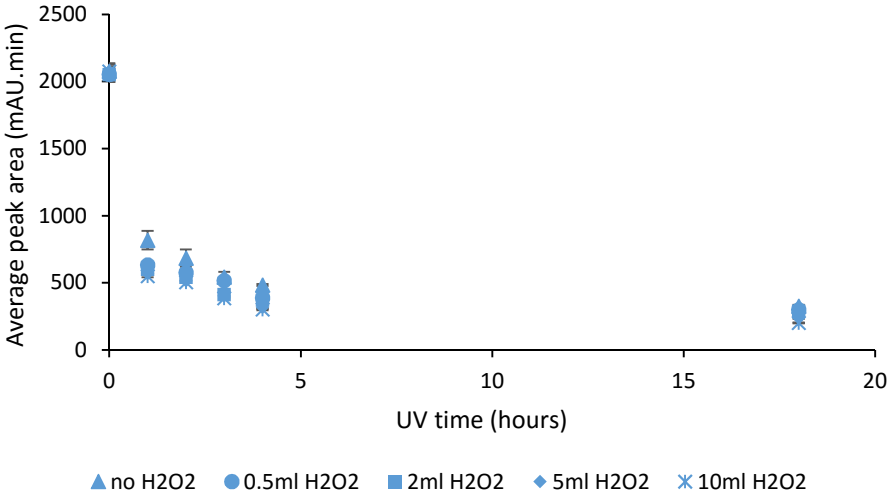

Figure 4-25-Relationship between UV light time with H_2O_2 supply and peak area geosmin.

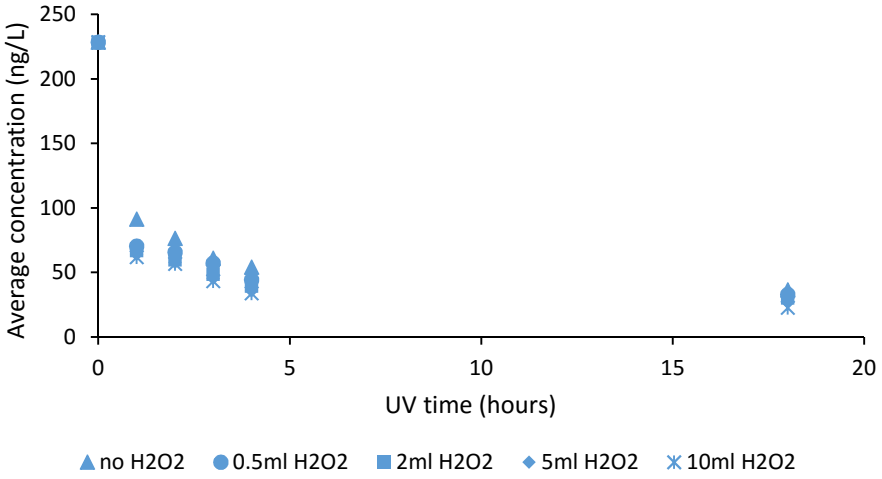

Figure 4-26-Relationship between UV light time with H_2O_2 supply and concentration of geosmin.

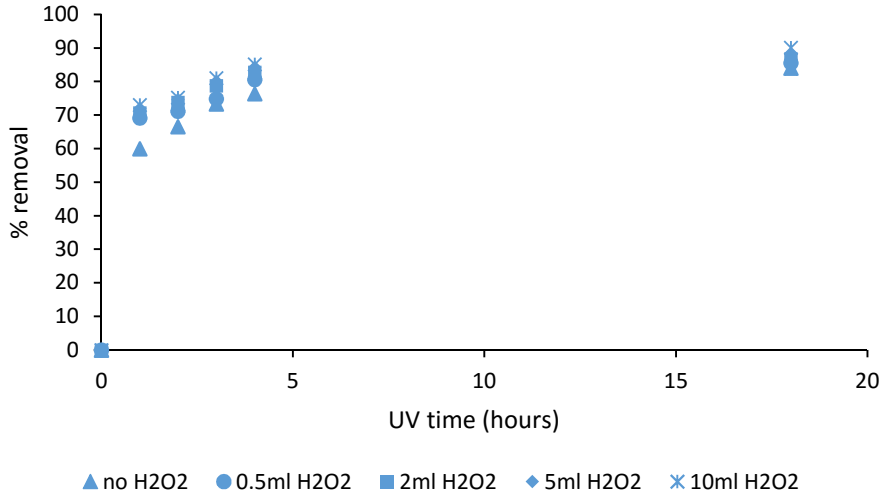

Figure 4-27-Relationship between UV light time with H_2O_2 supply and removal percentage of geosmin.

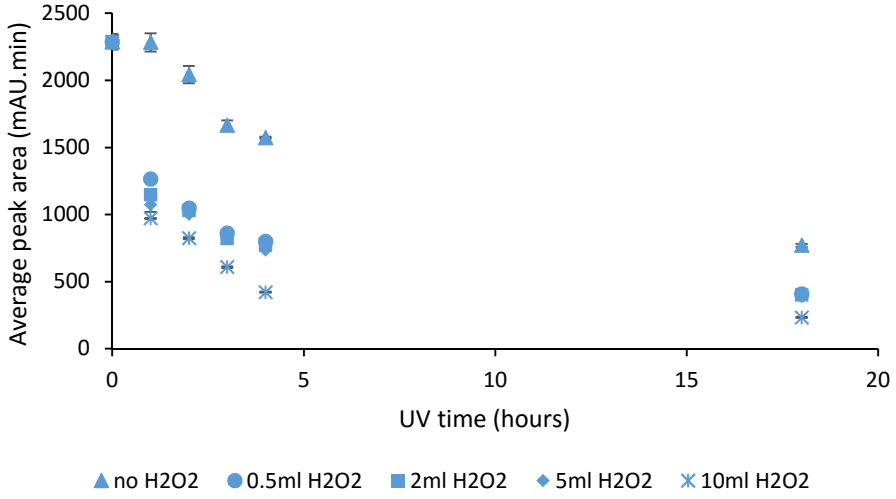

Figure 4-28-Relationship between UV light time with H_2O_2 supply and peak area of MIB.

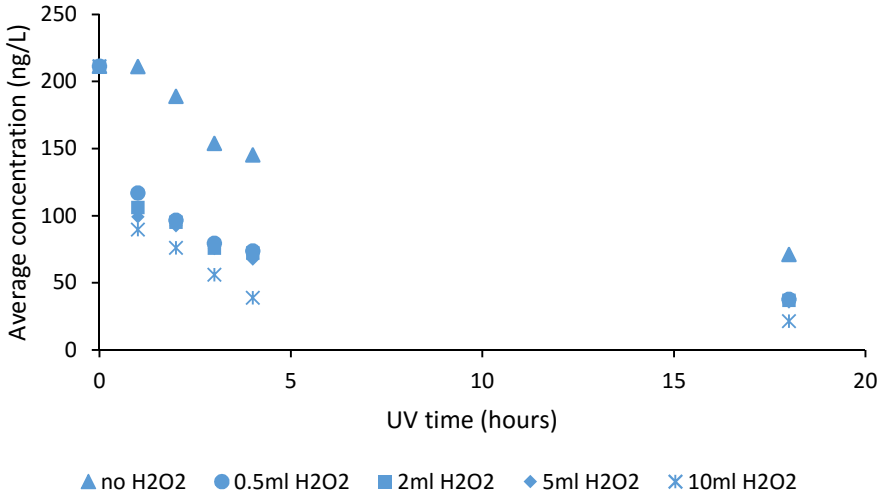

Figure 4-29-Relationship between UV light time with H_2O_2 supply and concentration of MIB.

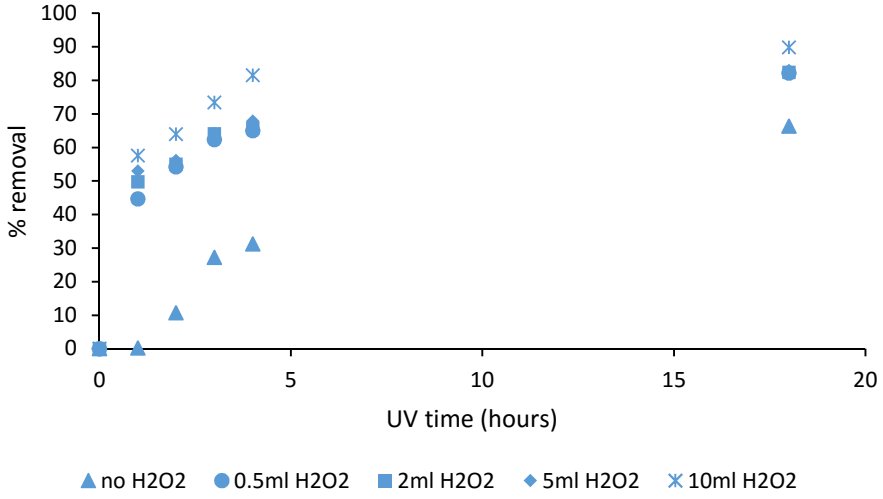

Figure 4-30-Relationship between UV light time with H_2O_2 supply and removal percentage of MIB.

To model the combined effect of UV light and hydrogen peroxide on geosmin and MIB, a simple model was developed, based on work by Hyun Jo (2008). This assumed that the bucket and the UV reactor were well mixed tanks, where water was circulated from the bucket to the UV lamp and back to the bucket. Volatilisation of MIB and geosmin was neglected (although future work should

examine rate of MIB and geosmin loss). The model also neglected the effect of partially oxidised compounds on rate of geosmin and MIB degradation.

The change in geosmin or MIB concentration (C_1) (ng/L) in the bucket with time t (min) is given by

$$\frac{dC_1}{dt} = \frac{Q(C_{in1} - C_{out1})}{V_1}$$

Where Q is flowrate in L/min, C_{in1} is the concentration of geosmin or MIB going into the bucket from the UV lamp, C_{out1} is the concentration of geosmin or MIB going out of the bucket into the UV lamp, and V_1 is the volume of the bucket.

Change in geosmin or MIB concentration (C_2) (ng/L) in the UV lamp with time t (min) is given by

$$\frac{dC_2}{dt} = \frac{Q(C_{out1} - C_{in1})}{V_2} - k_1 E {C_2}^{n_1} - k_2 E {C_2}^{n_2} C_{H2O2}$$

where k_1 is rate of geomsin or MIB degradation by UV light (1/J), k_2 is the rate of geomsin or MIB degradation by the hydroxide radicals from hydrogen peroxide produced by UV light (1/J), E is the energy emitted by the UV lamp (J/min) which was estimated by:

$$E = 60 P \eta T$$

Where P is rated power of the UV lamp (Watts or J/s), η is efficiency of the lamp in converting electrical energy to UV light (approximately 0.3), and T is the transmittance of UV light through the quartz cyclinder around the UV lamp (approximately 0.9). This was multiplied by 60 to convert from J/s to J/min. n_1 and n_2 are adjustable parameters (dimensionless) for fitting the model in case the model is not first order, and C_{H2O2} is the concentration of hydrogen peroxide in solution (L hydrogen peroxide / L solution)

The model was solved using a finite difference solution using a change in time for each iteration equal to the volume of the UV reactor divided by the flowrate, which was then divided by a factor of 3. For 18 hours simulation time, a total of

40500 iterations were used. UV degradation parameters k_1 and n_1 were obtained by fitting the model to UV degradation data for experiments using no hydrogen peroxide, and hydroxide degradation parameters k_2 and n_2 were obtained by fitting the model to data for experiments using hydrogen peroxide. Goodness of fit was determined by calculating the sum of squared errors (SSE) ((experimental result - model result)^2) and Excel Solver was used to adjust the model parameters to reduce SSE. Model parameters used are shown in Table 4-4, SSE results are shown in Table 4-5 and individual graphs in in Figure 4-31 and Figure 4-32.

Table 4-4-Model parameters used to simulate geosmin and MIB degradation.

Parameters	Geosmin	MIB
Bucket volume, V1 (L)	1.6	1.6
UV reactor volume, V2 (L)	0.4	0.4
UV rated power, P (Watts)	35	35
UV lamp efficiency (-)	0.3	0.3
UV lamp transmittance (-)	0.9	0.9
Lamp energy emitted as UV, E (J/min)	567	567
Flowrate (L/min)	5	5
Reactor residence time (min)	0.08	0.08
Division factor for change in time calculation (-)	3	3
Change in time (min)	0.027	0.027
Model run time (hr)	18	18
Time steps (-)	40500	40500
k1 (1/J)	7.07E-10	1.80E-10
n1 (-)	3.47	3.20
k2 (1/J)	6.69E-09	9.48E-06
n2 (-)	5.65	3.87
Starting concentration (ng/L)	228.4	211.6

Table 4-5-SSE of geosmin and MIB with different volume of H_2O_2.

H_2O_2 (ml)	SSE	
	Geosmin	MIB
0	63	1450
0.5	630	4103
2	706	88
5	569	1308
10	421	1032

Rate of degradation by UV light, k_1 was 7 times greater for geosmin than for MIB (Table 4-4), explaining the low % removal. With the addition of H_2O_2, it appears that MIB is more susceptible to hydroxide induced degradation than geosmin, because the k_2 value for MIB was over 1000 times greater than for geosmin. The adjustment factor n_2 for geosmin was greater than that for MIB which would steepen the initial slope of the geosmin curve. Goodness of fit was better for geosmin in almost all cases with SSEs being lower (Table 4-5). Comparisons of model curves to experimental data for all conditions are shown in Figure 4-31 and Figure 4-32.

A bad fit was achieved for MIB with 0.5 ml H_2O_2, because the model underestimated the extent of degradation. This set of experimental results would need to be repeated to see if the result was reproducible. The fit could be improved by individually fitting the model to each set of data and obtaining separate k and n parameters, but then this would not serve the purpose of having one set of parameters to model an entire set of conditions.

While predicting overall trends, the model does not predict the odd shaped curve between 1 hour and 4 hours UV exposure shown in Figure 4-31 and Figure 4-32. This would also need to be investigated further. Furthermore, to accurately predict what happens in the early stages, more data would need to be collected in the first hour, but this would also increase the amount of GC analysis required.

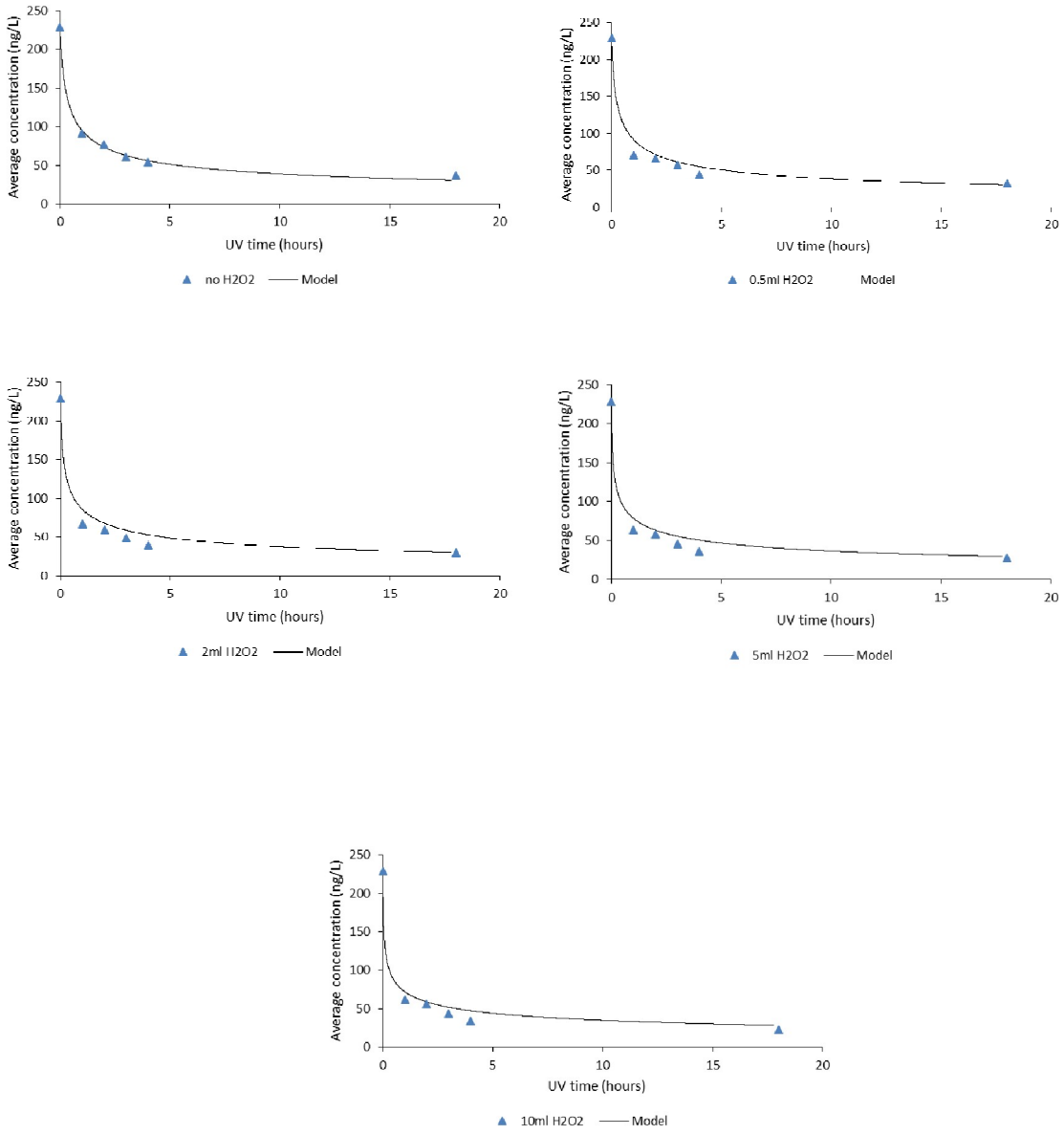

Figure 4-31-Degradation of UV with different volume of H_2O_2 for geosmin.

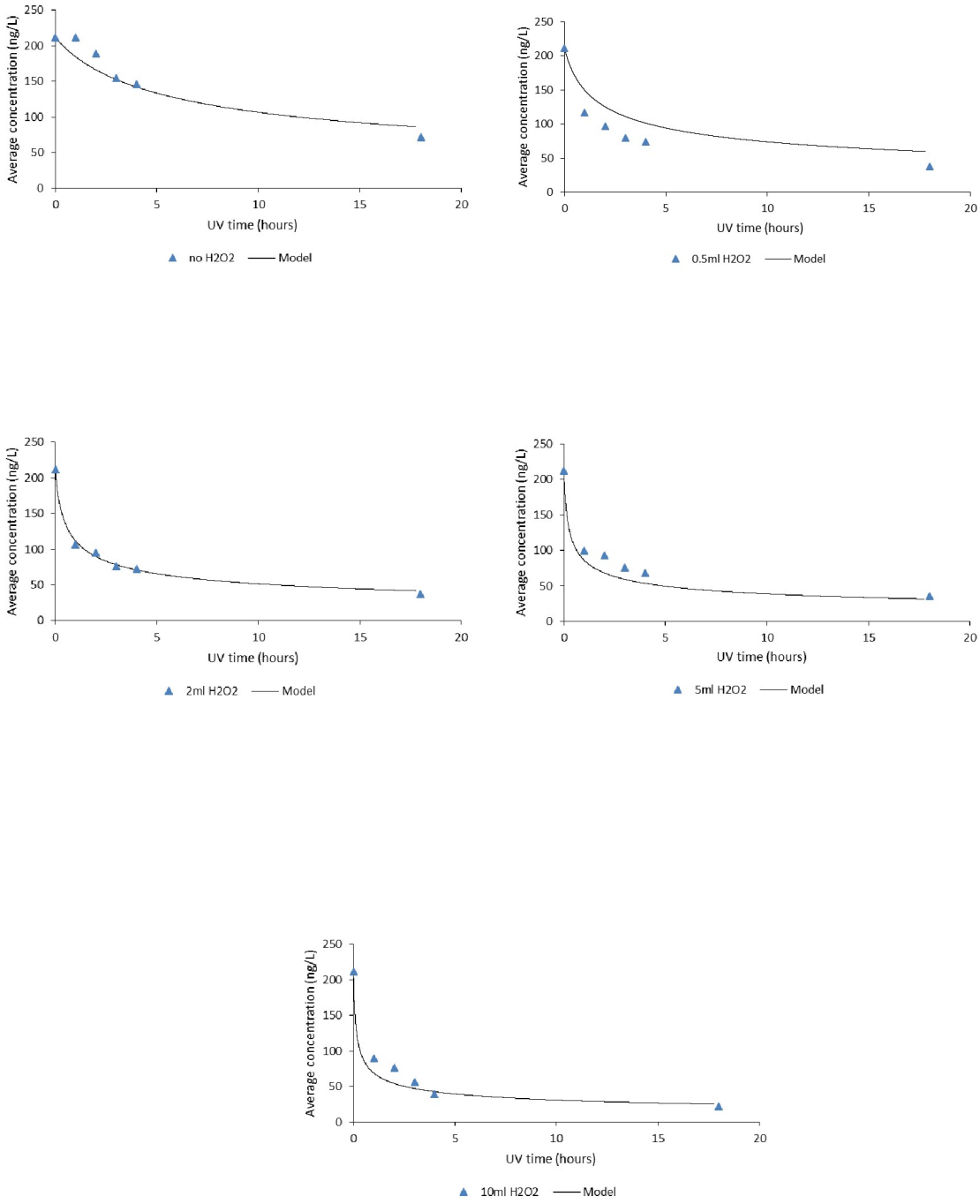

Figure 4-32-Degradation of UV with different volume of H_2O_2 for MIB.

5 CONCLUSION AND RECOMMENDATIONS

5.1 GC METHOD DEVELOPMENT

Headspace solid phase micro fibre extraction was used to extract geosmin and MIB from samples for analysis in GC-MS and GC-FID. This method was very reliable with standard deviations typically being less than 5% of the average peak area obtained from the GC. GC-FID typically showed lower standard deviations of less than 4% of average peak area.

Using napthalene D8 as an internal standard GC analysis was not successful as it bound preferentially to the microfiber and was unable to be removed with subsequent GC injections.

Headspace extractions where geosmin and MIB samples had salt added gave up to 40% lower GC peak areas compared to samples without salt, therefore salt was not used for subsequent analysis.

Increasing sample heating time increased GC peak area, and therefore potential to analyse very low concentrations of geosmin or MIB, but results in longer analysis time, so 30 minutes heating time was used for all analysis.

Increasing headspace extraction time also increased GC peak area, but 2 minutes extraction time was used as that gave peak areas 75% of when 10 minutes extraction time was used. Again, if greater GC sensitivity to low concentrations of MIB and geosmin is required, longer extraction times would be used.

GC-MS peak areas tended to decline during subsequent runs, possibly due to ionising filament fouling, therefore using an internal standard would be useful to correct for this, but the decline did not significantly affect results. GC-FID did not show the same trend because it used a different detector for measuring compounds.

5.2 GEOSMIN AND MIB REMOVAL

Activated carbon was effective at removing geosmin and MIB, with 500 mg GAC per L removing 90% of the geosmin and MIB. Geosmin absorption showed a type II isotherm suggesting monolayer followed by multilayer absorption, while MIB absorption was almost linear. Langmuir-Freundlich and Freundlich isotherms fitted the MIB data well but not as well for geosmin. An isotherm model similar to the BET isotherm would fit the geosmin model data better.

Oxidative treatment using H_2O_2 removed 84 % of geosmin and 49 % of MIB at 10 ml of H_2O_2 in 1 L of solution. UV degradation of geosmin and MIB using the Steriflo system removed up to 31 % of MIB and 76 % of geosmin after 4 hours. After 18 hours, geosmin had 84 % removal while MIB was only 66 %. Addition of H_2O_2 increased removal for MIB and geosmin up to 89 and 90 % respectively after 18 hours. Experimental results could be readily modelled using a simple model that accounted for UV degradation and hydrogen peroxide degradation, using one set of parameters over a range of conditions for each of MIB and geosmin. Additional data would need to be collected for the first hour of treatment to verify the model.

5.3 RECOMMENDATIONS

UV and oxidative treatment was carried out using the Steriflo UV system on distilled water containing geosmin and MIB. This would need to be repeated using water containing organic matter or water with various turbidity and salts to explore the effect of these constituents on the % removal and model parameters. It would be useful to develop the model further to account for these effects

The Steriflo UV system also seems to not be as effective compared to batch reactors used by other researchers, even though the estimated UV dose far exceeded that used in the batch reactor systems, so this would need to be investigated further as to why this might be.

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