NOVEL TECHNIQUES FOR THE RECOVERY OF SULPHUR AS USEFUL PRODUCTS FROM AIR POLLUTANTS USING AEROBIC BIOFILTERS

A dissertation submitted for the degree of
Doctor of Philosophy,
Murdoch University, Western Australia, June 2015

Khondkar Ayaz Rabbani
Declaration

I declare that this thesis is my own account of my research and contains as its main content work that has not previously been submitted for a degree at any tertiary education institution

Name: Khondkar Ayaz Rabbani

Signature:

Date: June 29th, 2015
For Pappa and Amma
Abstract

Biofilters and biotrickling filters are popular for the removal of odorous pollutants like hydrogen sulphide and ammonia from gaseous emissions in wastewater treatment plants because of their low capital costs, low energy requirements and environmental performance. In an aerobic environment, the microbes in biofilters oxidize hydrogen sulphide to non-odorous sulphate. Despite several advantages over conventional chemical systems, one of the consequences of maintaining a suitable pH and moisture content for the microbes in the biofilter is the production of large volumes of weakly acidic leachate which needs to be treated or disposed safely. In this research, weakly acidic leachate was considered as a sulphur resource rather than a waste stream and strategies to utilise this resource were investigated.

A novel laboratory scale biofilter system removed hydrogen sulphide with a removal efficiency of 98.8% and produced small volumes (1 mL of solution/L of reactor/day) of sulphuric acid with concentrations greater than 6M after 150 days of continuous operation. This was achieved by compensating for the loss of moisture in the upflow biofilter by intermittently trickling a minimum amount of nutrient solution. This created a moisture and pH gradient within the biofilter resulting in an environment at the top for the bacterial conversion of hydrogen sulphide while sulphuric acid was accumulated at the base. The small volume of high concentration sulphuric acid is a more valuable resource than a large volume of weakly acidic leachate produced in conventional biofilters.
Simultaneous removal of hydrogen sulphide and ammonia in contaminated air can also be achieved by aerobic biofilters, with biological oxidation by microbes producing sulphate and nitrate in the leachate. A pilot scale biofilter was setup at a local wastewater treatment plant for the simultaneous removal of hydrogen sulphide and ammonia from gaseous emissions but instead of biological oxidation of both the pollutants, the sulphate produced from the biological conversion of hydrogen sulphide in a biofilter was allowed to accumulate in a concentrated form first. The ammonia was then subsequently removed, not by biological oxidation, but by the chemical reaction of ammonium ion with sulphate to form ammonium sulphate which was washed down and accumulated in the bottom. This biofilter, which had been in continuous operation for more than 150 days, removed both hydrogen sulphide and ammonia at an average removal efficiency of 91.96% and 100% respectively. Unlike conventional biofilters which convert hydrogen sulphide to sulphate and ammonia to nitrate, this biofilter produced a solution of ammonium sulphate which can be harvested for further use.

The novel techniques explored in this research provide an alternative to conventional biofilters that allows recovery of the sulphur as useful products rather than waste.
Acknowledgement

First I would like to express my sincere gratitude to my principal supervisor, Professor Goen Ho, for his scientific input, guidance and patience for the duration of my studies. His calm and rational approach towards the scientific challenges brought up in this study is one of the main lessons that I will take away from being his student. I wish to thank my co-supervisor Dr. Ralf Cord-Ruwisch for his unbridled enthusiasm for academic inquiry and his assistance. My sincere and warm thanks are due to Dr. Wipa Charles without whose calm, guiding hand and almost daily encouragement this thesis would not at all have been possible. I gratefully acknowledge the Australian Research Council (ARC) and Water Corporation for their stipend and financial support of this research. I would like to express special thanks to my partners in scientific endeavours at Murdoch University – Liang, Emily and Raphael for sharing countless laughs, sweats and tears. A special thank you also goes to Murray Lindau, Senior Worshkop technician and John Snowball, Senior Electronics Technician for their excellent assistance during different stages of this thesis. Last, but not the least, a huge and special appreciation goes to my wife and my daughter for their love, support and understanding during the many nights and days I have neglected them while working on this thesis.

K. Ayaz Rabbani
Perth, June, 2015
Secondary Publications

The following work is being submitted as a thesis by publications/manuscripts and the following papers have been submitted for publication from this research:

a) A manuscript titled “Recovery of sulphur from contaminated air in wastewater treatment plants by biofiltration – A critical review” based on Chapter 2 of this thesis, authored by K. A. Rabbani, W. Charles, R. Cord-Ruwisch and G. Ho has been accepted by the journal titled Reviews in Environmental Science and Bio/Technology (DOI: 10.1007/s11157-015-9367-5).

b) A manuscript titled “Pilot-Scale biofilter for the simultaneous removal of hydrogen sulphide and ammonia at a wastewater treatment plant” based on Chapter 5 of this thesis, authored by K. A. Rabbani, W. Charles, A. Kayaalp, R. Cord-Ruwisch, G. Ho has been accepted in the journal titled Biochemical Engineering Journal. (DOI: 10.1016/j.bej.2015.11.018)

c) A manuscript titled “Novel biofilter for the removal of H₂S and generation of concentrated sulphuric acid” based on Chapter 4 of this thesis, authored by K. A. Rabbani, W. Charles, A. Kayaalp, R. Cord-Ruwisch and G. Ho has been submitted to the journal titled Biotechnology and Bioengineering.
Contribution of others

The work presented in this thesis was primarily designed, executed and interpreted by K. A. Rabbani. Contributions by co-authors for each chapter are described below.

CHAPTER 2
The literature review and primary author of the manuscript was K. A. Rabbani while W. Charles, R. Cord-Ruwisch and G. Ho provided intellectual input through discussions and contributed to the writing of the manuscript.

CHAPTER 3
K. A. Rabbani designed and conducted the experiments with assistance from W. Charles and R. Cord-Ruwisch. W. Charles, R. Cord-Ruwisch and G. Ho assisted in the interpretation of results and provided intellectual input through discussions.

CHAPTER 4
K. A. Rabbani designed and conducted the experiments with assistance from W. Charles and R. Cord-Ruwisch. W. Charles, R. Cord-Ruwisch and G. Ho assisted in the interpretation of results. The primary author of the manuscript was K. A. Rabbani while W. Charles, A. Kayaalp, R. Cord-Ruwisch and G. Ho contributed to the writing of the manuscript.

CHAPTER 5
K. A. Rabbani designed and conducted the experiments with assistance from W. Charles and A. Kayaalp. W. Charles, R. Cord-Ruwisch and G. Ho assisted in the interpretation of results. The primary author of the manuscript was K. A. Rabbani while W. Charles, A. Kayaalp, R. Cord-Ruwisch and G. Ho contributed to the writing of the manuscript.
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Chapter 1: Introduction

1.1 Background

Air pollution is one of the most important environmental health threats of our time, contributing to heart disease, cancer, and respiratory diseases in urban environments (Brunekreef and Holgate 2002, Chan and Yao 2008, Gurjar, Molina et al. 2010, Khan and Pappas 2011). Air pollutants such as particulate matter, nitrous oxides, sulphur dioxide, ozone and heavy metals damage our airways, lungs, heart, and circulatory systems (Schwartz, Ballester et al. 2001, Kidd, Kidd et al. 2006). The main source of these pollutants in most urban centres can be directly related to contaminated air from industries and the burning of fossil fuels for transportation (Chan and Yao 2008, Cooper and Alley 2011, Khan and Pappas 2011). The effect of air pollutants on human health depends on many factors including the potency of the pollutants, the concentration of the pollutant that people are exposed to and the duration of such exposures. Despite the success of several proven technologies for control and removal of air pollutants, there exist several challenges in the control and removal of air pollutants with concentrations in the parts per million range or lower (Burgess, Parsons et al. 2001, Cooper and Alley 2011). There is considerable interest in the development of new materials and technologies for the detection, removal and recovery of air pollutants which exist at low concentrations (Ozturk, Tasaltin et al. 2009, Agus, Lim et al. 2011, Lyu, Zhu et al. 2014, Micoli, Bagnasco et al. 2014, Nour, Berean et al. 2014, Aslam, Shawabkeh et al. 2015, Courtois, Andres et al. 2015). There is a potential for
systems that concentrate or accumulate air pollutants in an inexpensive and environmentally benign to yield useful products.

1.2 Air pollution from wastewater treatment plants

There is increasing concern worldwide of the air pollutants released from wastewater or sewage treatment plants (Gostelow and Parsons 2000, Burgess, Parsons et al. 2001, Lebrero, Bouchy et al. 2011). Unlike solid or liquid effluents, air pollutants from wastewater treatment plants have traditionally been given less importance (Pope and Lauria 1989). Complaints from wastewater treatment plants related to air pollution have typically been limited to unpleasant odours which are seen more as a nuisance than a genuine pollution problem (Lasaridi, Katsabanis et al. 2010). However, unpleasant odours are indicators of worsening air pollution which carry potential risks to human health (Schiffman and Williams 2005). Studies have shown relationships between odour and health complications like headaches, insomnia, loss of appetite and asthma (Shim and Williams 1986, Lebrero, Bouchy et al. 2011). Volatile emissions from wastewater treatment plants are composed of a mixture of hundreds of chemical compounds, typically at very low concentrations (Burgess, Parsons et al. 2001, Lebrero, Bouchy et al. 2011). The common odorous gases from wastewater treatment plants are the inorganic gases like ammonia, hydrogen sulphide and organic compounds like limonene, butanone, skatole and geosmin (Lebrero, Bouchy et al. 2011). One of the most hazardous air pollutants in wastewater treatment plants is hydrogen sulphide ($H_2S$). $H_2S$ is a broad spectrum poison and affects the
nervous system among other organs (Burgess, Parsons et al. 2001, Attene-Ramos, Wagner et al. 2006). It is a colourless gas and has a characteristic smell of rotten eggs which can be detected by the human nose at concentrations of 0.5 ppb (Gostelow and Parsons 2000). Control of H$_2$S is considered the most dominant odour control requirement from wastewater (Wang, Sivret et al. 2014). Domestic wastewater contains organic sulphur compounds and inorganic sulphur which act as a source of H$_2$S (Gostelow and Parsons 2000, Lebrero, Bouchy et al. 2011, Park and Allaby 2013). It should be noted that though “sulfur” is the spelling used in technical and scientific writing, according to the Macquarie Dictionary, “sulphur” is still the dominant spelling accepted in Australia and is, therefore, used in this thesis (Macquarie 2013).

1.3 Biofiltration

Biological treatment of waste gases, as an alternative to physical and chemical processes, has gained popularity in the last couple of decades because they operate under ambient temperatures and pressures and have low operating costs (Jensen and Webb 1995, McNevin and Barford 2000, Burgess, Parsons et al. 2001, Cox, Deshusses et al. 2002, Iranpour, Coxa et al. 2005, Shareefdeen and Singh 2005, Syed, Soreanu et al. 2006, Mudliar, Giri et al. 2010). Biological systems work on the principle that microorganisms act as catalysts for the conversion of volatile pollutants into a less harmful form (Burgess, Parsons et al. 2001, Shareefdeen and Singh 2005, Syed, Soreanu et al. 2006). There are different types of biological systems but biofilters and biotrickling filters are the most popular systems used for the removal of H$_2$S.
from wastewater treatment plants (Shareefdeen and Singh 2005, Mudliar, Giri et al. 2010, Estrada, Kraakman et al. 2011, Lebrero, Bouchy et al. 2011). Both systems work on the principle that contaminated air passes through a packed bed of suitably wet porous medium in it and the moisture content in these systems is the single most important parameter for performance (Williams and Miller 1992, McNevin and Barford 2000, Easter, Quigley et al. 2005). The moisture is introduced either by humidifying the contaminated air before it enters the system or by an intermittent trickling of water down the media or both. The amount of leachate produced from biological systems used in wastewater treatment plants ranges from 0.9 L of leachate/L of reactor/day to 1,147 L of leachate/L of reactor/day (Gabriel and Deshusses 2003, Lafita, Penya-Roja et al. 2012, Chen, Fan et al. 2014). With increased interest in maximizing resource recycling and integration of water and resource recycling in industrial production processes, eliminating or reducing the amount of leachate being produced in these systems would be a welcome innovation in industry.

1.4 Sulphur recovery from leachate

Anaerobic processes that recover elemental sulphur from H$_2$S are well known in industry (Sipma, Janssen et al. 2003, Janssen, Lens et al. 2009, Sorokin, Tourova et al. 2013). However, in most biofilters that remove H$_2$S, anaerobic environments are not favoured because the sulphur formed in the biofilter may convert back to odorous H$_2$S (Mudliar, Giri et al. 2010, Chaiprapat, Mardthing et al. 2011). The oxidation of H$_2$S in aerobic biofilters produces odourless
sulphuric acid and aerobic biofilters are considered more practical and cost-effective for use in a wastewater treatment plants as long as the pH is carefully controlled to maintain an environment suitable for microorganisms in the biofilter (Yang and Allen 1994, Mudliar, Giri et al. 2010, Chaiprapat, Mardthing et al. 2011, Montebello, Mora et al. 2014).

A common strategy to maintain the pH is to trickle water or chemicals like sodium hydroxide or sodium carbonate down the media inside the biofilter (Devinny, Deshusses et al. 1998, McNevin and Barford 2000, Burgess, Parsons et al. 2001, Syed, Soreanu et al. 2006). This leads to formation of a neutral or weakly acidic leachate which is usually redirected back into the plant process wastewater stream (Cox, Deshusses et al. 2002, Gabriel and Deshusses 2003, Shareefdeen and Singh 2005, Mudliar, Giri et al. 2010, Estrada, Kraakman et al. 2011, Lebrero, Bouchy et al. 2011). Sulphur analysis of the leachate formed in biofilters with inorganic media under aerobic conditions has shown that more than 90% of the sulphur in the leachate is in the form of sulphate at low concentrations (Shareefdeen, Herner et al. 2003, Montebello, Mora et al. 2014). Sulphur is one of the most important raw materials used in industry and sulphur recovery from dilute solutions of sulphuric acid has been considered as a viable source of sulphur (Selim, Gupta et al. 2013). Known industrial processes for the recovery of sulphur from dilute sulphuric acid involve high temperatures and expensive catalysts to produce $\text{SO}_2$ which is then subsequently converted to concentrated acid (Laursen and Karavanov 2006). Sulphur recovery from the leachate produced in a wastewater treatment plants which does not involve high amounts of energy or chemicals would be beneficial to the industry. The sulphur in
leachate produced in these processes should be considered a resource rather than a waste product.

1.5 Research question and Objective of Research

This thesis aims to answer an overarching research question of whether a novel approach can be developed that can minimise leachate production from an aerobic biofilter removing H\textsubscript{2}S as well as recovering sulphur as concentrated sulphate from the biofiltration process.

It aims to investigate a novel aerobic biofilter design and operation for the removal of hydrogen sulphide from contaminated air such that

- there is production of little to almost no leachate during the operation of the aerobic biofilter.

- sulphur can be recovered as a useable product like concentrated sulphuric acid from this aerobic biofilter.

- there is no requirement for pH control by addition of harsh chemicals (like sodium hydroxide) in the biofilter.

- there is simultaneous removal of hydrogen sulphide and ammonia in the contaminated air where ammonia is removed by acid stripping using concentrated sulphuric acid formed due to the H\textsubscript{2}S oxidation.
1.6 Thesis Structure

This following work is being submitted as a thesis by publications/manuscripts and is composed of six chapters and their brief descriptions are described below:

Chapter 1: Chapter one gives a brief background on the topic and the objectives of the research. The thesis structure is also outlined in this chapter.

Chapter 2: Chapter two describes a review of the current literature on hydrogen sulphide removal from air in an aerobic environment and discusses the possibility of recovering sulphur from contaminated air with special emphasis on contaminated air originating from wastewater treatment plants.

Chapter 3: Chapter three describes some of the modelling and lab scale experiments done to ascertain the scientific principles that were needed for the development, construction and operation of the novel biofilter.

Chapter 4: Chapter four describes the lab scale design and operation of the novel biofilter system together with the results and their discussion.
**Chapter 5:** Chapter five describes a pilot scale version of the novel biofilter system which concurrently removes hydrogen sulphide and ammonia and was setup at the local Subiaco Wastewater Treatment Plant based on the experience of the lab based biofilter.

**Chapter 6:** Chapter six contains the overall conclusion of the study together with the recommendation for further research.

Papers/manuscripts that have been submitted for publication from this research are outlined in a previous section titled Secondary Publications.
Chapter 2: Recovery of sulphur from contaminated air in wastewater treatment plants by biofiltration: A critical review

2.1 Abstract

Biofilters are popular as an alternative method for treatment of volatile air pollutants like hydrogen sulphide originating from wastewater treatment plants. Despite several advantages over conventional chemical systems, one of the concerns of biological treatment of hydrogen sulphide is the production of large volumes of neutral or acidic leachate which needs to be treated or disposed safely. Instead of treating as an unwanted product, a waste stream of weakly acidic leachate can be thought of as a sulphur resource. In this chapter, recent literature on H₂S removal by biofiltration in an aerobic environment is reviewed with special regard to the volume of leachate produced by the biofiltration process. After a short introduction in section 2.2 the relevant literature with regard to sulphur and H₂S in wastewater is provided in section 2.3. Some common chemical and physical methods for the removal of H₂S from air are summarised in section 2.4. The current literature on the biological methods for the removal of H₂S and the potential recovery of sulphur from leachate are described in section 2.5. Perspectives on future research and development needs in this area and a primary justification for the research conducted in this thesis are discussed in section 2.6.
2.2 Introduction

Volatile emissions from wastewater treatment plants (WWTP) are composed of a mixture of hundreds of chemical compounds, typically at very low concentrations (Stuetz and Frechen 2001, Stuetz, Gostelow et al. 2001, Lebrero, Bouchy et al. 2011, Lebrero, Rangel et al. 2013). The volatile emissions include ammonia, hydrogen sulphide, limonene, butanone, skatole, geosmin, toluene, benzene and other organic compounds (Escalas, Guadayol et al. 2003, Lee and Rasmussen 2006, Lebrero, Bouchy et al. 2011, Godayol, Besalu et al. 2015). Air pollution complaints from wastewater treatment plants have typically been limited to unpleasant odours which are seen as a nuisance for residential areas around the plants (Gostelow and Parsons 2000, Burgess, Parsons et al. 2001, Ziya Ozturk, Tasaltin et al. 2009). Recently, there is increasing emphasis on the health effects of air pollutants coming from wastewater treatment plants. (Gostelow and Parsons 2000, Schiffman and Williams 2005, Lee, Lee et al. 2006). Previous studies have shown relationships between odour and health complications like headaches and asthma (Herbert, Glick et al. 1967, Shim and Williams 1986, Sjaastad and Bakketeig 2006). Hydrogen sulphide (H₂S) control is considered the most dominant odour control requirement for wastewater (Wang, Sivret et al. 2014). H₂S is a colourless and toxic gas that is considered a broad spectrum poison which affects the nervous system among other organs Toxic exposure to hazardous chemicals in the air are described by threshold limit values (TLV) (Hodgson 2004). TLV-TWA (time weighted average) is the maximum concentration of contaminant that workers may be exposed to, without adverse health effects, during an 8 hour day. TLV-STEL (short term exposure limit) is
the maximum concentration that workers can be exposed to continuously, for a short period of time (usually 15 or 10 minutes) without adverse health effects (Hodgson 2004). The standard set by different authorities in some countries for H$_2$S are summarised in Table 2.1.

Table 2.1: Values of TLV-TWA and TLV-STE for H$_2$S for some selected countries

<table>
<thead>
<tr>
<th>Institution/Country</th>
<th>TLV-TWA</th>
<th>TLV-STE</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>OSHA (US)</td>
<td>20 ppm</td>
<td>50 ppm (69 mg/m$^3$) with 10 min exposure</td>
<td>(Occupational Safety &amp; Health Administration, Guidotti 2010)</td>
</tr>
<tr>
<td>SCOEL (EU)</td>
<td>5 ppm</td>
<td>10 ppm (14 mg/m$^3$) with 15 min exposure</td>
<td>(SCOEL, Guidotti 2010)</td>
</tr>
<tr>
<td>Safework Australia (Australia)</td>
<td>10 ppm (14 mg/m$^3$)</td>
<td>15 ppm (21 mg/m$^3$) with 15 minute exposure</td>
<td>(safe work australia)</td>
</tr>
</tbody>
</table>

Typical concentrations of H$_2$S emanating from WWTPs range from 7 to 590 mg/m$^3$ and are almost 1000 times the acceptable health limit (Gostelow and Parsons 2000, Cox, Deshusses et al. 2002, Converse, Schroeder et al. 2003, Gabriel and Deshusses 2003, Shareefdeen, Herner et al. 2003, Chen, Jiang et al. 2006, Lafita, Penya-Roja et al. 2012). There are several existing methods for removal of air pollutants from WWTP including incineration, physical adsorbents, chemical scrubbers and biological treatments (Burgess, Parsons et al. 2001, Estrada, Kraakman et al. 2011). Physical and chemical treatments of odours in WWTP are being replaced by biological treatments that use microorganisms for the removal of odours (McNevin and Barford 2000, Stuetz and Frechen 2001, Stanley and Muller 2002, Iranpour, Coxa et al. 2005,

2.3 Sulphur and H₂S in wastewater

Sulphur occurs naturally in the environment as sulphur, sulphide and sulphate minerals. The biogeochemical sulphur cycle is the mechanism by which sulphur is transported in and out of the atmosphere, water, soil minerals and living systems (Marshall and Fairbridge 1999, Park and Allaby 2013). A complete description of the global biogeochemical cycle is complex, however, it can be broken down into three cycles – the atmospheric cycle, the geochemical cycle (between the ocean and the land) and the microbial ecological cycle. An excellent description of the atmospheric cycle is given in the literature and the details are not included in this current description (Brimblecombe, Lein et al. 1989, Butcher 1992). A summary of the geochemical and microbial ecological cycle are given in Figure 2.1 and Figure 2.2 (Canfield, Erik et al. 2005). In the geochemical cycle, sulphur is released into the ocean by the erosion of soil and rocks on land, gases from hydrothermal vents and volcanic activity. The sulphur is converted and is found
in the ocean mainly in the form of sulphate. The sulphate in the ocean either precipitates back to the ocean floor (evaporite deposition) or is reduced to iron (II) sulphide and other sulphur-containing organic compounds (Canfield, Erik et al. 2005).

**Figure 2.1:** The sulphur cycle from a geochemical perspective (Canfield, Erik et al. 2005).

In the microbial ecological cycle, sulphide is formed from sulphate by processes known as assimilatory or dissimilatory sulphate reduction (Butcher 1992, Marshall and Fairbridge 1999). The sulphide is oxidized to sulphate through light mediated photosynthetic pathways, biologically mediated non-photosynthetic pathways or through inorganic reactions with metals. There are many other forms of sulphur with intermediate oxidation states during the formation of either sulphate or sulphide as can be seen in Figure 2.2 (Canfield, Erik et al. 2005).
Figure 2.2: The sulphur cycle from a microbial ecological perspective (Canfield, Erik et al. 2005).

Table 2.2 adapted from the literature includes some of the key naturally occurring sulphur compounds that are found in the air, water and soil arranged by the oxidation state of sulphur (Butcher 1992).

Table 2.2: Forms of naturally occurring sulphur compounds in nature

<table>
<thead>
<tr>
<th>Sulphur Oxidation state</th>
<th>Air</th>
<th>Water</th>
<th>Soil</th>
</tr>
</thead>
<tbody>
<tr>
<td>-2</td>
<td>H₂S, RSH, RSR, OCS, CS₂</td>
<td>HS⁻, S₂⁻, RS⁻</td>
<td>S²⁻, HS⁻, MS</td>
</tr>
<tr>
<td>-1</td>
<td>RSSR</td>
<td>RSSR</td>
<td>MS₂</td>
</tr>
<tr>
<td>0</td>
<td>CH₃SOCH₃⁺</td>
<td>-</td>
<td>S₈</td>
</tr>
<tr>
<td>2</td>
<td>-</td>
<td>S₂O₃²⁻</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>SO₂, HSO₃⁻ (as aerosol)</td>
<td>HSO₃⁻, SO₃²⁻</td>
<td>SO₃²⁻</td>
</tr>
<tr>
<td>6</td>
<td>SO₃ and H₂SO₄, HSO₄⁻, SO₄²⁻ (as aerosol)</td>
<td>SO₄²⁻, HSO₄⁻, RSO₃⁻</td>
<td>SO₄²⁻</td>
</tr>
</tbody>
</table>

*R represents organic functional groups and M represents metal.*
Domestic wastewater contains organic and inorganic sulphur compounds which act as the source of sulphur (Gostelow and Parsons 2000, Wang, Sivret et al. 2014). Degradation of organic sulphur compounds like cysteine and methionine in biological wastes, produces H$_2$S in wastewater (Stuetz, Gostelow et al. 2001). But the main source of sulphur in wastewater is dissolved inorganic sulphate (Araujo, de Oliveira et al. 2000, Pikaar, Sharma et al. 2014). According to Pikaar and his fellow researchers, there are three sources of inorganic sulphate in wastewater – the sulphate from the drinking water entering the waste stream, the sulphate added as coagulants in the water treatment process and human or industrial wastes discharged into wastewater (Pikaar, Sharma et al. 2014). Interestingly, the researchers have also shown that 52% of the inorganic sulphate in wastewater of Queensland originates from the aluminium sulphate added as a coagulant during the purification of the water supply indicating that the source of sulphur in sewer systems are mainly due to the addition of coagulants rather than any other sources (Pikaar, Sharma et al. 2014). The concentration of H$_2$S in sewer systems can be as high as 450 mg/m$^3$ and the conversion of sulphate to H$_2$S in sewer systems has been studied in great detail over the years primarily because of its effect on the corrosion of concrete pipes and several excellent reviews are available (Zhang, De Schryver et al. 2008, Oviedo, Johnson et al. 2012, Hao, Xiang et al. 2014, Park, Lee et al. 2014). In simple terms, the anaerobic regions of sewer systems convert sulphate to dissolved sulphide through the action of sulphate reducing bacteria (SRB) and the formation of H$_2$S is dependent on the temperature, pH and ventilation of air through the

2.4 H$_2$S removal in industry – chemical and physical methods

The most common industrial process for the conversion of H$_2$S to S in contaminated air is the Claus process (Hocking 2006, Khazini, Fatehifar et al. 2014, Li, Huang et al. 2014). H$_2$S is a by-product of processing natural gas and refining high sulphur crude oils and the Claus process is a multi-stage catalytic process that converts H$_2$S to elemental S according to the overall reaction:

$$2\text{H}_2\text{S} + \text{O}_2 \rightarrow 2\text{S} + 2\text{H}_2\text{O}$$

The process involves temperatures of 300 °C and the use of a catalyst like alumina or bauxite (Hocking 2006). The Claus process is suitable for air with high concentrations of H$_2$S (5 – 25%) and the high energy and cost of the catalyst makes this process unsuitable for use in removing the low concentration H$_2$S in wastewater treatment plants. H$_2$S can also be removed from the air by precipitation as metal sulphides using iron or metal salts (Al-Tarazi, Heesink et al. 2004, Shareefdeen and Singh 2005). Iron sponge processes use ferric oxide or ferric hydroxide coated on wood chips, wood shavings, ceramic beads, or diatomaceous earth to form iron sulphide as a solid, insoluble precipitate and several commercial products are available (Shareefdeen and Singh 2005, Cherosky and Li 2013). Iron solutions with EDTA have been used as a solvent in a patented system called LO-CAT for
H₂S removal from air (Kazemi, Malayeri et al. 2014). In this system, the ferric salt is used to react with H₂S to form ferrous ion and sulphur in one chamber while the ferrous ion is oxidized to ferric ion in the presence of oxygen in another chamber.

\[
H₂S + Fe^{3+} \rightarrow Fe^{2+} + 2H^+ + S
\]

\[
Fe^{2+} + O_2 + H_2O \rightarrow Fe^{3+} + OH^-
\]

The large cost of setup of systems like LO-CAT makes it unsuitable for use in WWTP. Use of other metals like nickel to remove H₂S can also be considered, however the high cost of metals make their use in WWTP unrealistic (Karbanee, Van Hille et al. 2008, Lewis 2010). Iron (oxyhydro) oxide minerals and ferrate (VI) compounds have also been investigated for the absorption of H₂S (Poulton, Krom et al. 2004, He, Li et al. 2009). Chemical scrubbers, which transfer H₂S from the gas phase to a suitable liquid solvent is also utilised in industry for the removal of H₂S (Stuetz and Frechen 2001, Estrada, Kraakman et al. 2011). Solvents like sodium hypochlorite, ozone, potassium permanganate, hydrogen peroxide and potassium carbonate oxidise the absorbed H₂S to either elemental sulphur or sulphate depending on the conditions (Shareefdeen and Singh 2005). H₂S can also be absorbed into solvents like sodium hydroxide and synthetic amines like monoethanolamine (MEA), methyl diethanolamine (MDEA), diglycolamine, and N-methyl-2-pyrrolidone and commercial mixtures like Sulfinol and Selexol (Judd 1978, Sweney 1980, Jensen and Webb 1995, Shareefdeen and Singh 2005, Lebrero, Bouchy et al. 2011, Ghanbarabadi and Khoshandam 2015). The amines have the advantage that they can be regenerated by heating the spent
solvent but the release of toxic H$_2$S during this step and the high cost of the solvent makes this process unsuitable for use in wastewater treatment plants (Rhodes 2013).

H$_2$S in air can also be physically adsorbed into many types of solid adsorbents. Activated carbon and surface modified activated carbon is the solid adsorbent of choice for the removal of H$_2$S with the highest adsorption capacity being 300 mg of S per gram of activated carbon (Bagreev, Rahman et al. 2000, Bandosz, Askew et al. 2000, Bagreev, Adib et al. 2001, Bagreev and Bandosz 2002, Bagreev and Bandosz 2002, Bagreev, Bashkova et al. 2002, Bandosz 2002, Duan, Yan et al. 2007, Zhou and Huo 2009). The problem with activated carbon and their modified versions is what to do with the activated carbon once they are used and high pressures are required to pass the gas through packed columns (Bagreev, Rahman et al. 2002, Bashkova, Baker et al. 2007). Natural zeolites, like clinoptilolite, have been used for the removal of H$_2$S, however their absorption capacities (87 mg/g) are very low compared to activated carbon (Yasyerli, Ar et al. 2002). Polymers like rubber and silica polyamine based carbon composites iron coated materials have also been used for H$_2$S adsorption but their adsorption capacities are very low compared to activated carbon (Herszage and Afonso 2000, Wilks and Rezac 2002, Bandosz, Seredych et al. 2007, Zakarina, Volkova et al. 2013). Molecular sieves for the removal of H$_2$S from contaminated air are still being developed and their removal capacities tend to be fairly low compared to other processes (Prabu and Ramalingam 2015) Other interesting absorbing materials considered for the absorption of H$_2$S include juglone and fulvic acid (Perlinger, Kalluri et al. 2015).
Like activated carbon, all solid adsorbents have the disadvantage of the safe disposal of the spent adsorbent (Bandosz and Le 1998). Synthetic membranes made from polymers and ceramic materials have received a lot of attention recently for the separation of gas mixtures (Jefferson, Nazareno et al. 2005, Basu, Khan et al. 2010, Jiang and Zhu 2013, Scholz, Melin et al. 2013). The main advantages of membrane systems are that they provide a constant surface area for separation and the low operating costs (Jefferson, Nazareno et al. 2005). This area of research is relatively new and practical membranes that can withstand real world conditions with acidic gases like H₂S and CO₂ are still being developed (Basu, Khan et al. 2010, Jiang and Zhu 2013, Scholz, Melin et al. 2013, Nour, Berean et al. 2014).

2.5 H₂S Removal in WWTP – biological methods

dimethyl sulphide and dimethyl disulphide using biofilters (Bobadilla Fazzini, Cortés et al. 2013, Malhautier, Soupramanien et al. 2015).

Not only are the biological systems cost effective, but they also produce innocuous products like N₂, CO₂ and H₂O (Mudliar, Giri et al. 2010). Biological systems work on the principle that microorganisms like bacteria act as catalysts for the conversion of volatile pollutants into a less harmful form (Stuetz and Frechen 2001, Shareefdeen and Singh 2005). The microorganisms are immobilised on the surfaces of a porous media forming a biofilm inside the biofilters (Kennes and Veiga 2002, Bernstein, Freger et al. 2014, Maksimova 2014). The microorganisms are attached to the surface of a medium by extracellular polymeric substances (EPS). EPS is a polymeric conglomeration generally composed of extracellular DNA, proteins, and polysaccharides (Maksimova 2014). The compositions of the microbial community in a biofilm that can be used in biological systems depend on the type, nature and concentration of the incoming gas stream. Start-up of biofilters in large-scale operations for odour removal involves the use of microbial consortia, mixed cultures or wastewater sludge rather than pure cultures (Shareefdeen and Singh 2005, Jensen, Nielsen et al. 2008, Jensen, Lens et al. 2011).

bioscrubber employs two reactors – one with a gas/liquid exchange column where the gas phase pollutant is dissolved onto a liquid phase and another where this liquid is constantly recirculated through an activated sludge unit which contain the microorganisms suspended in solution (McNevin and Barford 2000, Stuetz and Frechen 2001, Stanley and Muller 2002, Shareefdeen and Singh 2005). Bioscrubbers work best for pollutant that has a high solubility in liquid and is thus limited in its use for volatile organic compounds and poorly water soluble gases. The biomass growth in a bioscrubber also has to be controlled to reduce solid waste output and increase gas removal efficiency and since bioscrubbers require large amount of liquid, this is not considered a very popular method (Stuetz and Frechen 2001, Shareefdeen and Singh 2005). Membrane bioreactors, which have so far been used in lab-scale, consist of a membrane where the contaminated air is on one side and the biofilm is on the other side (Shareefdeen and Singh 2005). Nutrients, water and oxygen are provided to the side of the membrane that has the biofilm. The main advantage of the membrane system is that the contaminated air flow and biofilm are never in direct contact and this prevents the microorganisms from contaminating the gas phase (Maksimova 2014). Membrane bioreactors are best suited for volatile organic pollutants with low water solubility and the membranes can be designed for selective separation of pollutants (Basu, Khan et al. 2010, Nour, Berean et al. 2014). Other types of biological systems that have been tried are activated sludge diffusion (Burgess, Parsons et al. 2001), airlift bioreactors (Lohwacharin and Annachhatre 2010, Zytoon, AlZahrani et al. 2014), external loop airlift
bioreactor (Ritchie and Hill 1995) and spiral bioreactor (Shim, Jung et al. 1995).

Among all the biological methods, the biotrickling and biofilters are popular systems used for the removal of H$_2$S from WWTP (Shareefdeen and Singh 2005, Mudliar, Giri et al. 2010, Estrada, Kraakman et al. 2011, Lebrero, Bouchy et al. 2011). There are several examples of successful conversions of full-scale chemical scrubbers to biotrickling filters in industry (Gao, Keener et al. 2001, Cox, Deshusses et al. 2002, Gabriel and Deshusses 2003, Kraakman 2003, Gabriel, Cox et al. 2004, Santos, Guimera et al. 2015). Studies have demonstrated the economic advantage of this conversion to biofilters with better or comparable performance under equivalent operation conditions (Gabriel, Cox et al. 2004). One of the important parameters that need to be considered for the conversion from chemical to biological systems is the gas contact time or empty bed residence time. Empty Bed Residence Time (EBRT) is the time that a gaseous pollutant spends in a biofilter and is defined as the empty bed filter volume divided by the air flow rate (Shareefdeen and Singh 2005). The higher the EBRT, the larger the volume of the biofilter required and hence, the higher the capital cost. Chemical scrubbers typically have EBRTs of less than 5s and EBRTs of biofilters used to be around 10 to 30 s limiting their effectiveness as an alternative to chemical scrubbers (Wu et al., 2001). Only in the last couple of decades have biofilters with EBRTs lower than 2 s with comparable H$_2$S removal performances to chemical scrubbers been reported (Gabriel and Deshusses 2003, Santos, Guimera et al. 2015). A biofilter in Orange County, California with a 95% H$_2$S removal and EBRT of 1.6s was achieved by retrofitting an existing 1.73 m$^3$ chemical scrubber to a
biofilter using open polyurethane foam as the packing material (Gabriel and Deshusses 2003). A larger (4m$^3$) chemical scrubber in Barcelona, Spain was converted to a biofilter with a removal efficiency of 99% with an EBRT of 1.44s and this biofilter use Pall rings (open basket structure of thin plastic bars) as the packing material (Santos, Guimera et al. 2015). Due to the lower power requirements and the absence of chemicals in a biofilter, the operation costs of biotechnologies are between 2 and 4 times lower than those of chemical scrubbers (Comas et al., 1999; Gao et al., 2001; Hansen and Rindel, 2000).

Both biofilters and biotrickling filters have contaminated air passing through a suitably wet porous medium and the pollutant is transported from the gas phase to the water in the biofilm with the subsequent biological oxidation of the pollutant in the biofilm (Figure 2.3). However, biofilters and biotrickling filters differ in several aspects including the characteristics of the medium that carry the biofilm and the method of delivery of moisture or nutrients to the biofilm. In biofilters, the medium must have high surface area, high porosity, high buffer capacity, high nutrient availability and high moisture retention capacity (Shareefdeen and Singh 2005, Mudliar, Giri et al. 2010). In biofilters, the medium acts as the source of macronutrients (N, P, K, and S) and micronutrients (vitamins, metals) which are essential for growth of the microorganisms (Easter, Quigley et al. 2005, Mudliar, Giri et al. 2010). Examples of mediums that have been used in biofilters include soil, peat, compost, wood chips, bark mulch, perlite, sewage sludge and combinations of these (Easter, Quigley et al. 2005).
The medium used in a biotrickling filter is typically inert, synthetic materials such as plastic, polyurethane, polyethylene packing, ceramics and polyurethane foam (Burgess, Parsons et al. 2001, Easter, Quigley et al. 2005, Goncalves and Govind 2008). The advantage of synthetic materials is that because of their uniform particle sizes, they have uniform pore size distributions compared to soil, compost or peat media (Easter, Quigley et al. 2005). Typical media used in biotrickling filter also have high surface area per unit volume (>200 m²/m³), high porosity, good chemical resistance and good structural properties (Easter 2005). The inert media has to be inoculated initially with soil, compost or sewage sludge to assist development of the microbial cultures. The use of activated sludge as initial microbial inoculum

**Figure 2.3:** A schematic representation of the difference between a biotrickling filter and a biofilter (adapted from (Syed, Soreanu et al. 2006) and (Mudliar, Giri et al. 2010))
has been extensively reported (Cortinovis 1974, Lu, Lin et al. 2002, Rodríguez, Gómez et al. 2012, Shareefdeen 2015). Since the inert media is low on nutrients and moisture, it is necessary to supplement the media with nutrients for effective biofiltration to occur and the nutrients are typically supplied together with the recirculation water used in a biotrickling filter. In WWTP, the wastewater plant effluent water carries sufficient trace nutrients for use in a biotrickling filter (Easter, Quigley et al. 2005). Researchers have shown that good performance of biotrickling filters can be maintained by supplying a minimum amount of water and nutrient (Yang and Allen 1994, Yang and Allen 1994, Lu, Lin et al. 2002). A lab scale biotrickling filter with yard waste compost as the packing material and an EBRT of 60 seconds had a removal efficiency of 99.9 % even when the moisture content in the biofilter decreased to 30% (Yang and Allen 1994). One drawback of biotrickling filters is the accumulation of excess biomass in the filter bed and studies have shown that the biofilm thickness can be high enough to cause clogging, channelling and creation of anaerobic zones which eventually lead to deterioration in performance of the biotrickling filters (Mudliar, Giri et al. 2010, Yang, Chen et al. 2010). Measures to control biomass accumulation not only include physical, chemical and biological techniques but also improvements in biofilter designs and modes of operation (Yang, Chen et al. 2010).

The moisture content (MC) of the medium is the single most important parameter for the performance of a biofilter or biotrickling filter (Williams and Miller 1992, McNevin and Barford 2000, Easter, Quigley et al. 2005). Adequate moisture is necessary for the biological activity of the biofilm (Easter, Quigley
et al. 2005, Iranpour, Coxa et al. 2005, Shareefdeen and Singh 2005). The liquid water in these filters also functions to dilute the products of the biological reaction and provide pH buffering (Mudliar, Giri et al. 2010). Dilution has been found to be particularly important in maintaining the pH for hydrogen sulphide biofiltration (Yang and Allen 1994, Brennan, Donlon et al. 1996, McNevin and Barford 2000). The optimal moisture contents in the medium for use in both biofilter and biotrickling filter in the literature varied from 20 to 60% (McNevin and Barford 2000, Mudliar, Giri et al. 2010).

In biofilter, the moisture is introduced into the system either by humidifying the contaminated air before it enters the biofilter or by sprinkling water or nutrient solution from the top of the biofilter (Shareefdeen and Singh 2005, Mudliar, Giri et al. 2010). If the MC is too low in the biofilter medium cracks may open in the dry bed and channelling occurs which affects the performance of the biofilter (McNevin and Barford 2000). If the MC is too high, anaerobic zones are formed in the medium and the expected biological oxidation of pollutant does not occur (McNevin and Barford 2000). There can also be increasing backpressure due to reduced void volume and channelling of the gas within the bed (Mudliar, Giri et al. 2010). It is essential to develop an understanding of the loss of moisture in a medium due to changes in inlet air temperature and relative humidity and if the inlet air is not humidified to near 100% relative humidity, the airflow through the biofilter can dry up the media (Easter, Quigley et al. 2005, Mudliar, Giri et al. 2010). In a biotrickling filter, the moisture is provided by a continuous or intermittent stream of water or nutrient solution trickling down the media (McNevin and Barford 2000, Cox, Deshusses et al.
2002, Syed, Soreanu et al. 2006). The water or nutrient solution is supplied by
timed spray nozzles, or by a pump that recycles the leachate formed in the
biotrickling filter (Easter, Quigley et al. 2005, Shareefdeen and Singh 2005). If
the MC is too low in a biofilter medium, biological activity is hampered but,
unlike in a biofilter, cracks do not form in the inert medium and channelling is
avoided (McNevin and Barford 2000). If the MC is too high, anaerobic zones
are formed in the medium as in a biofilter and the expected biological oxidation
of pollutant does not occur (McNevin and Barford 2000).

Anaerobic biological processes for the removal of H₂S have been studied
extensively in the literature (Janssen, Lettinga et al. 1999, Oyarzun, Arancibia
et al. 2003, Mudliar, Giri et al. 2010). Green sulphur bacteria of the
Chlorobiaceae and Chromatiaceae family convert H₂S to elemental sulphur
under anaerobic conditions (Janssen, Lettinga et al. 1999). Since the bacteria
are photoautotrophic in nature, their use in large scale is limited by the
requirement that light be available to the biofilm at all times (Janssen, Lettinga
et al. 1999). A completely aerobic environment is more practical and cost-
effective in a wastewater treatment plant (Chaiprapat, Mardthing et al. 2011).
The biological oxidation of dissolved sulphide (HS⁻) in a biofilm under aerobic
environments is accomplished by sulphur oxidizing bacteria (SOB). Examples
of SOB include the bacteria from the genus Thiobacillus and Acidithiobacillus
which are responsible for the oxidation of sulphide (Friedrich, Rother et al.
2001, Oprime, Garcia et al. 2001, Lee, Lee et al. 2006, Chaiprapat, Mardthing
et al. 2011). In an aerobic environment, the sulphide in solution is oxidized by
the following reactions (Janssen, Lettinga et al. 1999):
Since the second reaction yields the most energy, sulphate is the main product in the presence of an excess oxygen and sulphur production will only proceed under oxygen-limiting conditions or at high sulphide loading rates oxygen (Buisman, Geraats et al. 1990). The formation of sulphuric acid by the bacteria leads to an increasingly low pH environment in the biofilter. Not only does low pH decrease the solubility of H\textsubscript{2}S in solution (Figure 2.4) but the pH can reach a level which is not favourable for the microorganisms (Table 2.3). Figure 2.4 has been derived from the acid dissociation constants (Ka\textsubscript{1} and Ka\textsubscript{2}) of the following equilibrium reactions and the details of the derivation are given in Appendix A:

\[ \text{H}_2\text{S} \rightleftharpoons \text{HS}^- + \text{H}^+ \quad \text{Ka}_1 = 1 \times 10^{-7} \]

\[ \text{HS}^- \rightleftharpoons \text{S}^{2-} + \text{H}^+ \quad \text{Ka}_2 = 1.3 \times 10^{-13} \]

Figure 2.4: Influence of pH on the fraction of sulphur in the form of H\textsubscript{2}S, HS\textsuperscript{-} and S\textsuperscript{2-} in aqueous solution
Table 2.3: pH for optimal growth of a few aerobic sulphur oxidizing bacteria

<table>
<thead>
<tr>
<th>Name of bacteria</th>
<th>pH range for optimal growth</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Thiobacillus thioparus</em></td>
<td>5.5-7.0</td>
<td>(Aroca, Urrutia et al. 2007)</td>
</tr>
<tr>
<td><em>Acidithiobacillus thiooxidans</em></td>
<td>1.8-2.5</td>
<td>(Aroca, Urrutia et al. 2007)</td>
</tr>
<tr>
<td><em>Acidithiobacillus thiooxidans</em></td>
<td>&lt;1</td>
<td>(Chaiprapat, Mardthing et al. 2011)</td>
</tr>
<tr>
<td><em>Acidithiobacillus thiooxidans AZ11</em></td>
<td>0.2</td>
<td>(Lee, Lee et al. 2006)</td>
</tr>
</tbody>
</table>

To maintain the optimal performance of the biofilter or the biotrickling filter that removes H₂S, the moisture content and pH is constantly monitored and carefully controlled (Mudliar, Giri et al. 2010). A common strategy to maintain the pH is to trickle water or a buffered solution of inorganic nutrients down the media inside the biofilter (Devinny, Deshusses et al. 1998, McNevin and Barford 2000, Burgess, Parsons et al. 2001, Syed, Soreanu et al. 2006). This leads to formation of a neutral or weakly acidic leachate which is usually redirected back into the plant process wastewater stream (Cox, Deshusses et al. 2002, Gabriel and Deshusses 2003, Shareefdeen and Singh 2005, Mudliar, Giri et al. 2010, Estrada, Kraakman et al. 2011, Lebrero, Bouchy et al. 2011). Sulphur analysis of the leachate with inorganic media under aerobic conditions has shown that more than 90% of the sulphur in the leachate is in the form of sulphate at low concentrations (0.02M H₂SO₄) (Shareefdeen, Herner et al. 2003).
The amount of leachate produced in industry range from 2 L/day to 10,800 L/day (Devinny, Deshusses et al. 1998, McNevin and Barford 2000, Shareefdeen and Singh 2005, Syed, Soreanu et al. 2006). Even though concentration of sulphate in leachate is low, since the volume of leachate being produced in WWTP is high, the amount of sulphur that can be recovered from the leachate can potentially be significant (Table 2.4). There are many lab-scale biological systems in the literature that have been shown to remove H₂S, but for the recovery of sulphur in leachate, the interest is more in the industrial scale where the biofilter units perform under fluctuations of temperature and pollutant concentrations.

**Table 2.4**: Summary of biological systems used in WWTP for the removal of H₂S and potential recoverable sulphur

<table>
<thead>
<tr>
<th>H₂S concentration of foul air</th>
<th>Flow rate</th>
<th>Removal Efficiency</th>
<th>Sulphur removed / Recoverable sulphur per day</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>mg/m³</td>
<td>m³/h</td>
<td>%</td>
<td>g S/day</td>
<td></td>
</tr>
<tr>
<td>28</td>
<td>27,694</td>
<td>99.0</td>
<td>17,189</td>
<td>(Shareefdeen, Herner et al. 2003)</td>
</tr>
<tr>
<td>7-49</td>
<td>16,300</td>
<td>98.0</td>
<td>2,504 – 17,526</td>
<td>(Gabriel and Deshusses 2003)</td>
</tr>
<tr>
<td>14 -69</td>
<td>42.5</td>
<td>99.3</td>
<td>13-66</td>
<td>(Converse, Schroeder et al. 2003)</td>
</tr>
<tr>
<td>1-139</td>
<td>3,500</td>
<td>98.0</td>
<td>108-10,752</td>
<td>(Lafita, Penya-Roja et al. 2012)</td>
</tr>
<tr>
<td>14-69</td>
<td>600</td>
<td>98.0</td>
<td>184-922</td>
<td>(Cox, Deshusses et al. 2002)</td>
</tr>
<tr>
<td>125 – 590</td>
<td>14</td>
<td>90.0</td>
<td>36-168</td>
<td>(Chen, Jiang et al. 2006)</td>
</tr>
</tbody>
</table>
The amount of sulphur removed from the contaminated air depends on several factors including the concentration of inlet H₂S, air flow rate and efficiency of H₂S removal. Literature data on industrial-scale installations are scarce in comparison with laboratory results, but an overview of the parameters of recent biological systems operating in WWTP is summarized in the Table 2.4.

Depending on the flow rate and concentration of H₂S being removed, the amount of sulphur being removed from a biofilter could be as high as 17.5 kg of sulphur per day (Table 2.4). Sulphur is an important industrial raw material that is mainly used as a precursor for the manufacture of other chemicals. In 2013, the worldwide production and reserves of sulphur was 69 million tonnes with the China and US as top producers with 10 million tonnes and 9.1 million tonnes respectively (U.S. Geological Survey 2014). The most important industrial chemical manufactured from sulphur is sulphuric acid. Sulphuric acid production is considered one of the most important factor to determine the extent of industrialization of a country. The leading use of sulphuric acid is the production of phosphate fertilizer but it is also used in the manufacture of detergents, dyes, explosives, drugs and plastic. In an aqueous solution, the first hydrogen in sulphuric acid is completely ionized, the second hydrogen ionizes only partially (Brown 2006):

\[
\begin{align*}
\text{H}_2\text{SO}_4 \rightarrow & \text{H}^+ + \text{HSO}_4^- \\
\text{HSO}_4^- \rightarrow & \text{H}^+ + \text{SO}_4^{2-} \quad K_a = 1.1 \times 10^{-2}
\end{align*}
\]
Sulphur recovery from dilute solutions of sulphuric acid has been considered as a viable source of sulphur (Selim, Gupta et al. 2013). Simply heating dilute sulphuric acid to form concentrated sulphuric is not economically favourable because of the cost of water evaporation (Bartholomew 1952). Known industrial processes for the recovery of sulphur from dilute sulphuric acid involve high temperatures and/or expensive catalysts to produce SO₂ which is then subsequently converted to concentrated acid (Laursen and Karavanov 2006). Other methods suggested for concentrating dilute acid solutions include membrane distillation technology (Tomaszewska 1993, Tang and Zhou 2006), solvent extraction (Agrawal and Sahu 2009, Kesieme, Aral et al. 2013) and a microbial electrochemical system (Pikaar, Rozendal et al. 2011, Liu, Feng et al. 2014). For the recovery of sulphur from the leachate produced in a biofilter or biotrickling filter, the ideal recovery would not involve high amounts of energy or chemicals. One possible chemical recovery process was suggested by Wang and his co-workers who showed that H₂S reacts with sulphuric acid at high concentrations to form elemental sulphur that can be harvested (Wang, Dalla Lana et al. 2003).

2.6 Future scope for research

Biological treatment is suitable for the removal of H₂S in WWTP compared to physical and chemical methods, because of the low concentration of H₂S in the air stream and low cost. The amount of sulphur that can be potentially recovered from the leachate of biofilters in WWTP (17.5 kg of S/day) indicates that there is a scope for the development of an aerobic process for the removal of H₂S from contaminated air in WWTP but with production of concentrated
sulphuric acid leachate rather than large volumes of waste streams of weak acid. This can be achieved by intermittently trickling a minimum amount of solution down an upflow biofilter which will wash the ions out of the biofilter and accumulate them at the bottom. This will also create moisture and pH gradient within the biofilter resulting in an environment at the top for the bacterial conversion of H_2S while sulphuric acid will accumulate at the base. Recent studies have shown that a biochemical ammonia removal process, where the amount of water percolating through a biofilter is controlled, can achieve a pH and soluble ion gradient with the production of no leachate (Van Eckstaedt, Ho.G. et al. 2013). In this process, the top of the biofilter encouraged biological conversion of ammonia to nitrate and nitrite while the bottom favoured a chemical reaction of ammonium and nitrite (Van Eckstaedt, Ho.G. et al. 2013). If a biofilter can be developed to incorporate this strategy then the setup will encourage the formation of concentrated sulphuric acid as a usable product.
3.1 Abstract

The chapter describes modelling and bench scale experiments done to ascertain some of the scientific principles that were needed for the development, construction and operation of the novel biofilter. This chapter also describes some of the methodology used to analyse the samples collected during the experiments conducted for this thesis. The proposed biofilter system will produce a minimal amount of leachate while maintaining condition for biological removal of \( \text{H}_2\text{S} \). This will be achieved by controlling the optimum amount of water in the system. An understanding of incoming and outgoing humidity and the relationship to the amount of water a biofilter is modelled in section 3.2. The moisture content is a crucial element of the analysis planned for this biofilter and a method was developed for the determination of moisture and this is explained in section 3.3. A column is constructed for a proof of concept study to test the modelled behaviour of moisture control in the proposed biofilter and formation of a gradient in moisture and is described in section 3.4. The proposed biofilter system is predicted to produce sulphuric acid at concentrations higher than conventional biofilters and the reaction of hydrogen sulphide (\( \text{H}_2\text{S} \)) and sulphuric acid (\( \text{H}_2\text{SO}_4 \)) at high concentrations are examined in section 3.5.
3.2 Modelling of moisture control in a biofilter

The amount of water vapour in air is typically expressed in the form of relative humidity. Relative humidity (RH) is defined as the ratio of the partial pressure of water vapour \( P_{H_2O} \) in a system to the saturated vapour pressure of water \( P^{*}_{H_2O} \) at a given temperature (McCabe, Smith et al. 2001).

\[
\% \text{ RH} = \left( \frac{P_{H_2O}}{P^{*}_{H_2O}} \right) \times 100
\]

The saturated vapour pressure of water is the amount of water held by a parcel of air at a particular temperature just before turning into liquid water (McCabe, Smith et al. 2001). The Clausius-Clapeyron equation, derived from first and second Laws of Thermodynamics, is used to characterize the phase boundary between a liquid and gas phase and can be used to describe the relationship between the saturated vapour pressure above a liquid and the temperature of the liquid (Atkins and De Paula 2010):

\[
p_s = p_0 \cdot \exp \left[ \left( \frac{\Delta H_{\text{vap}}}{R} \right) \cdot \left( \frac{1}{T_0} - \frac{1}{T} \right) \right]
\]

where, \( p_s \) is the saturation vapour pressure,

\( p_0 \) is the pressure at temperature \( T_0 \),

\( H_{\text{vap}} \) is the enthalpy of evaporation,

\( R \) is the universal gas constant,

\( T \) and \( T_0 \) is temperature.

When comparing tabulated values of saturated vapour pressure in the literature (Haynes 2014), with the predicted values of the Clausius-Clapeyron equation, the fit is poor (Figure 3.1). It is common practice to use empirical
equations to determine the saturated vapour pressure of water over air and the most common one used is the Teten equation which gives a better fit to the data and will be used to determine the saturated vapour pressure.

\[ e_s = 610.78 \times \exp\left[17.2694 \cdot \frac{T}{(T+238.3)}\right] \]

where, \( e_s \) is the saturation vapour pressure in kPa,

\( T \) is temperature in Celsius.

Figure 3.1: Saturated vapour pressure of water at different temperature according to the Clausius-Clapeyron equation, the Teten equation and data from literature (Haynes 2014).

The Teten equation is used to model the amount of water that can be lost from a system with an inlet gas flow with lower humidity than the outlet. If the humidity of a gas entering a system is lower than the humidity of gas coming out, then there will be a net loss of moisture from the system. The amount of water lost over time will depend on several factors including the temperature, pressure, flow and humidity of the inlet and outlet gas and the surface area of
the liquid contact to the gas. A simple mathematical model to predict the volume of moisture that can be lost from a system with different inlet humidity under set conditions has been set up for use in this thesis.

**Table 3.1:** Sample calculation from model (Conditions of model: Temperature = 25 °C, Pressure = 1 atm., inlet flow = 1 L/min; Time = 1 hour)

<table>
<thead>
<tr>
<th>% RH of Outlet</th>
<th>% RH of Inlet</th>
<th>Mass of water lost from system</th>
<th>Rate of volume of water loss from system</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>g/m³</td>
<td>mg/min</td>
<td>mL/h</td>
</tr>
<tr>
<td>100</td>
<td>23.02</td>
<td>23.02</td>
<td>13.81</td>
</tr>
<tr>
<td>40</td>
<td>9.21</td>
<td>9.21</td>
<td>0.83</td>
</tr>
</tbody>
</table>

Figure 3.2 shows the amount of volume that is predicted to be lost from the reactor in one hour at different temperatures according to this model. Since the temperature in laboratory conditions will be between 30 to 20 °C, the volume of water needed to replenish this loss water due to the difference in humidity between the inlet and outlet can be predicted. The water lost by the system is the minimum amount of water need to be replenished in order to avoid drying of the biofilter.
Figure 3.2: Model predictions of the effect of different relative humidity of inlet air on water lost from a biofilter (Temperature = 25 °C, Pressure = 1 atm., inlet flow = 1 L/min; Time = 1 hour).

3.3 Determination of moisture content in biofilter

The determination of the moisture content and the concentration of water soluble ions in the different sections of the biofilter are crucial to the analysis of the operation of this biofilter. It is important that the moisture is determined without affecting or destroying the biofilm since the same biofilm will be analysed for water soluble ions (like sulphate and sulphide). If one sample of the medium is taken for moisture analysis and a different sample taken for the ion analysis, then questions may be raised on whether both samples of the media was touched by the trickling water media. This is specially relevant in this system where a very small volume of water will be used to wash the medium. The oven drying method, which is the conventional technique for the
determination of moisture content in a media, destroys the biofilm being measured and this will affect the analysis of water soluble ions if done on the same biofilm. In this study, it is important to determine the volume of water on the medium without destroying the biofilm, so that the water soluble ions can be extracted for later analysis. For this reason, in this study, the moisture content was determined by a simple mass difference method – the moisture content was determined by calculating the difference in mass of the medium with the biofilm on it and the mass of the original dry medium. This can be done because the medium being used, when dry, has a very consistent weight (Mean = 0.2618, SD = 0.0029, n = 20) and the inert medium will not degrade over time. An experiment was done to compare the moisture content determined by the oven-drying method with the moisture content determined by mass difference method. It is important to note that no microbes are introduced at this stage of the experiment.

3.3.1 Materials and Methods

The weight of the sample was determined using the Kern AEJ 220-4M Analytical balance (Kern and Son GmbH). The samples were heated in a Contherm Series 1300 Incubator (Contherm Scientific Ltd.). Sample pieces of AMB Biomedia Bioballs (ABB media), a commercially available polyethylene packing material, used in this study was previously washed with detergent, 10% nitric acid, rinsed with distilled water and air dried before use.
Oven-Dry method: 10 pieces of previously dried ABB media was washed with distilled water and the water from the media was allowed to drain. The weight of the wet media was recorded and is shown as an average in Table 3.2. The media was heated to 100° C in the incubator for four hours, cooled in a desiccator to room temperature and the weight determined. The media is again heated and weighed till the difference in weight is less than 0.01%. The weight of the dry medium was recorded and is shown as an average in Table 3.2.

\[
\text{Moisture content (g/g)} = \frac{\text{(Mass of wet medium} - \text{Mass of dry medium)}}{\text{(Mass of dry medium)}}
\]

Mass difference method: 10 pieces of previously dried ABB media was taken and their weights recorded. The media was washed with distilled water and was allowed to drain and the weight of the wet media was recorded and is shown as an average in Table 3.2. This is compared to the original weight of the dried ABB media.

\[
\text{Moisture content (g/g)} = \frac{\text{(Mass of wet medium} - \text{Mass of dry medium)}}{\text{(Mass of original dry)}}
\]
3.3.2 Results and Discussion

Table 3.2 gives the moisture content determined by the oven-dry method and the mass difference method.

**Table 3.2: Comparison between the oven-dry method and the mass difference method**

<table>
<thead>
<tr>
<th>Method</th>
<th>Average Mass of dry media</th>
<th>Standard Deviation</th>
<th>Average Mass of wet media</th>
<th>Standard Deviation</th>
<th>Mean moisture content g/g</th>
<th>Standard deviation of moisture content</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oven dry</td>
<td>0.2617</td>
<td>0.0028</td>
<td>0.3485</td>
<td>0.0507</td>
<td>0.3320</td>
<td>0.1917</td>
</tr>
<tr>
<td>Mass difference</td>
<td>0.2618</td>
<td>0.0029</td>
<td>0.3934</td>
<td>0.0425</td>
<td>0.2516</td>
<td>0.1103</td>
</tr>
</tbody>
</table>

A Student's t-test was used to compare the mean moisture content determined by the oven-dry method and the mass difference method. The two-tailed P value equals 0.1123 and this difference is considered to be not statistically significant at $P < 0.01$. The average moisture content determined by the oven dry method does not differ significantly from the moisture content determined by the mass difference method.

3.4 Establishment of gradient of moisture content in biofilter

The model described in section 3.2 predicts the amount of water that will be lost from a system due to the humidity of the air entering a biofilter. The amount
of water in the biofilter, or the moisture content of the medium supporting the biofilm, is one of the most important parameters in a biofilter (Williams and Miller 1992, McNevin and Barford 2000, Easter, Quigley et al. 2005). If the moisture content of the medium in the biofilter is too low, then it will hamper the performance of the activity of the biofilm (Easter, Quigley et al. 2005, Iranpour, Coxa et al. 2005, Shareefdeen and Singh 2005). The volume of water that will be added to the proposed biofilter will be calculated based on the model to maintain steady moisture content in all parts of the biofilter. Since the biofilter is being designed to operate for an extended period of time, it is important to examine whether this modelled volume does in reality provide a steady and adequate gradient of moisture in the biofilter. This must be done before seeding the biofilter with a biological medium (like activated sludge) to avoid unnecessary drying up of the biofilter and loss of biofilm which will only lead to renewed start-up of the experiment.

The objective of this experiment is to monitor the moisture content of the media under the conditions of the experiment involving the proposed biofilter. Therefore, a column was constructed that will be used later during the experiments involving biofiltration. It is important to note that no microbes are introduced at this stage of the experiment.

3.3.1 Column for experiment

A column was constructed with PVC piping (Holman Industries) with an internal diameter of 5.5 cm. The column had three detachable sections (the
top, middle and bottom sections) and a detachable glass measuring cylinder at the bottom for the collection of leachate with dimension as shown in Figure 3.3. The sections were filled with equal amounts of a polyethylene packing material called AMB Biomedia Bioballs (ABB media) washed in distilled water. The sections were filled with the wet ABB media to a height of 13.0 cm in each section giving a total working volume of 308.86 cm³ or 0.309 L for each section.

**Figure 3.3:** Diagram of the biofilter without biofilm (column)
The bed volume of the media in the column was 0.93 L. The flow rate for the inlet gas is set at 0.9 L/min to ensure that the media has a contact time of 1 minute. The packing material in each section was supported by sieve plates made of acid resistant Plexiglas which also operated as a separator for each section. A peristaltic pump (Masterflex C/L Dual-Channel Variable-Speed Tubing Pump, Cole Palmer Instrument Company) was used to control the amount of distilled water delivered to the top of the column. The timing of the delivery by the pump was controlled using a simple on-off controller implemented by the LabView™ (version 7.1) controlled computer. The humidity of the inlet air supplied under laboratory conditions was monitored using the HOBO Pro v2 external temp/RH probe and data logger (Onset Computer Corp.).

3.3.2 Sampling and measurement

10 pieces of ABB media was randomly chosen from each section. The moisture content in each section was determined by the mass difference method as given in Section 3.3 and expressed as the gravimetric water content:

\[ M_n = \frac{M_w}{M_0} \]

where, \( M_n \) is the moisture content, 
\( M_w \) is the mass of medium with water 
\( M_0 \) is the mass of the medium without water
3.3.3 Results and Discussion

After allowing the excess water in the wet ABB media in the column to drain out, the initial moisture content in the medium was measured (Time “0” in Figure 3.4). The inlet air is then allowed to flow through the column. The %RH measured in the inlet air had an average value of 40.378 % (SD = 3.120 %.) and the outlet moisture content had an average value of 99.547 % (SD = 2.054 %.). Using the model described in Section 3.2, the amount of moisture that will be lost from the column in these conditions is 0.74 mL/h.

It is important to remember that the proposed biofilter system is being designed to produce a minimal amount of leachate while maintaining the conditions for biological removal of H₂S. The amount of water added to the biofilter will not only compensate for the volume of water lost due to the difference in relative humidity of the inlet and outlet but also be sufficient to wash down the water soluble ions down the biofilter. This is a crucial part of the design as the idea is to accumulate all the sulphate in the biofilter formed by the biological oxidation of H₂S into the smallest possible volume of leachate leading to a concentrated solution. Based on the dimensions of the column setup (Section 3.3.1) and preliminary experiment, 3mL of water was determined as the minimum volume of water required to wash down this column. This volume for the wash down was confirmed once again during the full operation with the microbes present where the sulphate being produced in the biofilter was washed down to the bottom during the operation of the lab scale biofilter described in Chapter 4. It was decided that 3mL of water will be
introduced to this column every 4 hours to facilitate the wash down of ions formed in the biofilter. The volume of water entering the column (3 mL) will be just enough to compensate for the water lost by evaporation (2.96 mL) during the 4 hours. In the preliminary experiment, the “top up” water was supplied to the biofilter from the top and the moisture content of the sections over a 12 hour period is given in Figure 3.4.

![Figure 3.4: Moisture content of medium in each section](image)

The results show that the column starts with all three sections having the similar moisture content (0.5280, 0.5821 and 0.4939 g/g in the top, middle and bottom sections respectively). As dry air entered the column from the bottom, the bottom section started to dry up leading to a decrease in the moisture content in this section. After every 4 hours, when the “top-up” water is added, water trickles down the column and there is an increase in the moisture content of the bottom section. The bottom section never completely dries out and the
top and the middle sections maintain their moisture content during this period providing a steady moisture environment for the biological activity to take place in these sections of the proposed biofilter.

3.5 Reaction of Hydrogen sulphide with Sulphuric Acid

Since the suggested biofilter was expected to produce sulphuric acid, it was important to determine the maximum concentration of sulphuric acid that can be produced in this biofilter which has an inlet relative humidity of around 40%. Sulphuric acid is known to be a dehydrating agent at high concentrations and the concentration of sulphuric acid at a specific temperature depends on the interphase moisture content (relative humidity). The water vapour concentration in equilibrium with different concentrations of sulphuric acid at 25 °C and 1 atm. adapted from the literature (Perry and Chilton 1973) is summarised in Figure 3.5.

![Figure 3.5: Water vapour concentration in equilibrium at different concentrations of sulphuric acid.](image_url)
With a relative humidity of around 40\% in the inlet air, the maximum concentration of sulphuric acid than can be expected from the biofilter is a little above 6M. At high concentrations, it is known that H\textsubscript{2}SO\textsubscript{4} can react with H\textsubscript{2}S to form elemental sulphur (Zhang, Dalla Lana et al. 2000, Wang, Dalla Lana et al. 2002, Wang, Dalla Lana et al. 2003). It was necessary to investigate the possibility of a chemical reaction of H\textsubscript{2}S and the H\textsubscript{2}SO\textsubscript{4} at this concentration that may be generated by the proposed biofilter.

At pH greater than 6, most of the H\textsubscript{2}S exists as HS\textsuperscript{-} (Figure 2.4) and there have been several studies of the reaction of H\textsubscript{2}S with H\textsubscript{2}SO\textsubscript{4} at pH greater than 6 (Chen and Morris 1972, Jolley and Forster 1985, Wilmot, Cadee et al. 1988, Buisman, Geraats et al. 1990). The major products of this reaction are solid sulphur, thiosulphate, sulphate or polysulphides and the form of the final product depends on the oxygen concentration and H\textsubscript{2}S loading rates (Chen and Morris 1972). There is a wide variety of rate expressions and rate laws in the literature for the oxidation of H\textsubscript{2}S in solutions in this pH range and the rate constant, k in the literature ranges from as low as 2.8 \times 10^{-7} \text{ mol/L/min} to as high as 67.6 \text{ mol/L/min} (Chen and Morris 1972, Jolley and Forster 1985, Wilmot, Cadee et al. 1988, Buisman, Geraats et al. 1990).

There have been fewer studies on the chemical reaction of H\textsubscript{2}S and H\textsubscript{2}SO\textsubscript{4} where the concentration of the acid is greater than 1M (Zhang, Dalla Lana et al. 2000, Wang, Dalla Lana et al. 2002, Wang, Dalla Lana et al. 2003). H\textsubscript{2}S has been shown to react with H\textsubscript{2}SO\textsubscript{4} concentrations greater than 5.6M to form
elemental sulphur (Zhang, Dalla Lana et al. 2000). The following overall reaction has been proposed in this study for the production of elemental sulphur (Zhang, Dalla Lana et al. 2000):

$$3 \text{H}_2\text{S} + \text{H}_2\text{SO}_4 \rightarrow 4 \text{S} + 4\text{H}_2\text{O}$$

Kinetic studies have shown that for acid concentrations greater than 16.5 M, the reaction is first order with respect to H$_2$S (Wang, Dalla Lana et al. 2002). The general rate expression for the reaction in this study is

$$R = k P_{\text{H}_2\text{S}}$$

where, R is the rate law,

$$k$$ is the rate constant,

$$P_{\text{H}_2\text{S}}$$ is the pressure of H$_2$S

In this study Wang and his co-workers found a rate constant, $k$ of $1.4 \times 10^{-4}$ mol/L/min. However, the authors noted that their particular experimental setup was unsuitable for detecting reaction rates for acids below 16.5M.

In order to determine the feasibility of the reaction of H$_2$S with sulphuric acid at lower concentrations of acid, a series of bench scale experiments to investigate the reaction of H$_2$S and H$_2$SO$_4$ at different concentrations of acid and H$_2$S were conducted and is described below. At this stage, it is important to note that the term “concentrated acid” encompasses a wide range of concentrations in the literature and in this section of the thesis, the concentrations of the acid will be explicitly mentioned and the use of the term
“concentrated acid” or “dilute acid” will be avoided.

3.5.1 Materials and Methods

In the first batch experiment, 120 mL air-tight serum bottles sealed with rubber bungs were flushed with 1% of \( \text{H}_2\text{S} \) in \( \text{N}_2 \). Duplicate bottles were injected with 30mL of sulphuric acid with concentrations of 6M, 12M and 18M respectively and stirred with a magnetic stirrer. 0.2mL sample of the headspace of the serum bottles was withdrawn at each time interval by means of a syringe and the amount of \( \text{H}_2\text{S} \) determined using GD 2529 Hydrogen Sulphide Sensor (GasTech Australia Pty. Ltd.). A bottle with 10.2M HCl and 1% \( \text{H}_2\text{S} \) was used as negative control.

In the second batch experiment, 30mL of 6M sulphuric acid was injected into 120 mL serum bottles sealed with rubber bungs. Duplicate bottles were flushed with 1%, 0.5% and 0.1% \( \text{H}_2\text{S} \) in \( \text{N}_2 \) and stirred with a magnetic stirrer. 0.2mL sample of the headspace of the serum bottles was withdrawn at each time interval by means of a syringe and the amount of \( \text{H}_2\text{S} \) determined using GD 2529 Hydrogen Sulphide Sensor (Accuracy: 0.5%; GasTech Australia Pty. Ltd.). A bottle with 10.2M HCl and 1% \( \text{H}_2\text{S} \) was used as negative control.

3.5.2 Results and Discussion

The results of the first batch experiment are presented in Figure 3.6. There was no reaction between \( \text{H}_2\text{S} \) in the headspace and the negative control (HCl) which confirms that very little \( \text{H}_2\text{S} \) will be absorbed into a solution with such a
low pH as predicted in Figure 2.4. When sulphuric acid is used, there is an initial decrease (between 0 min and 5 min in Figure 3.6) in the amount of H₂S in the headspace and the rate of decrease increases with increasing H₂SO₄ concentration.

![Graph showing reaction of H₂S with different concentrations of H₂SO₄](image)

**Figure 3.6:** Reaction of H₂S with different concentrations of H₂SO₄

This indicates that there is a reaction between H₂S and sulphuric acid. The initial rate of decrease in H₂S (between 0 min and 5 min in Figure 3.6) is calculated and is summarised in Table 3.3.
Table 3.3: Experimentally determined initial rate of disappearance of H$_2$S at different concentrations of acid

<table>
<thead>
<tr>
<th>H$_2$SO$_4$ concentration</th>
<th>Rate of disappearance of H$_2$S</th>
</tr>
</thead>
<tbody>
<tr>
<td>M</td>
<td>mol/L/min</td>
</tr>
<tr>
<td>0</td>
<td>$4.3 \times 10^{-6}$</td>
</tr>
<tr>
<td>6</td>
<td>$4.6 \times 10^{-5}$</td>
</tr>
<tr>
<td>9</td>
<td>$5.0 \times 10^{-5}$</td>
</tr>
<tr>
<td>18</td>
<td>$1.1 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

The rate of disappearance of H$_2$S is higher for 18M sulphuric acid compared to the 9M and 6M acid which show similar reaction rates. After 4 hours (not shown in the graph), the amount of H$_2$S in the headspace had reached a steady state concentration of 0.034mmol for the blank, 0.002mmol for the 15M acid, 0.016mmol for the 10M acid and 0.024mmol for the 5M acid. This indicated that after the initial drop in H$_2$S concentration, there was no appreciable reduction in H$_2$S in the headspace. The results seem to indicate that at the acid concentrations expected in the proposed biofilter (6M), it is feasible that there will be the reaction of H$_2$S with H$_2$SO$_4$. 
Interestingly, results from the second batch experiment (Figure 3.7) showed that the concentration of H$_2$S had little bearing on the rate of the reaction of H$_2$S with H$_2$SO$_4$. This is important because this indicates that in the proposed biofilter, the inlet concentrations of H$_2$S will not be a factor for the reaction between H$_2$S and concentrated H$_2$SO$_4$. 

**Figure 3.7**: Reaction of H$_2$SO$_4$ with different concentrations of H$_2$S
Chapter 4: Biofilter for the removal of H$_2$S and generation of concentrated sulphuric acid

4.1 Abstract

Fixed-film biofilters with chemotrophic bacteria are suitable for conversion of odorous hydrogen sulphide (H$_2$S) to odourless sulphate (SO$_4^{2-}$) in wastewater treatment plants under the right conditions of moisture and pH. One of the consequences of maintaining the suitable pH and moisture content in the biofilter is the production of large volumes of weakly acidic leachate. This chapter presents a biofilter for the removal of H$_2$S that produces small volumes (1 mL of solution/L of reactor/day) of sulphuric acid of up to 6M after 150 days of continuous operation. This was achieved by intermittently trickling a minimum amount of nutrient solution down the upflow biofilter which created a moisture and pH gradient within the biofilter resulting in an environment at the top for the bacterial conversion of H$_2$S while sulphuric acid was accumulated at the base. Genetic diversity profiling of samples taken from different sections of the biofilter confirm that the upper sections of the biofilter had the best environment for the bacteria to convert H$_2$S to sulphate. The maximum elimination capacity of the biofilter was 16.3 g/m$^3$/h and the removal efficiency of the biofilter was 98.8% for H$_2$S. The formation of concentrated sulphuric acid presents an opportunity for the recovery of sulphur from the waste stream as a usable product.
4.2 Introduction

Domestic sewage contains organic sulphur, sulphonates and inorganic sulphur (as sulphates) which all act as a source of hydrogen sulphide (Gostelow, Parsons et al. 2001, Carrera-Chapela, Donoso-Bravo et al. 2014). Hydrogen sulphide is a colourless and toxic gas that is considered a broad spectrum poison and affects the nervous system among other organs (Burgess, Parsons et al. 2001, Guidotti 2010). It has a characteristic smell of rotten eggs which can be detected by the human nose at concentrations as low as 10 ppb. Typical concentrations of H$_2$S emanating from wastewater treatment plants range from 5 to 100 ppm (Churchill and Elmer 1999, Stanley and Muller 2002). Removal of hydrogen sulphide is considered the most dominant odour control requirement from wastewater (Gostelow, Parsons et al. 2001). Biofilters are becoming common as a treatment for H$_2$S emanating from wastewater or sewage treatment plants (McNevin and Barford 2000, Dumont, Andres et al. 2008, Mudliar, Giri et al. 2010, Lebrero, Gondim et al. 2014). Biofilters use biofilm - microorganisms immobilised on the surface of porous media that degrade the pollutants to oxidised and often less harmful compounds. In biofilters contaminated air flows up through the media and a continuous stream of water trickles down the media to keep the biofilms moist and biologically active. The pollutants in the air come in contact with the active biofilms and are degraded to harmless products. The advantages of biofilters are that they work at ambient temperatures and pressure and have low capital costs. The disadvantage of biofilters is that the microorganisms require sufficient moisture, nutrients and a suitable pH (Mudliar, Giri et al. 2010). In
the case of biofilters used to remove hydrogen sulphide in an aerobic environment, the overall biological reaction that occurs is given below (Oyarzun, Arancibia et al. 2003, Wang, Dalla Lana et al. 2003):

\[ \text{H}_2\text{S} + 2\text{O}_2 \rightarrow \text{SO}_4^{2-} + 2\text{H}^+ \]  \hspace{1cm} \text{Equation 1}

H\textsubscript{2}S can be oxidised to either elemental sulphur or SO\textsubscript{4}\textsuperscript{2-} depending on the ratio of H\textsubscript{2}S to O\textsubscript{2} in the treated air (Jensen and Webb 1995, Chaiprapat, Mardthing et al. 2011, Montebello, Mora et al. 2014). In their study of aerobic acidic biofilters for the removal of H\textsubscript{2}S, Chaiprapat and his co-workers (Chaiprapat, Mardthing et al. 2011) showed that the highest efficiency of conversion of H\textsubscript{2}S to sulphate or sulphuric acid was when the H\textsubscript{2}S to O\textsubscript{2} ratio was 1:4. If the oxygen is supplied in a limited amount, incomplete oxidation of H\textsubscript{2}S occurred to produce elemental sulphur. Examples of microorganisms that can oxidise H\textsubscript{2}S include *Thiobacillus denitrificans*, *Thiobacillus thioparus* and *Acidithiobacillus thiooxidans*. The pH range for optimal growth of *T. denitrificans* is 6.8 to 7.4, *T. thioparus* is 5.5 - 7.0 and *A. thiooxidans* is 1.8 - 2.5 (Aroca, Urrutia et al. 2007, Lors, Chehade et al. 2009, Solcia, Ramirez et al. 2014). However, studies have shown that the production of sulphuric acid by these microorganisms can drop the pH in the biofilter to below 1 and *A. thiooxidans* has been shown to operate even at a pH of 0.2 (Lors, Chehade et al. 2009, Solcia, Ramirez et al. 2014). A common strategy to control pH in conventional biofilters is to wash out the accumulated acidity in the biofilm with a buffered media or chemicals like sodium hydroxide or calcium carbonate (Shareefdeen, Herner et al. 2003, Jover, Ramirez et al. 2012, Solcia, Ramirez et al. 2014).
et al. 2014). This leads to production of as much as 2,000 mL/L/day of neutral or slightly acidic leachate (pH = 2) which is treated as waste and requires proper disposal (Abdehagh, Namini et al. 2011, Chaiprapat, Mardthing et al. 2011, Park, Evans et al. 2011, Solcia, Ramirez et al. 2014).

Removal and recovery of elemental sulphur from coal, natural gas and high sulphur crude oils is well-recognized processes, but recovery of sulphur from dilute streams of acid from wastewater treatment plants has not been previously attempted (Babich and Moulijn 2003, Bachmann, Johnson et al. 2014, Shu, Sun et al. 2014, Jiang, Zhu et al. 2015, Meshram, Purohit et al. 2015). Dilute sulphuric acid solutions produced in industry are concentrated by energy intensive processes using high temperature conversion of acid to sulphur dioxide and subsequent catalytic conversion of sulphur dioxide to concentrated sulphuric acid (Smith and Mantius 1978). Dilute sulphuric acid has also been concentrated in laboratory scale evaporators, where droplets of dilute sulphuric acid undergo a loss in water by evaporation to produce acid with concentrations of as much as 14M (Zhou and Liu 2007). A recent study has shown that it is possible to remove high concentrations of hydrogen sulphide using a biofilter even under extreme acidic conditions (pH < 1) (Ben Jaber, Couvert et al. 2016). The elimination efficiency decreased with increasing acidity and the maximum elimination capacity of the biofilter was 24.7 g/m3/h (Ben Jaber, Couvert et al. 2016). Another study has shown that in a biochemical ammonia removal process, where the amount of water percolating through the biofilter is controlled, a pH and soluble ion gradient can be achieved in a biofilter with the production of no leachate (Van Eckstaedt, Ho.G. et al. 2013). In this patented process, the top of the biofilter encouraged
biological conversion of ammonia to nitrate and nitrite while the bottom favoured a chemical reaction of ammonium and nitrite which is only possible at high concentrations (Van Eckstaedt, Ho.G. et al. 2013).

Gold-film based sensors, where H$_2$S molecules are absorbed into a thin gold film, are one of the most common sensors for the measurement of H$_2$S (Yoo, Sorensen et al. 1994, Stuetz and Frechen 2001, Cox, Deshusses et al. 2002, Gabriel, Cox et al. 2004). They are used extensively in experiments where H$_2$S is the sole source of sulphur, but because reduced sulphur compounds can also be adsorbed onto a gold film, the sensor is susceptible to interference from other reduced sulphur compounds in air (Yoo, Sorensen et al. 1994, Stuetz and Frechen 2001). A study on a typical gold-film sensor showed that the sensors showed excellent response to H$_2$S and also responded to a series of reduced sulphur compounds, including methyl marcaptan, dimethyl sulphide and carbon disulphide (Winegar and Schmidt 1998). However, the lower response factors and lower abundance of reduced sulphides in gas samples mean that golf-film based sensors are suitable for quantitative detection of hydrogen sulphide (Winegar and Schmidt 1998). Gold-film based sensors are suitable for lab scale biofilter studies where the only source of sulphur is H$_2$S but they have also been used in pilot scale or full scale studies (Lipták 1995, Cox, Deshusses et al. 2002, Gabriel, Cox et al. 2004).

This chapter proposes an aerobic biofilter for the removal of H$_2$S producing a small amount of concentrated sulphuric acid. A moisture and pH gradient is
maintained in the biofilter by adding a minimal amount of solution to the top of the biofilter, so that the top section is favourable for the growth of microorganisms while the bottom accumulates sulphuric acid. This setup encourages sulphur recovery rather than producing waste streams of diluted sulphuric acid.

4.3 Materials and Methods

4.3.1 Experimental Setup

The investigation was carried out in a lab-sale up flow biofilter and the schematic of the experimental setup is given in Figure 4.1. H₂S was supplied to the reactor using Tedlar gas sampling bags (CEL Scientific Corp.) made of DuPont’s 2mil Tedlar PVF film with PTFE fittings which were non-reactive to hydrogen sulphide (CPLabSafety, DuPont). Concentrated H₂S in the Tedlar bag was dosed using a peristaltic pump (Masterflex L/S economy variable-speed drive, Cole-Palmer Instrument Company) into the pressure regulated laboratory compressed air leading to the biofilter. The flow rate of the peristaltic pump was adjusted to attain the desired H₂S concentration and the flow rate never exceeded more than 0.1L/min. This was done to ensure that the oxygen to H₂S ratio entering the biofilter was always high and there is an aerobic environment during the operation of the biofilter. The Tedlar bags, stored at room temperature was changed every 30 hours and the H₂S concentration and humidity of the gas entering the biofilter was measured in real time.
Figure 4.1: Schematic diagram of experimental setup

4.3.2 Biofilter column

The biofilter was constructed from acid-proof PVC piping (Holman Industries) with an internal diameter of 5.5 cm. The biofilter had three detachable sections (the top, middle and bottom sections as shown in Figure 4.1) and a glass flask at the bottom for the collection of acidic product. Each section was filled with equal amounts of acid resistant polyethylene packing material (AMB Biomedia Bioballs (ABB media)). The sections were filled with the ABB media to a height of 13.0 cm in each section giving a total working volume of 308.86 cm$^3$ or 0.309L for each section. The packing material in each section was supported by sieve plates made of Plexiglas. Empty Bed Residence Time (EBRT) is the time that a gaseous pollutant spends in a biofilter and is defined as the bed
volume of the reactor divided by the air flow rate (Shareefdeen and Singh 2005). In this system, the bed volume was 0.926 L and the flow rate was set at 0.9 L/min giving an EBRT of 1.03 min.

4.3.3 Seeding procedure

At the start of the study period, the biofilter was seeded with a mixture containing 1L of activated sludge (sourced from a local wastewater treatment facility in Woodman Point, Perth) and 1L of nutrient solution with the following composition modified from the *Thiobacillus novellus* medium as described in Atlas (2005): KH$_2$PO$_4$ (4.0g), K$_2$HPO$_4$ (1.5g), MgCl$_2$.6H$_2$O (0.2g), NH$_4$Cl (0.1g) and 10mL of trace metal solutions (Na$_2$EDTA 50 g/L, NaOH 11g/L, CaCl$_2$.2H$_2$O 7.34g/L, FeCl$_2$, MnCl$_2$.7H$_2$O 2.5g/L, ZnCl$_2$, CoCl$_2$.6H$_2$O 0.5g/L, (NH$_4$)$_6$Mo$_7$O$_{24}$.4H$_2$O 0.5g/L, CuCl$_2$). To ensure that the incoming H$_2$S was the only source of sulphur in the biofilters, there was no thiosulphate or sulphate in the nutrient solution. The magnesium sulphate, ammonium sulphate, zinc sulphate and copper sulphate were replaced with equimolar amounts of the respective metal chlorides. After the initial incubation period, a peristaltic pump (Masterflex C/L Dual-Channel Variable-Speed Tubing Pump, Cole Palmer Instrument Company) was used to control the amount of this nutrient delivered to the top of the column. The timing of the delivery by the pump was controlled by a connected computer using a Labjack USB interface and National Instruments LabView 7.1 control software.
4.3.4 Sampling and chemical analysis

The H$_2$S concentration was measured in real time by means of an inline sensor (GD 2529 Hydrogen Sulphide Sensor, GasTech Australia Pty. Ltd) which was calibrated against a Calgaz 100ppm Hydrogen Sulphide (H$_2$S) calibration gas cylinder with nitrogen balance (Air Liquide). The sensor output was converted to H$_2$S concentration by means of a calibration curve and an example is provided in Appendix D.2. Humidity and temperature of the gas mixture were measured using the HOBO Pro v2 external temp/RH probe and data logger (Onsetcomp). Five pieces of randomly chosen ABB media was used to determine the moisture content in the different sections of the biofilter and was expressed as the gravimetric water content:

\[ M_n = \frac{M_w}{M_o} \]

where, \( M_n \) is the moisture content,
\( M_w \) is the mass of medium with water
\( M_o \) is the mass of the medium without water

The concentration of sulphate, sulphide, thiosulphate, elemental sulphur and hydrogen ion concentration were also determined in the different sections of the biofilter. The previously mentioned five pieces of randomly chosen ABB media was added to 10mL of distilled deionized water in a 30mL glass vial and shaken for 10 minutes. Triplicate samples of 1mL solution with the extracted water soluble ions were then analysed for sulphate (SO$_4^{2-}$), sulphide (HS$^-$),
thiosulphate ($S_2O_3^{2-}$), elemental sulphur (S) and hydrogen ion ($H^+$) concentration.

Sulphate was determined based on precipitation as $BaSO_4$ followed by photo spectrometric quantitation at 420nm with the HACH DR 2700 Portable Spectrophotometer (Rice and Bridgewater 2012). Sulphide ($HS^-$) was determined based on the reaction of copper sulphate ($CuSO_4$) in an acidic solution producing CuS precipitate which was measured photometrically at 480 nm (Cord-Ruwisch 1985). Thiosulphate ($S_2O_3^{2-}$) was determined based on the standard method for the standardisation of sodium thiosulphate with potassium iodate (Vogel and Mendham 2000). Elemental sulphur was determined using extraction with chloroform and HPLC analysis (Henshaw, Bewtra et al. 1997). 0.8 mL chloroform (ChemSupply) and 0.2 mL of 10% nitric acid were added to 1 mL sample and shaken for 15 minutes. The tube was then centrifuged at 1350 rpm for 5 minutes. The bottom 0.5 mL chloroform layer was added to 1mL of methanol and injected into Agilent 1200 HPLC Liquid Chromatography System with an Eclipse DB C-18 column (4.6 X 150mm) with a diode array and multiple wavelength detector set at 254 nm. The eluent was HPLC grade methanol (Honeywell Burdick & Jackson) at a flow rate of 1.5 mL/min. The pH of the medium was determined by titration with NaOH using methyl orange as an indicator.
4.4 Results and Discussion

The objective of the biofilter was the removal of H\textsubscript{2}S from the air with the generation of a small volume of concentrated acid leachate. The key findings of this study with regard to our objective will be discussed first (section 4.4.1., 4.4.2, 4.4.3) and subsequent details of the process in the biofilter will be discussed next (section 4.4.4, 4.4.5, 4.4.6).

4.4.1 Removal of H\textsubscript{2}S from the inlet air

The biofilter initially operated continuously for more than 24 weeks with H\textsubscript{2}S in the inlet air. Inlet mass load (ML\textsubscript{i}) is the quantity of pollutant that enters the system and is defined as the product of flow rate (F\textsubscript{R}) and concentration of pollutant entering the biofilter (C\textsubscript{IN}) divided by the reactor volume (Shareefdeen and Singh 2005):

\[
\text{ML}_i = \frac{\text{F}_R \times \text{C}_{\text{IN}}}{V_R}
\]

where, ML\textsubscript{i} is the inlet mass load,
F\textsubscript{R} is the airflow rate,
C\textsubscript{IN} is the inlet pollutant concentration,
V\textsubscript{R} is the bed volume of the reactor.

During the first 17 weeks of the operation of the biofilter, the inlet mass loading of H\textsubscript{2}S varied between 0.14 to 0.12 g/m\textsuperscript{3}/min (102 to 87 ppm/min) (Figure 4.2). Removal Efficiency (RE) is a measure of how effective the biofilter is at removing the pollutant (Shareefdeen and Singh 2005):
RE = \left(\frac{C_{IN} - C_{OUT}}{C_{IN}}\right) \times 100 \quad \text{where, RE is the removal efficiency,}
\text{C}_{IN} \text{ is the inlet pollutant concentration,}
\text{C}_{OUT} \text{ is the outlet pollutant concentration.}

After an initial seven day incubation period, the removal efficiency of H$_2$S was continuously greater than 95% for the first 17 weeks, indicating that the biofilter was removing H$_2$S from the contaminated air. The mass loading was stepped up to between 0.30 to 0.25 g/m$^3$/min (216 to 177 ppm/min) from week 17 to week 22 by increasing the amount of dosing of H$_2$S from the Tedlar bag (Figure 4.2). After an initial decline in removal efficiency to 35%, the response of the biofilter was rapid as the removal efficiency reached 95% within 4 days of continued operation under the same conditions. Finally the mass loading was stepped up to greater than 0.54 g/m$^3$/min (380 ppm/min) after week 22 (Figure 4.2). The removal efficiency at this stage reduced to less than 10% and did not improve after more than 10 days of continued operation under the same conditions indicating that biological oxidation had ceased in the biofilter.
Figure 4.2: $\text{H}_2\text{S}$ concentration in the inlet and the outlet of the biofilter during the study period.

The parameters for this biofilter are summarised in Table 4.1. Some of the parameters used in the table that have not been defined are the Volumetric Load and Elimination Capacity. Volumetric Load ($V_L$) is a term used to normalize the volume of air entering the system and is defined as the airflow rate ($F_R$) divided by the volume of the reactor ($V_R$) (Shareefdeen and Singh 2005). Elimination capacity (EC) is the mass of pollutant removed by the biofilter ($C_{\text{IN}} - C_{\text{OUT}}$) and normalized for the flow rate and the volume of the reactor (Shareefdeen and Singh 2005) and is defined as –

$$EC = \frac{F_R \times (C_{\text{IN}} - C_{\text{OUT}})}{V_R}$$

where, EC is elimination capacity,

$F_R$ is the airflow rate,

$V_R$ is the bed volume of the reactor.
\( C_{IN} \) is the inlet pollutant concentration, \\
\( C_{OUT} \) is the outlet pollutant concentration.

### Table 4.1: Relevant parameters during the operation of biofilter.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Week 1 – 17</th>
<th>Week 17 – 22</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average ( \text{H}_2\text{S} ) concentration of inlet air</td>
<td>0.14 g/m(^3)</td>
<td>0.28 g/m(^3)</td>
</tr>
<tr>
<td>Volume of reactor</td>
<td>0.00093 m(^3)</td>
<td>0.00093 m(^3)</td>
</tr>
<tr>
<td>Inlet Flow rate</td>
<td>0.0009 m(^3)/min</td>
<td>0.0009 m(^3)/min</td>
</tr>
<tr>
<td>EBRT</td>
<td>1.03 min</td>
<td>1.03 min</td>
</tr>
<tr>
<td>Volumetric Load</td>
<td>0.97 m(^3)/m(^3)/min (^a)</td>
<td>0.97 m(^3)/m(^3)/min (^a)</td>
</tr>
<tr>
<td>Inlet mass load</td>
<td>0.13 g/m(^3)/min (^b)</td>
<td>0.27 g/m(^3)/min (^b)</td>
</tr>
<tr>
<td>Elimination capacity</td>
<td>7.6 g/m(^3)/h (0.13 g/m(^3)/min) (^c)</td>
<td>16.3 g/m(^3)/h (0.27 g/m(^3)/min) (^c)</td>
</tr>
<tr>
<td>Removal Efficiency</td>
<td>95.55%</td>
<td>98.82%</td>
</tr>
</tbody>
</table>

\(^a\) m\(^3\)/m\(^3\)/min refers to \(m\(^3\)\) of air flow/m\(^3\) of reactor volume per minute  
\(^b\) g/m\(^3\)/min refers to gram of \(\text{H}_2\text{S}\)/ m\(^3\) of reactor per minute  
\(^c\) both the units of g/m\(^3\)/h and g/m\(^3\)/min are common in the literature

There is a wide range of elimination capacities (8 g/m\(^3\)/h to 22 g/m\(^3\)/h) in the literature for biofilters that remove \(\text{H}_2\text{S}\) based on different operating conditions and types of support medium (Converse, Schroeder et al. 2003, Kim, Rene et al. 2008, Chaiprapat, Mardthing et al. 2011, Park, Evans et al. 2011, Roshani, Torkian et al. 2012, Solcia, Ramirez et al. 2014). For the biofilter described in this chapter, the maximum elimination capacity was 16.3 g/m\(^3\)/h which is within the range of similar lab scale biofilters (Converse, Schroeder et al. 2003, Kim, Rene et al. 2008, Chaiprapat, Mardthing et al. 2011, Park, Evans et al. 2011, Roshani, Torkian et al. 2012, Solcia, Ramirez et al. 2014).
The pressure drop in the biofilter was periodically measured during the course of the operation of the biofilters with an in-house water differential manometer and the change was found negligible. Pressure drop occurs in biofilters due to excessive growth of biomass or the compaction and breakdown of the medium (like soil or wood chips) leading to a reduction in the porosity of the medium (Yang and Allen 1994, Chung, Huang et al. 2001, Elias, Barona et al. 2002, Kennes and Veiga 2002, Kim, Rene et al. 2008). No excessive biomass growth was noticed during the operation of the biofilter and the maximum pressure drop in this biofilter was 0.0375 cm H₂O/m filter bed. This value is lower than the pressure drop in conventional biofilters treating H₂S (Yang and Allen 1994, Chung, Huang et al. 2001, Elias, Barona et al. 2002, Kim, Rene et al. 2008). In this biofilter, the inert plastic medium did not breakdown and maintained its porosity. The conversion of H₂S to H₂SO₄ is dependent on the ratio of H₂S and O₂ and since the intention of this study is to harvest H₂SO₄, it was important to avoid the formation of anaerobic zones inside the biofilter (Jensen and Webb 1995, Chaiprapat, Mardthing et al. 2011).

4.4.2 Production of leachate

One of the objectives of this biofilter is the production of a minimum amount of leachate and since the amount of leachate produced in the biofilter is dependent on the humidity of the air, both the humidity of the incoming air and the outgoing air from the biofilter was monitored using the HOBO Pro v2 external temp/RH probe and data logger (Onset Computer Corp.). The inlet gas had an average relative humidity of 44% (10.15 g/m³ at 25º C) during this
study period and as the gas travelled up the biofilter, it picked up moisture resulting in the outlet to have an average relative humidity of 100% (23.00 g/m$^3$ at 25º C). The amount of moisture lost due to the difference in humidity between the inlet and outlet was modelled to be 0.70 g/h (approximately 0.7 mL/h or 16.8 mL/d) and this water loss was compensated by delivering 3 mL of nutrient solution at the top of the reactor every 4 hours (18 mL/d) or excess water of about 1.2 mL/d. Experimentally 178.59 mL of excess liquid was collected over the 172 days of operation of this biofilter. This figure is comparable to the excess nutrient solution added over this period considering possible inaccuracy in metering of the small volume of nutrient solution intermittently added and the estimation of water loss through calculating the difference between moisture content of air entering and leaving the biofilter (Figure 4.3). The acidic product produced per volume of biofilter was a 1.15 mL/L of reactor/day. This is considerably less than similar systems which produced leachate in the range of 38 to 2,000 mL/L/day (Yang and Allen 1994, Gabriel and Deshusses 2003, Shareefdeen, Herner et al. 2003, Abdehagh, Namini et al. 2011, Chaiprapat, Mardthing et al. 2011, Solcia, Ramirez et al. 2014).
4.4.3 Accumulation of ions in leachate

Water-soluble ions produced by the biological oxidation of H₂S are washed down and accumulated at the bottom. The ions that accumulated in the leachate were monitored during the study period and are presented in Figure 4.4. There was an increase in the amount of both the sulphate and hydrogen ion in the leachate over time and the hydrogen ion concentration is twice that of the concentration of sulphate in the leachate. This is expected since the biological oxidation of H₂S produces H₂SO₄ (Equation 1). In Figure 4.4, the dashed line represents the model H⁺ that is expected from the amount of SO₄²⁻ in the leachate. The amount of H⁺ experimentally detected, specially after the first 8 weeks, shows a good agreement with the model H⁺.
Figure 4.4: Amount of sulphate ion and hydrogen ion accumulated in the leachate.

The concentration of sulphuric acid collected as a leachate (Figure 4.5) is much more concentrated than the sulphate concentrations of similar biofilters in the literature where the concentrations in the leachate are 0.2M or less (Chen, Fan et al. 2014, Solcia, Ramirez et al. 2014).
There was no sulphide (HS⁻) and thiosulphate (S₂O₃²⁻) in the leachate at any time during the operation of the biofilter, providing further evidence that the biofilter operated in an aerobic environment.

The concentration of sulphuric acid achieved in this biofilter is not surprising considering that the inlet gas for this study had an average relative humidity of 44% (10.15 g/m³ at 25º C). As shown in Figure 3.5, we would expect a 6M sulphuric acid to be formed by this biofilter. It should be noted that elemental sulphur was detected in the leachate after 10 weeks of the operation of the biofilter; however the amount formed was less than 1% of the total sulphur in the system. It is possible that the high concentration of sulphuric acid in the bottom section of this biofilter may provide a chemical pathway for the formation of elemental sulphur in the biofilter as explained in section 3.4. Batch experiments conducted in-house to determine the feasibility of the reaction of
H$_2$S with sulphuric acid at lower concentrations of acid have shown that the rate of the reaction at concentrations (6M) that is found in this biofilter is 4.6 X $10^{-5}$ mol/L/min and cannot be considered as a possible route for the formation of elemental sulphur from H$_2$S by chemical reaction. Besides, biological oxidation of H$_2$S even in an aerobic environment has been shown to produce small quantities of elemental sulphur which seems the more likely explanation (Jensen and Webb 1995, Chaiprapat, Mardthing et al. 2011, Montebello, Mora et al. 2014).

4.4.4 Removal of H$_2$S by each section of the biofilter

The biofilter was constructed so that each of the sections could be detached and the performance of each section in removing H$_2$S was measured (Figure 4.6) A summary of the results of the H$_2$S removed by each section are summarised in Figure 4.7.

![Figure 4.6: Sampling of H$_2$S for analysis of H$_2$S removal in different sections of the biofilter](image-url)
Interestingly, the bottom section did not remove any significant amount of the incoming H₂S (Figure 4.7) indicating that these parts of the biofilter did not have an environment conducive to the formation of microorganisms for the removal of H₂S. This is further explored in section 4.3.5. When the inlet concentration of H₂S was around 100 ppm (for example week 14 in Figure 4.7), the middle section removed almost all of the H₂S. When the inlet H₂S concentration was stepped up to 200 ppm (for example week 21 in Figure 4.7), the bottom section continued to be poor in removing H₂S and the middle section removed about half of the H₂S. The addition of the top section removed H₂S from the inlet gas at greater than 98% removal efficiency.

![Figure 4.7: H₂S in the outlet from different points of the biofilter as shown in Figure 4.6](image)

With the increase in the inlet concentration of H₂S, the top section was almost as important as the middle sections in removing H₂S from the inlet, whereas
in previous weeks, with lower inlet H$_2$S concentration, the middle section alone was sufficient to remove most of the H$_2$S. Stepping up the inlet concentration once again to 400ppm led to the failure of the whole biofilter in removing H$_2$S.

4.4.5 Moisture and ion gradient in biofilter

One of the expected characteristics of this biofilter was that there would be a gradient of moisture content and ion concentrations in the different sections of the biofilter.

![Graph](image)

**Figure 4.8:** Average moisture content and concentration of sulphate and hydrogen ion over 17 weeks in the different sections of the biofilter.

The moisture content in each section was determined and is summarised in Figure 4.8. The average moisture content of the bottom section was lower than the top and middle sections of the biofilter. Since air with low humidity (44%) entered the biofilter from the bottom, the bottom section was on average drier than the top and middle sections. Compared to the top and middle sections, the bottom section had a high sulphate and hydrogen ion concentration.
According to Yang and his co-workers (Yang and Allen 1994) microorganisms that convert H$_2$S to sulphate are inhibited when the sulphate concentrations are greater than 0.8 M sulphate. From Figure 4.7, it was evident that the bottom section did not remove any H$_2$S from the air and with the sulphate concentration being on average greater than 2M; it is no surprise that the bottom section did not remove H$_2$S. The middle and top sections with an average sulphate concentration of 0.83M and 0.12M respectively, however, do allow the biological oxidation of H$_2$S to take place. This biofilter operated effectively with one of the sections or one-third of the biofilter not participating in the biological oxidation of H$_2$S. Unlike conventional biofilters which need to be constantly washed down to maintain a pH of 7, the top section of the biofilter had a pH of 0.5 which is just within the range of operation for _A. thiooxidans_ for the conversion of H$_2$S to H$_2$SO$_4$ (Lors, Chehade et al. 2009, Solcia, Ramirez et al. 2014). This design of the biofilter enables the biofilter to function even though there is an accumulation of high acidity at the bottom.

Samples from each section at the end of week 14 were sent to Australian Genome Research Facility (AGRF) at the University of Queensland for diversity profiling using the two bacterial 16s amplicons of 16S:27F – 519R (V1-V3) and the results are summarised in Table 4.2. The results show that the top, middle and bottom sections contain organisms identified as being of the _Acidithiobacillus_ family but only the top and middle sections contained organisms identified as being of the _Thiobacillus_ family because the bottom section did not have a pH favourable for the growth of _Thiobacillus_. In the middle section, there were 4 times more sequences of the _Acidithiobacillus_ family than in the top and bottom section indicating that the middle section has
the most number of *Acidithiobacillus* which correlated to the fact that the middle section was doing most of the work in removing H₂S from the inlet (Table 4.2).

**Table 4.2**: Summary of diversity profiling in different sections of the biofilter

<table>
<thead>
<tr>
<th></th>
<th>Total sequences</th>
<th>Sequences with <em>Acidithiobacillus</em></th>
<th>Sequences with <em>Thiobacillus</em></th>
</tr>
</thead>
<tbody>
<tr>
<td>Top Section</td>
<td>125279</td>
<td>15</td>
<td>186</td>
</tr>
<tr>
<td>Middle Section</td>
<td>104996</td>
<td>61</td>
<td>24</td>
</tr>
<tr>
<td>Bottom Section</td>
<td>99915</td>
<td>20</td>
<td>0</td>
</tr>
</tbody>
</table>

According to the microbial diversity profiling of the mixed culture samples collected in week 14, the most prominent microorganisms in the biofilter were of the genus *Streptococcus, Rhodanobacter, Haemoophilus, Acinetobacter, Neisseria, Fulvimonas* and *Rhodopseudomonas*.

4.4.6 Sulphur balance

The mass balance in this system over the study period is summarized in Figure 4.9. The amount of sulphur entering the biofilter was calculated by considering the H₂S (g) removed by the biofilter as the only source of sulphur. A sample calculation is given below:

Let the H₂S concentration in the inlet (in g/m³) be designated as [H₂S]ᵢₐₜ and the H₂S concentration in the outlet inlet (in g/m³) be designated as [H₂S]ₒᵤᵗ. The mass of H₂S entering the biofilter per volume of air is given as ([H₂S]ᵢₐₜ -...
[H₂S]_{\text{out}}). If the flow rate is designated as \( \text{flow}_{\text{in}} \) in m³/min, then the mass of H₂S entering the biofilter per minute designated as \( \text{H}_2\text{S}_{\text{g/min}} \) is given as

\[
\text{H}_2\text{S}_{\text{g/min}} = ([\text{H}_2\text{S}]_{\text{in}} - [\text{H}_2\text{S}]_{\text{out}}) \times \text{flow}_{\text{in}}
\]

\( \text{H}_2\text{S}_{\text{g/min}} \) is converted to the mass of sulphur in the biofilter S_{g/day}.

The total amount of all forms of S in the biofilter was determined by measuring the amount of sulphate (SO₄^{2-}) and elemental sulphur (S) in the accumulated leachate and on the biofilm in all the sections of the biofilter. Sulphide (HS⁻) and thiosulphate (S²O₃^{2-}) were not detected in this biofilter.

Total Sulphur Mass =

\[
(\text{S from SO}_4^{2-} \text{ in leachate}) + (\text{S from elemental S in leachate}) + (\text{S from SO}_4^{2-} \text{ in biofilter sections}) + (\text{S from elemental S in biofilter sections})
\]
**Figure 4.9:** Mass balance of sulphur in the system

Representative data for Figure 4.9 is given in Table 4.3 and it is clear that, in this biofilter, the S from the sulphate in the leachate accounted for more than 90% of the mass of sulphur in the system after the initial acclimation period showing that almost all the sulphuric acid produced in the biofilter had been collected in the leachate as sulphate.

**Table 4.3** Representative data for the mass balance of sulphur in the biofilter

<table>
<thead>
<tr>
<th>Week</th>
<th>S from SO$_4^{2-}$ in leachate</th>
<th>S from elemental S in leachate</th>
<th>S from SO$_4^{2-}$ in biofilter sections</th>
<th>S from elemental S in biofilter sections</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>g</td>
<td>mg</td>
<td>g</td>
<td>mg</td>
</tr>
<tr>
<td>2</td>
<td>0.90</td>
<td>0.00</td>
<td>0.06</td>
<td>0.00</td>
</tr>
<tr>
<td>10</td>
<td>11.05</td>
<td>1.02</td>
<td>0.74</td>
<td>0.00</td>
</tr>
<tr>
<td>17</td>
<td>19.36</td>
<td>1.42</td>
<td>0.33</td>
<td>52.1</td>
</tr>
<tr>
<td>21</td>
<td>26.74</td>
<td>1.62</td>
<td>0.87</td>
<td>66.7</td>
</tr>
</tbody>
</table>
Previous researchers have shown that $\text{H}_2\text{S}$ is converted to sulphuric acid in an aerobic biofilter with $>90\%$ efficiency (Moghanloo, Fatehifar et al. 2010, Chaiprapat, Mardthing et al. 2011, Montebello, Mora et al. 2014).

4.5 Conclusion

Wastewater or sewage can be considered as a source of water, materials, bioplastics and energy (Guest, Skerlos et al. 2009, Schaubroeck, De Clippeleir et al. 2015). For example, biosolids derived from WWTP have being used as fertilizer both in the US and UK and there have been recent developments in harvesting of struvite from solids treatment process (de-Bashan and Bashan 2004, Guest, Skerlos et al. 2009). Environmental scientists have started to view WWTPs as a resource recovery system rather than a pollutant removal system (Guest, Skerlos et al. 2009). Polluted air being treated at WWTPs has never been considered as a potential source for substances like sulphur because of their low concentrations in air. But as shown in this thesis in Table 2.4 and Table 5.1, the amount of recoverable sulphur from contaminated air in wastewater treatment plants is significant. The biofilter system described in this chapter minimised leachate production from an aerobic biofilter removing $\text{H}_2\text{S}$ which lead to recovering sulphur as concentrated sulphate. This has been achieved without the addition of any harsh chemical, high temperatures or expensive catalysts. This original idea of recovering sulphur from low concentration gas streams can be applied to other contaminated air streams in industry which has low concentrations of sulphur or ammonia.
In this study, an aerobic biofilter that removed hydrogen sulphide from air with a removal efficiency of 98.8% produced a very small amount (1 mL/L/day) of concentrated sulphuric acid (6M) by controlling the amount of water going into the biofilter and collecting all the sulphate produced. A sulphate and hydrogen ion concentration gradient from low to high was achieved along the biofilter where the top section of the biofilter had a pH favourable for the growth of microorganisms and the high concentration of hydrogen ion and sulphate in the bottom of the biofilter could be collected as sulphuric acid for further use.

4.6 Acknowledgement

The authors would like to acknowledge the Australian Research Council (ARC) and Water Corporation of Western Australia for their financial support of this research and Dr Lucy Skillman for her assistance in with interpreting the data obtained from the Australian Genome Research Facility (AGRF) at the University of Queensland.
Chapter 5: Pilot-Scale biofilter for the simultaneous removal of hydrogen sulphide and ammonia from gas emissions at a wastewater treatment plant

5.1 Abstract

Biofilters are popular for the removal of odours from gaseous emissions in wastewater treatment plants because of their low capital costs and low energy requirements. In an aerobic environment, the microbes in biofilter oxidize odorous gases like hydrogen sulphide (H$_2$S) and ammonia (NH$_3$) to non-odorous sulphate and nitrate. Simultaneous biological removal of H$_2$S and NH$_3$, however, requires the monitoring and careful control of pH in the biofilter for optimal operation. This chapter describes a pilot plant biofilter setup at a local waste water treatment plant (WWTP) for the simultaneous removal of H$_2$S and NH$_3$ from gaseous emissions. This biofilter, which has been in continuous operation for more than 150 days, removes both H$_2$S and NH$_3$ at an average removal efficiency of 91.96% and 100% respectively. Unlike a conventional biofilter, the pH of this biofilter was not adjusted by addition of chemicals or buffers and the H$_2$SO$_4$ produced from the biological conversion of H$_2$S is periodically washed down and allowed to accumulate in a concentrated form at the base of the biofilter. NH$_3$ entering at the base is removed, not by biological oxidation, but by the chemical reaction of
ammonium with sulphate to form ammonium sulphate. The ammonium sulphate produced in biofilter is washed down and the volume of leachate produced is less than 0.2mL of leachate/L of reactor/day. Estimated cost savings of converting the current chemical scrubber used at the WWTP to a similar biofilter described in this study is included with this chapter.

5.2 Introduction

Air pollutants emanating from wastewater treatment plants (WWTP) are composed of a mixture of hundreds of chemical compounds including ammonia (NH$_3$), hydrogen sulphide (H$_2$S), limonene, butanone and other organic compounds (Stuetz, Gostelow et al. 2001, Escalas, Guadayol et al. 2003, Lee and Rasmussen 2006, Lebrero, Bouchy et al. 2011, Lebrero, Rangel et al. 2013, Godayol, Besalú et al. 2015). Air pollution complaints from WWWTP have been limited to unpleasant odours which are seen as a nuisance for residential areas around the plants (Gostelow and Parsons 2000, Burgess, Parsons et al. 2001, Ozturk, Tasaltin et al. 2009). Of all the odours originating from wastewater treatment plants, the rotten egg smell of H$_2$S and the pungent smell of NH$_3$ is the most distinctive (Liang, Quan et al. 2000, Malhautier, Gracian et al. 2003, Chen, Yin et al. 2005). Chemical scrubbers are the most common method for removing odours in industry because of their high efficiency at low contact times and large volumes of air can be treated in relatively small plants (McNevin and Barford 2000, Shareefdeen and Singh 2005, Mudliar, Giri et al. 2010, Lebrero, Bouchy et al. 2011). The disadvantage of using chemical scrubbers is the use of hazardous chemicals like sulphuric
acid and sodium hydroxide (Santos, Guimera et al. 2015). The hazardous chemicals adds not only to the cost of daily operations but also to the cost of maintaining the health and safety requirements for the operators. Biofilters are becoming more popular as a treatment for gases like H₂S and NH₃ emanating from wastewater treatment plants because they work at ambient temperatures and pressure, have low capital costs and have better environmental performance than chemical methods (McNevin and Barford 2000, Dumont, Andres et al. 2008, Mudliar, Giri et al. 2010, Lebrero, Gondim et al. 2014, Alfonsin, Lebrero et al. 2015). The first use of a biofilter in wastewater treatment was in 1893 with rock or slag being used as the support media (Chaudhary, Vigneswaran et al. 2003). Examples of mediums that have been used in biofilters since then include soil, peat, compost, wood chips, bark mulch, perlite, activated carbon, sewage sludge and combinations of these (Ergas, Schroeder et al. 1995, Weber and Hartmans 1996, Zilli, Fabiano et al. 1996, Easter, Quigley et al. 2005, Morgan-Sagastume and Noyola 2006). Most biofilters in the last decade have used synthetic media made of plastic or polymers as the support medium (Kennes and Veiga 2002). The synthetic media has the advantage of being inert, having uniform pore size distributions, high porosity, good chemical resistance and high surface area (Easter, Quigley et al. 2005). Older biofilters in Australia typically use organic medium but all new biofilters in WWTP located in Australia and around the world use synthetic materials such as plastic, polyurethane, polyethylene packing and ceramics as the support material (Burgess, Parsons et al. 2001, Easter, Quigley et al. 2005, Goncalves and Govind 2008).
In aerobic conditions, sulphur oxidizing bacteria (SOB) in biofilters convert H$_2$S in contaminated air to sulphate (SO$_4^{2-}$). Examples of SOB include *Thiobacillus denitrificans*, *Thiobacillus thioparus* and *Acidithiobacillus thiooxidans*. The pH range for optimal growth of *T. denitrificans* is 6.8 to 7.4, *T. thioparus* is 5.5 - 7.0 and *A. thiooxidans* is 1.8 - 2.5 (Aroca, Urrutia et al. 2007, Lors, Chehade et al. 2009, Solcia, Ramirez et al. 2014). In an aerobic environment, NH$_3$ is oxidized to nitrite (NO$_2^-$) by ammonia oxidizing bacteria (AOB) like those of the genera *Nitrosomonas* and the conversion of nitrite (NO$_2^-$) to nitrate (NO$_3^-$) is achieved by nitrite oxidizing bacteria (NOB) like those of the genus *Nitrobacter* (American Public Health Association 2012). For optimal operation, *Nitrosomonas* prefer a pH of 6.0 – 9.0 and *Nitrobacter* prefer pH between 7.3 and 7.5. For the microorganisms to operate at optimal performance, the pH of the biofilter has to be controlled and this is typically achieved by washing the biofilter with chemicals or a buffered solution (Mudliar, Giri et al. 2010). In an industrial scale biofilter, this leads to production of large volumes of leachate which contains ions like SO$_4^{2-}$, NO$_2^-$ and NO$_3^-$ which needs to be measured and the leachate requires proper disposal (Cox, Deshusses et al. 2002, Gabriel and Deshusses 2003, Shareefdeen and Singh 2005). Studies done on removal of H$_2$S and NH$_3$ using biofilters show efficiencies greater than 90% for both the gases (Gracian, Malhautier et al. 2002, Gabriel and Deshusses 2003, Oyarzun, Arancibia et al. 2003, Pagans, Font et al. 2005, Chen, Jiang et al. 2006, Taghipour, Shahmansoury et al. 2008, Lafita, Penya-Roja et al. 2012).

However, simultaneous biological removal of H$_2$S and NH$_3$ from air by biofiltration have shown that oxidation of high concentrations of H$_2$S (140 mg/m$^3$) affects the growth and activity of the nitrifying bacteria leading to
reduction in the NH\textsubscript{3} removal efficiency (Chung, Huang et al. 2000, Kim, Kim et al. 2002, Malhautier, Gracian et al. 2003). This is because the oxidation of H\textsubscript{2}S produces an acidic environment in the biofilter which does not promote the growth of AOB or NOB and thus hampers the removal of NH\textsubscript{3} (Chung, Huang et al. 2000, Kim, Kim et al. 2002, Malhautier, Gracian et al. 2003).

In chapter 4 of this thesis, a novel lab scale biofilter that remove H\textsubscript{2}S with the production of a concentrated sulphuric acid was described. In this alternative to conventional biofilter, the top region of the upflow biofilter had a suitable environment for the biological conversion of H\textsubscript{2}S while a concentrated solution of H\textsubscript{2}SO\textsubscript{4} formed in the bottom of the biofilter. A similar biofilter can be setup where the H\textsubscript{2}SO\textsubscript{4} can be used to remove NH\textsubscript{3} through acid stripping and formation of ammonium sulphate. This will avoid the problems associated with the AOB or NOB growing in an acidic environment since the removal of NH\textsubscript{3} will be achieved by the chemical reaction with sulphate to produce ammonium sulphate. No nitrate or nitrite will be formed in this process and the ammonium sulphate formed can be washed down the biofilter and collected as a product to be recovered from the process.

This study aims to investigate the pilot-scale feasibility of simultaneous H\textsubscript{2}S and NH\textsubscript{3} removal from waste air stream from a local municipal WWTP (Subiaco WWTP, Western Australia) using a combined biological oxidation of H\textsubscript{2}S and chemical NH\textsubscript{3} stripping using acid produced from H\textsubscript{2}S oxidation.
5.3 Materials and Methods

5.3.1 Biofilter Construction

A pilot plant biofilter was set up at the Subiaco WWTP and a schematic diagram of the biofilter is given in Figure 5.1.

![Schematic diagram of the pilot scale biofilter](image)

**Figure 5.1**: Schematic diagram of the pilot scale biofilter
The biofilter was constructed from acid-proof PVC piping (Holman Industries) with an internal diameter of 15 cm. The biofilter had three detachable sections (the top, middle and bottom sections) with dimension as shown in Figure 5.1 and a 5L Schott glass bottle at the bottom for the collection of solution. Each section was filled with equal amounts of acid resistant polyethylene packing material (AMB Bioballs (ABB media)) with dimensions of 11mm x 7mm and a total surface area of 834 m²/m³. Each section was filled with packing material to a height of 47cm giving a total working volume of 24.93 L. The packing material in each section was supported by sieve plates made of Plexiglas. The three sections and the bottom glass bottle could be detached for sample collection. Flow of air into the biofilter was controlled using a flow meter (Cole Palmer Instrument Company) and a peristaltic pump (Masterflex C/L Dual-Channel Variable-Speed Tubing Pump, Cole Palmer Instrument Company) was used for intermittent supply of deionized water to the biofilter.

5.3.2 Biofilter setup at the Subiaco WWTP

There are odour control units in all of the four large scale wastewater treatment plants in Perth located in Subiaco, Woodman Point, Beenyup and Alkimos (Water Corporation of WA). The Woodman Point and Beenyup WWTP have biotrickling filters to treat odorous gases from the extracted air collected from the covered tanks and treatment buildings while the Alkimos WWTP has a photoionisation unit which consists of UV lamps followed by an activated carbon unit (Water Corporation of WA). Using the methodology developed in Section 2.5, the maximum amount of sulphur that can be recovered from the
odorous gases at Woodman Point, Beenyup and Subiaco WWTPs are summarised in Table 5.1.

**Table 5.1:** Summary of potential sulphur recovery from WWTP in Perth

<table>
<thead>
<tr>
<th>WWTP based in Perth</th>
<th>H₂S concentration of foul air (mg/m³)</th>
<th>Average Flow rate (m³/h)</th>
<th>Sulphur removed / Recoverable sulphur per day (g S/day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Woodman Point</td>
<td>278</td>
<td>18,000</td>
<td>196</td>
</tr>
<tr>
<td>Beenyup</td>
<td>137</td>
<td>66,000</td>
<td>356</td>
</tr>
<tr>
<td>Subiaco</td>
<td>42</td>
<td>50,000</td>
<td>29</td>
</tr>
</tbody>
</table>

Of all the WWTPs in Perth, the Subiaco WWTP has a chemical scrubbing tower as the sole type of odour control unit. The pilot scale biofilter was set up at Subiaco Wastewater Treatment Plant (WWTP), Western Australia. The WWTP treats domestic wastewater collected from the Perth central metropolitan area and is designed to treat up to 61.4 million L/day and produces 65,000 m³ of contaminated gas per hour with maximum concentrations of H₂S and NH₃ at 75ppm and 5 ppm respectively (Water Corporation of WA). Currently, a series of chemical scrubber system is used to remove H₂S and NH₃ (Figure 5.2). The first scrubber uses 34% sulphuric acid as the scrubbing solution and the second scrubber uses 50% sodium hydroxide as the scrubbing solution. The outlet from the second scrubber is fed, together with the gaseous emissions from the secondary treatment area, to the last two scrubbers which are washed with a mixture of 12.5% sodium hypochlorite and 50% sodium hydroxide to remove trace amounts of any other
odorous gases before discharging the uncontaminated air into the atmosphere.

**Figure 5.2:** Schematic diagram of chemical odour control setup at Subiaco WWTP.

The pilot scale experiment at the Subiaco WWTP was conducted in two stages. In stage I of the experiment, the biofilter was placed after the first acid scrubber (Stage I in Figure 5.2) where NH₃ in the gaseous emissions had been removed by the acid scrubber. The inlet to the biofilter at stage I contained H₂S and the biological oxidation of H₂S forms H₂SO₄ at the bottom of the biofilter. The aim of this stage was generate sufficient H₂SO₄ at the base of the biofilter to remove incoming NH₃ in stage II.
In stage II of the experiment, the same biofilter was moved and placed in the main inlet of the chemical scrubber where the gaseous emissions contained a mixture of H$_2$S and NH$_3$ (Stage II in Figure 5.2).

5.3.3 Seeding method and moisture control

At the start of the study period, the biofilter was seeded with an inoculum from an existing lab scale aerobic biofilter which removed H$_2$S as described in Chapter 4 of this thesis. In order to maintain suitable media moisture levels for bacterial growth and to wash the ions down the biofilter, 250 mL of deionised water was trickled from the top of the biofilter once every week. The 250 ml water had been previously tested to be the minimum amount of water sufficient to wash contaminants from top to the base of this particular biofilter. Other than water, no additional nutrients, chemicals, or inoculums were added to the biofilter during the course of the study.

5.3.4 Sampling and chemical analysis:

The H$_2$S concentration in the inlet and outlet of the biofilter was measured in real time by means of an inline sensor (GD 2529 H$_2$S Sensor, GasTech). The NH$_3$ concentration in the inlet and outlet of the biofilter was measured twice a week using Dräger Tubes (Ammonia 2/a) with Accuropump (Accuracy: 10-15%; Dräger Safety, Inc.). Humidity and temperature of the gas mixture in
the inlet and outlet of the biofilter were measured in real time using the HOBO Pro v2 external temp/RH probe and data logger (Onsetcomp). All sensors and the water pump were controlled by connected computer using a Labjack USB interface and National Instruments LabView 7.1 control software. Ten pieces of randomly chosen ABB media was used to determine the moisture content in the different sections of the biofilter and was expressed as the gravimetric water content:

\[ M_n = \frac{M_w}{M_o} \]

where, \( M_n \) is the moisture content,

\( M_w \) is the mass of medium with water

\( M_o \) is the mass of the medium without water

The concentration of soluble ions in the biofilter was determined by collecting samples from different sections of the biofilter once a week. At each sampling event duplicate samples of 10 pieces of the packing material, sampled from the top, middle and bottom sections of the biofilter was shaken with 10 mL of distilled deionized water for 15 minutes in a glass vial to extract the water soluble ions. This solution and the leachate was analysed once a week for pH, sulphate (\( \text{SO}_4^{2-} \)), sulphide (\( \text{HS}^- \)), ammonium ion (\( \text{NH}_4^+ \)), nitrate (\( \text{NO}_3^- \)) and nitrite (\( \text{NO}_2^- \)). The pH of the samples solution was determined using an Ecoscan pH meter (Eutech instruments). Sulphate was determined by the standard method based on precipitation as \( \text{BaSO}_4 \) followed by photo spectrometric quantitation at 420nm with a HACH DR 2700 Portable Spectrophotometer (American Public Health Association 2012). Sulphide (\( \text{HS}^- \)) was determined based on the reaction of copper sulphate (\( \text{CuSO}_4 \)) in an acidic solution producing copper sulphide precipitate which was measured
photometrically at 480 nm (Cord-Ruwisch 1985). NH$_4^+$, NO$_3^-$ and NO$_2^-$ was determined by the standard photometric analysis as described in the literature (American Public Health Association 2012).

### 5.4 Results and Discussion

A pilot scale experiment was conducted at Subiaco WWTP that converts H$_2$S by biological oxidation to sulphate and the NH$_3$ is removed by forming ammonium sulphate. The system achieves simultaneous removal of H$_2$S and NH$_3$ without the use of high concentrations of sulphuric acid or sodium hydroxide as in a chemical scrubber, with high efficiency and the production of minimal amount of leachate. In stage I of the experiment, biological oxidation of H$_2$S produces SO$_4^{2-}$ in the biofilter which is accumulated in the bottom. In stage II, the NH$_3$ in the gaseous emissions is removed by the formation of ammonium sulphate - while the sulphur oxidizing bacteria (SOB) in the biofilter continues to remove H$_2$S from the gaseous emissions. The low pH of the biofilter prevents the growth of nitrifying bacteria in the biofilter thus avoiding the problems associated with the biological oxidation of H$_2$S and NH$_3$ (Chung, Huang et al. 2000, Kim, Kim et al. 2002, Malhautier, Gracian et al. 2003).
5.4.1 Stage I – Removal of H$_2$S with production of sulphate solution

5.4.1.1 H$_2$S removal efficiency

In the first stage of the experiment, the objective was to remove H$_2$S from the incoming air and accumulate the H$_2$SO$_4$ produced in the leachate. The biofilter was placed after the acid scrubber in the chemical scrubber system (Figure 5.2) and operated continuously for 15 weeks. Empty bed residence time (EBRT) is defined as the working volume of the biofilter divided by the air flow rate. The average flow rate through the biofilter was 25 L/min at this stage of the experiment giving an EBRT of 1 minute. The average concentration of H$_2$S entering the biofilter over the first 15 weeks was 31.85 ppm (0.04 g/m$^3$) and after an initial incubation period of about 4 days, the biofilter removed H$_2$S from the inlet air at an average removal efficiency of 94.38% (Figure 5.3). At this stage of the experiment, the H$_2$S was effectively removed from the gaseous emissions from the WWTP by the biofilter and the results show the robustness of the system over a wide range of inlet loads.
Figure 5.3: Removal of $\text{H}_2\text{S}$ in stage I of the experiment

5.4.1.2 Moisture and pH gradient in biofilter

Conventional biofilters have their pH maintained by adding a buffer solution or chemicals like sodium hydroxide to the biofilter (Shareefdeen, Herner et al. 2003, Jover, Ramirez et al. 2012, Solcia, Ramirez et al. 2014). In this biofilter, deionized water ($\text{pH} = 7$) was added intermittently to the top of the biofilter which washed the ions down from the biofilm to create a gradient of pH in the biofilter. The moisture content and the pH in the biofilter were monitored over the study period and the average values of these parameters are shown in Table 5.2. Because the air with a lower %RH entered the biofilter at the bottom, the lowest section dried out leaving the top and middle sections with almost
the same amount of moisture content. The pH of the bottom section was lower than the top and middle sections, but was still in the range for the operation of sulphur oxidizing bacteria (SOB) (Aroca, Urrutia et al. 2007, Lors, Chehade et al. 2009, Solcia, Ramirez et al. 2014). The low pH in the bottom section favoured the transfer of NH$_3$ from gaseous phase to liquid phase and will be used to replace the current acid scrubber used at the WWTP.

**Table 5.2:** Gradient of moisture and pH in the biofilter during stage I.

<table>
<thead>
<tr>
<th>Moisture content</th>
<th>Top section</th>
<th>Middle section</th>
<th>Bottom Section</th>
</tr>
</thead>
<tbody>
<tr>
<td>g / g*</td>
<td>1.21</td>
<td>1.27</td>
<td>0.99</td>
</tr>
<tr>
<td>pH</td>
<td>5.34</td>
<td>4.95</td>
<td>3.67</td>
</tr>
</tbody>
</table>

* g/g refers to grams of water per gram of supporting medium

5.4.1.3 Volume of leachate produced

The leachate produced by the biofilter was collected at the bottom in a sealed Schott glass bottle and the cumulative volume collected over time is given in Figure 5.4. The solution collected in stage I (week 0-15) was only 163mL per week, significantly less than the 250 mL per week delivered to the biofilter but is reasonable considering the estimation of water loss due to temperature fluctuations and the difference in moisture content of air entering and leaving the biofilter. During stage I, the average humidity of the air entering the biofilter was 98 (± 4 %). The high humidity was expected since the gaseous emissions passes through the acid scrubber (Figure 5.2) and carries the moisture before entering the biofilter. By washing down the biofilter once a week as described
in this study, the amount of leachate produced by this biofilter was less than 1mL of leachate/L of reactor/day.

![Graph showing leachate production over time](image)

**Figure 5.4:** Actual and expected cumulative volume of leachate

During stage II, the volume of deionized water used to wash the biofilter remained at 250 mL but the average humidity of the air entering the biofilter was 64 (± 23 %) due to placing the biofilter at the entrance to the chemical scrubber system (Figure 5.2). The lower humidity and the larger deviation at this stage compared to stage I led to a smaller volume of leachate being produced (Figure 5.4). 195mL of leachate was collected from the 24.93 L biofilter during the 7 weeks of stage II leading to a leachate production rate of less than 0.2 mL of leachate/L/day. This is significantly less than similar pilot scale systems which produce leachate in the range of 80 to 714,000 mL of
leachate/L of reactor/day (Abdehagh, Namini et al. 2011, Chaiprapat, Mardthing et al. 2011, Park, Evans et al. 2011, Solcia, Ramirez et al. 2014). This biofilter produces a small amount of leachate which reduces the need for the leachate treatment and disposal.

5.4.1.4 Concentration of ions in leachate

The increase in the concentration of the sulphate and hydrogen ion in the leachate over the study period is shown in Figure 5.5. The sulphate concentration steadily increases during the course of the experiment; the hydrogen ion concentration is roughly double that of the concentration of sulphate in the leachate giving an indication that H$_2$SO$_4$ is being accumulated in the leachate (Figure 5.5).

![Figure 5.5: Sulphate and hydrogen ion concentration in leachate](image-url)
The pH of the leachate was just below 1 at the end of this stage, which was important as this would prevent the growth of NOB and AOB when NH$_3$ was introduced into the biofilter.

5.4.2 Stage II – Simultaneous removal of H$_2$S and NH$_3$

5.4.2.1 H$_2$S and NH$_3$ removal efficiency

In stage II, the biofilter prepared in stage I was placed at the entrance to the chemical scrubber system (Figure 5.2). The inlet to the biofilter contained both NH$_3$ and H$_2$S. The aim was to use acid stripping to remove NH$_3$ in the gaseous while the sulphur oxidizing bacteria (SOB) in the biofilter continued to remove H$_2$S from the gaseous emissions. The biofilter was operated continuously for 7 weeks. The airflow rate at this stage was 50 L/min giving an EBRT of 30s. The average concentration of H$_2$S and NH$_3$ entering the biofilter over the 7 weeks was 31.86 ppm (0.04 g/m$^3$) and 1.94 ppm (1.35 mg/m$^3$) respectively. The biofilter removed H$_2$S and NH$_3$ from the inlet air at an average removal efficiency of 91.96% and 100% respectively (Figure 5.6, Figure 5.7). Since no NO$_3^-$ or NO$_2^-$ was detected in the biofilter or the leachate, it can be inferred that the removal of NH$_3$ as shown in Figure 5.7 was not due to biological oxidation. Mass loading rate is defined as the mass of contaminant entering the biofilter per unit volume of filter material per unit time (Lebrero, Bouchy et al. 2011). This biofilter at its current configuration had a mass loading rate of 5.37 mg of S/L/hr and 0.14 mg of N/L/hr. There was no appreciable change in
the removal efficiency for \( \text{H}_2\text{S} \) in stage II compared to stage I where there was no \( \text{NH}_3 \) in the incoming gaseous emissions. The operation of the biofilter for the removal of \( \text{H}_2\text{S} \) had not been hampered in any way by the presence of \( \text{NH}_3 \) in the inlet.

![Stage II](image)

**Figure 5.6:** Removal of \( \text{H}_2\text{S} \) in stage II of the experiment
Figure 5.7: Removal of NH$_3$ by solution at low pH in stage II of the experiment

5.4.2.2 Concentration of ions in leachate

During stage II, when the NH$_3$ was introduced into the biofilter, the sulphate concentration continued to increase indicating that the biological oxidation of H$_2$S continues after the addition of NH$_3$ in the gaseous emissions (Figure 5.6). There was no evidence of NO$_3^-$ and NO$_2^-$ in the biofilter or leachate indicating that biological oxidation of NH$_3$, which was unlikely at this low pH, was not occurring. There was also evidence of some NH$_4^+$ in the bottom section of the biofilter indicating that the ammonia with the inlet gas was absorbed by the bottom section of the biofilter before it could go to the middle or top sections (Table 5.3). Periodic washing of the biofilter washed down the ammonium ion to the leachate avoiding the accumulation of ammonium sulphate in the biofilter. The concentration of ammonium ion steadily increased in the leachate (Figure 5.8).
Figure 5.8: Sulphate, ammonium and nitrate concentration in leachate during stage II.

Table 5.3: Gradient of pH and ammonium ion concentration at the end of stage II.

<table>
<thead>
<tr>
<th></th>
<th>Top section</th>
<th>Middle section</th>
<th>Bottom Section</th>
<th>Leachate</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>5.34</td>
<td>4.95</td>
<td>3.67</td>
<td>0.74</td>
</tr>
</tbody>
</table>
| NH$_4^+$
| concentration | mM          | 0.00           | 0.00           | 1.2      | 81.90    |

Analysis of the hydrogen ion concentration of the leachate at this stage provided further evidence for the neutralization of the sulphuric acid by the ammonia being trapped in the biofilter. In stage I, hydrogen ion concentration in the leachate was almost twice that of the sulphate ion concentration indicating that there was almost complete dissociation of the sulphuric acid
produced in the biofilter (Figure 5.5). In stage II, the measured H+ concentration is less than expected from the sulphate ion alone. Figure 5.9 shows the measured concentration of H+ in the leachate labelled as ‘H+ concentration measured in leachate’. This is less than the theoretical hydrogen ion concentration based on the complete dissociation of the sulphuric acid produced in the leachate (labelled ‘Expected H+ from dissociation of H2SO4’ in Figure 5.9). The NH3 in the gaseous emissions was being converted to NH4+ in the acidic leachate leading to a reduction in the concentration of hydrogen in the leachate and the hydrogen ion concentration due to the sulphate concentration minus the amount reacting with ammonia is labelled ‘Calculated H+ from sulphate and ammonium concentration’ in Figure 5.9. The pH of the leachate at the end of this stage of the experiment was still below 1 which still did not encourage the growth of ammonia oxidizing bacteria (AOB) or nitrite oxidizing bacteria (NOB).
The overall biological reaction that occurs in an aerobic biofilter that removes hydrogen sulphide is given below (Oyarzun, Arancibia et al. 2003, Wang, Dalla Lana et al. 2003):

\[
\text{H}_2\text{S} + 2\text{O}_2 \rightarrow \text{SO}_4^{2-} + 2\text{H}^+
\]

The uniqueness of the biofilter setup described in this study is the use of the sulphuric acid formed by the biological oxidation of \( \text{H}_2\text{S} \) for the removal of \( \text{NH}_3 \) in the contaminated air and accumulating the ions that are washed down from the biofilter. Since 2 moles of \( \text{H}^+ \) can potentially be produced from one mole of \( \text{H}_2\text{S} \), as long as the ratio of \( \text{H}_2\text{S} \) to \( \text{NH}_3 \) in the contaminated air is greater than 0.5, there will be enough \( \text{H}^+ \) to remove \( \text{NH}_3 \) from air. In this study, the ratio of
the amount of H\textsubscript{2}S to NH\textsubscript{3} in the contaminated air is greater than 15, which is more than adequate for the removal of NH\textsubscript{3} in the air.

By operating the biofilter as described in this study, ammonium sulphate is obtained as a product. The formation of ammonium sulphate has been observed previously in other biofilters, but they are usually considered a nuisance, specially when wood chips or compost were used as filter media (Yang and Allen 1994, Kim, Kim et al. 2002, Shareefdeen and Singh 2005). Ammonium sulphate is useful as a fertilizer that provides sulphur and nitrogen to plants as nutrients and has been shown to be better than ammonium nitrate (Chien, Gearhart et al. 2011, Wang, Yang et al. 2013). Industrial processes for the production of ammonium sulphate from flue-gas desulfurization has been studied but they involve high temperatures and long residence times (Chou, Bruinius et al. 2005). There is potential for an inexpensive process that produces ammonium sulphate at ambient conditions as is the case in this biofilter. At the Subiaco WWTP, the average concentration of NH\textsubscript{3} in the contaminated air with an average flow of 62,500 m\textsuperscript{3}/h is 2 ppm. Complete conversion of this ammonia to ammonium sulphate has the potential to produce 17kg of ammonium sulphate per day. Since the solubility of ammonium sulphate in water is 74.4g/100mL, a biofilter system like the one proposed in this chapter, which completely removes NH\textsubscript{3} and produces a minimal amount of leachate, can be potentially used to form ammonium sulphate as a solid product.
Samples from each section of the pilot scale biofilter at the end of week 22 were sent to Australian Genome Research Facility (AGRF) at the University of Queensland for diversity profiling using the two bacterial 16s amplicons of 16S:27F – 519R (V1-V3) and is summarised in Table 5.4. The results show that the organisms identified as being of the *Thiobacillus* family, which have optimal growth at around 5, were found only in the top section of the biofilter. It is important to note that the top section of the biofilter had a pH of greater than 5, while the middle and bottom sections had pH < 5 (Table 5.3). No sequences with *Thiobacillus* was found in the middle or bottom sections which were more acidic than the top section. The results also show that there were a negligible number of organisms identified as being of the *Nitrobacter* family, which prefer a pH > 6.

**Table 5.4:** Summary of diversity profiling in different sections of the pilot scale biofilter

<table>
<thead>
<tr>
<th></th>
<th>Total sequences</th>
<th>Sequences with <em>Thiobacillus</em></th>
<th>Sequences with <em>Nitrobacter</em> and <em>Nitrosomonas</em></th>
</tr>
</thead>
<tbody>
<tr>
<td>Top Section</td>
<td>122570</td>
<td>4262</td>
<td>9</td>
</tr>
<tr>
<td>Middle Section</td>
<td>99915</td>
<td>0</td>
<td>8</td>
</tr>
<tr>
<td>Bottom Section</td>
<td>19687</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
5.4.2.3 Mass Balance

Over the study period, the mass balance in this system was calculated by considering the inlet gas as the only source of sulphur and nitrogen into the biofilter. Since all sulphur was converted to sulphate, the mass of sulphur in biofilter was the sum of the sulphur as SO\(_4^{2-}\) in leachate and in the biofilter sections. The mass of sulphur entering the system was 10.25 g/week and the mass accounted for sulphur as sulphate was 0.40 g/week leading to 3.92% of the mass of sulphur being accounted for (Mass balance of sulphur: presence of RSCs). Since all the nitrogen was converted to ammonia in this biofilter, the total mass of nitrogen in biofilter was the sum of the nitrogen as NH\(_4^+\) in leachate and in the biofilter sections. The mass of nitrogen entering the system was 0.51 g/week and the mass of nitrogen as ammonium in the biofilter was 0.48 g/week leading to 95.7% of the mass of nitrogen being accounted for.

5.5 Full scale conversion of chemical scrubber to novel biofilter setup

Successful conversion of chemical scrubbers to biofilters has been described in the literature (Gao, Keener et al. 2001, Gabriel and Deshusses 2003, Gabriel, Cox et al. 2004, Iranpour, Coxa et al. 2005, Santos, Guimera et al. 2015). The operating cost of a biofilter range from one fourth to one tenth the operating cost of a chemical scrubber (Hasnaa Jorio et Michele 1999, Gao, Keener et al. 2001). As the biofilter process described above relies on acid produced by H\(_2\)S oxidation to strip off ammonia, the application is suitable for waste air stream containing higher concentrations of hydrogen sulphide.
compared to ammonia. This scenario is common in wastewater treatment plants where the air stream has a higher concentration of hydrogen sulphide compared to ammonia (Chung, Huang et al. 2000, Lebrero, Bouchy et al. 2011). A convenient ten step protocol was developed by Deshusses and his co-workers as a general procedure for the conversion of chemical scrubbers to biofilters in WWTP (Gabriel, Cox et al. 2004, Shareefdeen and Singh 2005). Following this protocol, the conversion of chemical scrubbers at Subiaco WWTP to biofilters can be achieved by using the same chemical scrubber tank, packing material and recirculation pump that is being currently used in the chemical scrubber system. For the existing chemical system at the Subiaco WWTP, each of the scrubbers have a volume of 17.18 m$^3$ and the hypo scrubber has a volume of 40 m$^3$. If all the scrubbers at the Subiaco WWTP are converted to a biofilter, then an EBRT of 8.2 s can be achieved with the minimum allowed flow rate of 50,000 m$^3$/h for the incoming gas. Further reduction in the flow rate would risk the safety of the workers at the WWTP as this would lead to high H$_2$S and NH$_3$ concentrations. The pilot scale biofilter system described in this chapter has an EBRT of 30s at the final stage (Stage II). To test the effectiveness of the pilot scale biofilter system at low EBRT, both the top and middle sections of the biofilter were removed leaving a biofilter with only one section and a volume of 8.31L and an EBRT of 9.33s. This was the most convenient way to come as close to the desired EBRT of 8.2s without making significant changes to the pilot scale biofilter
Table 5.5: Gradient summary of results of the biofilter with all three sections and only one section.

<table>
<thead>
<tr>
<th></th>
<th>All three section</th>
<th>One section only</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average H$_2$S concentration of inlet air</td>
<td>31.86 ppm (0.04 g/m$^3$)</td>
<td>30.98 ppm (0.04 g/m$^3$)</td>
</tr>
<tr>
<td>Average NH$_3$ concentration of inlet air</td>
<td>1.94 ppm (1.35 mg/m$^3$)</td>
<td>1.96 ppm (1.36 mg/m$^3$)</td>
</tr>
<tr>
<td>Volume of reactor</td>
<td>0.025 m$^3$</td>
<td>0.0083 m$^3$</td>
</tr>
<tr>
<td>Inlet Flow rate</td>
<td>0.05 m$^3$/min</td>
<td>0.05 m$^3$/min</td>
</tr>
<tr>
<td>EBRT</td>
<td>27.98 s</td>
<td>9.33 s</td>
</tr>
<tr>
<td>Mass Loading Rate for H$_2$S</td>
<td>5.37 g of S/m$^3$/hr.</td>
<td>15.66 g of S/m$^3$/hr.</td>
</tr>
<tr>
<td>Mass Loading Rate for NH$_3$</td>
<td>0.14 mg of N/m$^3$/hr.</td>
<td>0.43 mg of N/m$^3$/hr.</td>
</tr>
<tr>
<td>Removal Efficiency for H$_2$S</td>
<td>91.96 %</td>
<td>90.24 %</td>
</tr>
<tr>
<td>Removal Efficiency for NH$_3$</td>
<td>100 %</td>
<td>100 %</td>
</tr>
</tbody>
</table>

After an initial incubation period of a few hours, the removal efficiency was 90.24% for H$_2$S and 100% for NH$_3$. The result of the experiment comparing the biofilter with all three sections and a biofilter with only one section is summarized in Table 5.5.

It should be noted that there are examples in the literature of biofilters treating H$_2$S with EBRT of 9 seconds but with pH control using buffered solutions and open pore polyurethane foam as the support material (Chen, Jiang et al. 2006). In another pilot scale study, an EBRT of 2-10 seconds was sufficient for the removal of ammonia (Dorado, Gabriel et al. 2015). It could be possible to convert only the first or second chemical scrubber in the odour control system into a biofilter (leading to biofilters with EBRT of 2s) leaving the last two hypo scrubbers (which are washed with a mixture of sodium hypochlorite and sodium hydroxide) to remove trace amounts of any other odorous gases.
before discharging into the air (Figure 5.2). This would give EBRTs closer to the residence times of the pollutants in each tank of the chemical scrubber process, however, it is important that the suitability of the conversion needs to be tested by running a full scale trial of the biofilter. The economic viability of a conversion of the chemical scrubber to a full scale biofilter setup on the principles described above is dependent on the savings obtained from capital and operating costs. Since the proposed biofilter system will intermittently add water instead of harsh chemicals, there will be savings on reagent consumptions. The cost calculation is summarized in Table 5.6 based on the current cost of the chemicals in the Australian market. Savings on electricity due to the intermittent use of the recirculation pump instead of the continuous use is also summarized in Table 5.6. The total saving on operating cost from not using chemicals and curtailed use of the recirculating pump comes to a total of $56,794/yr. This does not include saving from reduced water use, cost associated with waste stream treatment or disposal. Furthermore, there will also be savings in the form of reduced insurance derived from elimination of chemical handling issues.
Table 5.6: Summary of cost savings in converting from chemical scrubber to a biofilter

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Amount of reagent used</th>
<th>Reagent cost</th>
<th>Savings per year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid</td>
<td>40 L/day</td>
<td>$0.40/L</td>
<td>$5,840</td>
</tr>
<tr>
<td>Caustic</td>
<td>200 L/day</td>
<td>$0.50/L</td>
<td>$36,500</td>
</tr>
</tbody>
</table>

**Savings from electricity consumption**

<table>
<thead>
<tr>
<th>Power</th>
<th>Electricity cost per unit</th>
<th>Usage</th>
<th>Savings per year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pump</td>
<td>11 kW</td>
<td>$0.18 /kWh&lt;sup&gt;a&lt;/sup&gt;</td>
<td>20 h/day</td>
</tr>
</tbody>
</table>

Total savings per year $56,794

<sup>a</sup>(Finance and Australia 2015)

It is being assumed that the current packing material being used at the chemical scrubber is suitable for the conversion to the biofilter. However, if the packing material needs to be changed then the removal of the old packing material and installation of new packing material would add to the cost. Some modifications of the pump controls may also be required. All these would be better estimated by running a full scale trial of the system rather than a small scale described in this chapter.
5.6 Conclusion

A biofilter setup at a local wastewater treatment plant removed both \( \text{H}_2\text{S} \) and \( \text{NH}_3 \) from gaseous emissions with average removal efficiency of 91.96\% and 100\% respectively. This novel biofilter process produced a very small amount of leachate (0.2mL of leachate/L of reactor/day) and the ammonium and sulphate ions were accumulated at the bottom of the biofilter. The results of this pilot scale study show that there was no change in the \( \text{H}_2\text{S} \) removal efficiency of the biofilter due to the presence of ammonia (Figure 5.3, Figure 5.6). There was a change in the pH of the leachate due to the presence of ammonia which could be accounted for by the neutralization of the sulphuric acid by the ammonia being trapped in the biofilter (Figure 5.9). The diversity profiling of the microorganisms in the biofilter show that there were a negligible number of organisms identified as being of the \emph{Nitrobacter} family and the removal of \( \text{NH}_3 \) was not achieved by the use of microorganisms but by the acid scrubbing of \( \text{NH}_3 \) to form ammonium sulphate with no production of nitrate or nitrite. This process provides a possible alternative to the current chemical scrubber used in the plant that uses harsh chemicals and produces large volumes of waste stream. Within the parameters of the study conducted at the wastewater plant, the concentration of ammonium sulphate in the leachate of the biofilter kept increasing but further investigations on the suitability of this biofilter for the harvesting of ammonium sulphate as a solid should be investigated.
5.7 Acknowledgements

The authors would like to acknowledge the Australia Research Council (ARC) and the Water Corporation of Western Australia for providing financial support for this project and the personnel of Subiaco Waste Water Treatment Plant at Perth, Australia for their help and support during the field work.
Chapter 6: Conclusions and recommendations for further work

6.1 Conclusions

This thesis aimed to develop a novel approach to biofiltration that minimised leachate production from an aerobic biofilter removing H$_2$S as well as recovering sulphur as concentrated sulphate. Two biofilters were described in this thesis to examine this principle – a lab scale biofilter described in Chapter 4 that operated for more than 150 days with a H$_2$S removal efficiency of 98.8% to produce concentrated sulphuric acid and a pilot scale biofilter described in Chapter 5 that also operated for more than 150 days that simultaneously removed H$_2$S and NH$_3$ at removal efficiencies of 91.96% and 100% respectively and produced ammonium sulphate.

- One of the objectives of the thesis was the development and testing of an aerobic biofilter that produced little or almost no leachate. The lab scale aerobic biofilter produced only 1.15 mL of leachate/L of reactor/day. The relative humidity of the air entering the biofilter was consistently less than 45% and the amount of moisture lost due to the difference in humidity between the inlet and outlet was modelled and this water loss was compensated by trickling water down the biofilter so that the moisture content in the biofilter was maintained. The pilot scale biofilter had a larger variability of relative humidity (64(±23) %) entering the biofilter and this
biofilter produced less than 0.2 mL of leachate/L of reactor/day while simultaneously removing H$_2$S and NH$_3$.

- Another objective of this thesis was to recover sulphur from biofilter as sulphuric acid. The lab scale aerobic biofilter with an elimination capacity of 16.3 g/m$^3$/h produced 6M or 30% sulphuric acid as product at the end of the study period. The H$_2$S and humidity in the inlet and outlet of the biofilter was measured in real time by means of an inline sensor. The mass balance of the sulphur in the system showed that the sulphate ion concentration in the leachate accounted for more than 90% of the mass of sulphur in the system indicating that almost all the sulphuric acid produced in the biofilter was collected in the leachate. This allowed for the recovery of sulphur from the leachate rather than producing waste streams of diluted sulphuric acid.

- The third objective of this thesis was to operate the biofilter without the use of harsh chemicals like sodium hydroxide to adjust the pH. A moisture and pH gradient was developed within the lab scale biofilter by trickling a minimum volume of buffer solution resulting in an environment at the top for the bacterial conversion of H$_2$S while sulphuric acid accumulated at the base. The pH was adjusted not by the addition of sodium hydroxide, but by washing down the accumulated acid down the biofilter. The same strategy was employed in the pilot scale biofilter, where the H$_2$SO$_4$ produced from the biological conversion of H$_2$S was periodically washed down and allowed to accumulate at the base of the biofilter.
The fourth objective was to develop a biofilter that simultaneously removed ammonia and hydrogen sulphide and this was achieved in the pilot scale biofilter. A pilot plant biofilter setup at a local WWTP removed both H$_2$S and NH$_3$ at an average removal efficiency of 91.96% and 100% respectively. NH$_3$ entering at the base was removed, not by biological oxidation, but by the chemical reaction of ammonium with sulphate to form ammonium sulphate. The pH in the biofilter was in the range of 4.6 to 1.5 which was not conducive to the biological oxidation of NH$_3$ and this was backed up by the lack of NO$_3^-$ or NO$_2^-$ in the biofilter.

6.2 Recommendations for further work

In this final chapter, future recommendations and ideas based on the findings presented above are presented.

- It is recommended that the further studies are conducted on the simultaneous removal of NH$_3$ and H$_2$S in lab scale for the production of ammonium sulphate crystals as a product. A lab scale biofilter can setup like the one described in Chapter 4 of this thesis, where there is an inlet of relatively dry air and the ammonium sulphate produced is washed down to accumulate at the bottom of the biofilter as ammonium sulphate crystals. In the lab scale, the ratio of H$_2$S to NH$_3$ required for the optimal production of ammonium sulphate can also be examined.
• It would also be interesting to look at the design of biofilters (size and shape) and investigate how to maximize the formation of concentrated solutions in a biofilter. Biofilters may be redesigned so that the pollutants spend more time passing through the concentrated products rather than the biofilter. With the design of this biofilter allowing for production of concentrated solutions of product, there is potential to investigate reactions that are typically not possible in ambient conditions but can now be feasible due to the high concentrations in the biofilter. Concentrated product can react with other pollutants in the air that would normally not react because of their low concentrations in air.

• The concentrated product could also react with the media—specially if synthetic media or “designed” polymers are used. One could envisage reactions where the media would be inert at low concentrations of product but would react or be activated when the concentration of the product has reached a certain threshold.

• The extreme nature of the environment in this biofilter (high concentration of reagents, low moisture content, low pH, etc.) could also be used for nurturing extremophiles— that is, microbial organisms that thrive in extreme physical conditions. They provide a fascinating area of research and the applicability of extremophiles in real world situations is a tantalising prospect.


Appendix

Appendix A: Derivation of the plot of the fractions of H₂S that exists as H₂S (aq), HS⁻ (aq) and S²⁻ (aq) with respect to pH.

Once in solution, H₂S acts as a weak acid and releases H⁺ in solution (Shareefdeen and Singh 2008).

\[ \text{H}_2\text{S (aq)} \rightleftharpoons \text{H}^+ (aq) + \text{HS}^- (aq) \quad \text{K}_1 = \frac{[\text{H}^+][\text{HS}^-]}{[\text{H}_2\text{S}]} \quad \text{pK}_1 = 7.0 \text{ (Equation K}_1) \]

\[ \text{HS}^- (aq) \rightleftharpoons \text{H}^+ (aq) + \text{S}^{2-} (aq) \quad \text{K}_2 = \frac{[\text{H}^+][\text{S}^{2-}]}{[\text{HS}^-]} \quad \text{pK}_2 = 12.9 \text{ (Equation K}_2) \]

The derivation of the plot of the fractions of H₂S that exists as H₂S (aq), HS⁻ (aq) and S²⁻ (aq) with respect to pH is given below.

Let, the total sulphur species in solution be [S]ₜ, the amount of H₂S in water be [H₂S], the amount of bisulphide ion be [HS⁻], and the amount of sulphide ion be [S²⁻].

Since,

\[ [\text{S}]_\text{t} = [\text{H}_2\text{S}] + [\text{HS}^-] + [\text{S}^{2-}] \]

The fraction of H₂S in solution compared to [S]ₜ (A₁) is

\[ A_1 = \frac{[\text{H}_2\text{S}]}{[\text{S}]_\text{t}} = \frac{[\text{H}_2\text{S}]}{[\text{H}_2\text{S}]+[\text{HS}^-]+[\text{S}^{2-}]} \]
\[
\frac{[H^+][HS^-]}{K_1} + \frac{[H^+][S^{2-}]}{K_1} + \frac{K_2[HS^-]}{[H^+]} = \frac{[H^+][HS^-]}{K_1} + \frac{K_2[HS^-]}{K_1}\]

\[
\frac{[H^+][HS^-]}{K_2[H^+]} + \frac{K_1[H^+][S^{2-}]}{K_2[H^+]} + \frac{K_2[H^+]}{K_2[H^+]} = \frac{[H^+][HS^-]}{K_2[H^+]} + \frac{K_1[H^+][S^{2-}]}{K_2[H^+]} + K_1K_2[H^+]
\]

\[
\frac{[H^+][HS^-]}{K_2[H^+]} + \frac{K_1[H^+][S^{2-}]}{K_2[H^+]} + \frac{K_2[H^+]}{K_2[H^+]} = \frac{[H^+][HS^-]}{K_2[H^+]} + \frac{K_1[H^+][S^{2-}]}{K_2[H^+]} + K_1K_2[H^+]
\]

Similarly, the expression for \(\frac{[HS^-]}{[S]_{tot}} (A_2)\) and \(\frac{[S^{2-}]}{[S]_{tot}} (A3)\) can be derived.

A plot of \(A_1\), \(A_2\) and \(A_3\) with the values of \(K_1\) and \(K_2\) from Equation \(K_1\) and Equation \(K_2\) respectively gives a plot as shown in Figure 2.4.
Appendix B: Determination of sulphate and hydrogen concentration on the medium

The proposed biofilter produced high concentrations of sulphuric acid and pH and the sulphate concentration on the media was measured to monitor the performance of the biofilter. Since this analysis is the base for analysis on the small volume of water on the medium, it was necessary to ensure that the analytical methods used are precise enough for this study. The following experiment establishes the analytical methods for the determination of sulphate and hydrogen ion concentration on the biofilm.

B.1 Sampling and Measurement

5 pieces of previously dried ABB media was washed with 15M sulphuric acid, allowed to drain and the amount of moisture on the medium was determined using the method described in section 3.3. 10mL of distilled deionized water was added to the sample in a 30mL glass vial and shaken for 10 minutes. 1mL of solution with the extracted water soluble ions were then analysed for sulphate ($\text{SO}_4^{2-}$) and hydrogen ion ($\text{H}^+$) concentration. The $\text{SO}_4^{2-}$ concentration was determined by the standard method based on precipitation as BaSO$_4$ followed by photo spectrometric quantitation at 420nm with the HACH DR 2700 Portable Spectrophotometer (American Public Health Association 2012). The $\text{H}^+$ concentration was determined by titration with NaOH using methyl
orange as an indicator. The experiment was repeated for 10M and 5M sulphuric acid.

B.2 Results and Discussion

The volume of water on the medium was determined from the moisture content of the media (as described in section 3.3) and assuming that the density of water was 1.00 g/mL. The concentration of H\(^+\) and SO\(_4^{2-}\) was determined and is summarized in the Table B.1.

<table>
<thead>
<tr>
<th>Standard H(_2)SO(_4) acid concentration</th>
<th>SO(_4^{2-}) concentration determined by spectrophotometric method</th>
<th>H(^+) concentration determined by titration</th>
</tr>
</thead>
<tbody>
<tr>
<td>M</td>
<td>Average</td>
<td>SD</td>
</tr>
<tr>
<td>10.00</td>
<td>10.00</td>
<td>0.11</td>
</tr>
<tr>
<td>5.00</td>
<td>5.02</td>
<td>0.08</td>
</tr>
<tr>
<td>2.50</td>
<td>2.49</td>
<td>0.04</td>
</tr>
</tbody>
</table>

The results show that if the biofilter is operated under the conditions of this experiment, the concentration of sulphuric acid can be determined by the analytical method being used, inspite the small volumes being analysed. This also shows that the sampling method and the determination of the moisture content is suitable for use in further studies by this setup.
Appendix C: Confirmation of washdown of ions in biofilter on addition of intermittent volume of solution.

During the operation of the biofilter in Chapter 4, the water soluble ions in the biofilter are washed down and accumulated in the biofilter. 3mL of water was added to the biofilter every 4 hours to wash the all the soluble ions out of the biofilter. To confirm that the sulphate ions were being washed out of the biologically active biofilter, the concentration of sulphate on the medium in each section was determined both before and after the addition of water. A comparison of the mass of sulphur in each section before and after the wash showed that the ions were being washed down the biofilter.

C.1 Sampling and Measurement

Five pieces of randomly chosen ABB media from the different sections of the biofilter were collected before washing the biofilter with water. The biofilter was washed with 3mL of water and then five further pieces of randomly chosen ABB media from the different sections of the biofilter were collected. The moisture content of the medium was determined as in section 3.3. The concentration of SO$_4^{2-}$ on the medium was determined as in Appendix B. The leachate was also analysed for SO$_4^{2-}$. 
C.2 Results and Discussion

The mass of sulphur in each section was calculated by determining the concentration of sulphate from the medium sampled. A sample calculation for determination of the mass of sulphur on the medium is given below:

Let the moisture content determined on each media be $Y_{MC}$ g/g (mass of water/mass of media) and the concentration determined by the method of sulphate on each media be $C_{SO4}$ mol/L. If there is $M_1$ g of media in a section, then the mass of water in each section will then be $(Y_{MC} \times M_1)$ g. Assuming that the density of water is 1 g/mL, the volume of water in each section is $(Y_{MC} \times M_1)$ mL. The amount of sulphate in each section will be $(C_{SO4} \times ((Y_{MC} \times M_1)/1000))$ mol. Since the mass of sulphur per mole of sulphate is 32g, the mass of S in the section is $32 \times (C_{SO4} \times ((Y_{MC} \times M_1)/1000))$ g. The value is then converted to mg and the results of the experiment are given in the Table C.1 below.

<table>
<thead>
<tr>
<th></th>
<th>Total amount of sulphur in each section (mg of S)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Before wash down</td>
</tr>
<tr>
<td>Top Section</td>
<td>0.4116</td>
</tr>
<tr>
<td>Middle Section</td>
<td>3.5614</td>
</tr>
<tr>
<td>Bottom Section</td>
<td>5.0085</td>
</tr>
<tr>
<td>Leachate</td>
<td>$8.46 \times 10^3$</td>
</tr>
</tbody>
</table>
As seen in Table C.1, the amount of sulphur in the top section was almost the same before and after the wash. As explained in Chapter Section 4 of this thesis, the top section of the biofilter was not as biologically active as the middle section and there is not much change in the mass of sulphur in this section after the wash. The middle section, which is the most biologically active of the three sections, shows the biggest loss in sulphur mass after the wash. The sulphate produced in the middle section is washed down and accumulated in the bottom section. The bottom section has an increase in the mass of sulphur after the wash. The change in mass of the leachate was not noticeable because the mass of sulphur entering the leachate in this time period is negligible.
Appendix D: Experiments to verify selected analytical procedures

All the analytical procedures used in this thesis were adapted from standard sources or from the literature. The following sections describe some of the analytical procedures that needed further information regarding their precision and accuracy.

D.1 Determination of elemental sulphur in aqueous solution

The procedure has been taken from the literature where elemental sulphur in aqueous solution is extracted into chloroform and then detected in HPLC (Henshaw, Bewtra et al. 1997). 0.8 mL Chloroform (ChemSupply Inc.) and 0.2 mL of 10% nitric acid were added to 1 mL sample and shaken for 15 minutes. The tube was then centrifuged at 1350 rpm for 5 minutes. Using a syringe, the bottom 0.5 mL chloroform layer was carefully extracted and the solution shaken with 1 mL of methanol and injected into Agilent 1200 HPLC Liquid Chromatography System with an Eclipse DB C-18 column (4.6 X 150mm) with a diode array and multiple wavelength detector set at 254 nm. The eluent was HPLC grade methanol (Honeywell Burdick & Jackson) at a flow rate of 1.5 mL/min. Standard elemental sulphur solutions were prepared as specified in the literature (Henshaw, Bewtra et al. 1997).
<table>
<thead>
<tr>
<th>mg/L</th>
<th>Set 1</th>
<th>Set 2</th>
<th>Set 3</th>
<th>Average</th>
<th>Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>25</td>
<td>242.70</td>
<td>249.32</td>
<td>236.08</td>
<td>242.70</td>
<td>6.62</td>
</tr>
<tr>
<td>50</td>
<td>517.17</td>
<td>494.49</td>
<td>539.85</td>
<td>517.17</td>
<td>22.68</td>
</tr>
<tr>
<td>75</td>
<td>725.64</td>
<td>748.16</td>
<td>703.12</td>
<td>825.64</td>
<td>40.83</td>
</tr>
<tr>
<td>100</td>
<td>1232.87</td>
<td>1234.28</td>
<td>1231.46</td>
<td>1232.87</td>
<td>1.41</td>
</tr>
</tbody>
</table>

### Standard curve of elemental sulphur

![Standard curve of elemental sulphur](image)

\[ y = 11.581x \]

\[ R^2 = 0.9857 \]

---

D. 2 Determination of H\(_2\)S in air:
GD 2529 Hydrogen Sulphide Sensor (GasTech) was used as the gas detector with a 2 wire 4-20mA loop powered device. It has an electrochemical sensing unit which is temperature compensated.

Specifications of the sensor are as follows:

<table>
<thead>
<tr>
<th>Specification</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>Range</td>
<td>0-100ppm</td>
</tr>
<tr>
<td>Operating Voltage</td>
<td>12 - 32v dc</td>
</tr>
<tr>
<td>Output Type</td>
<td>4 - 20 mA loop powered</td>
</tr>
<tr>
<td>Output Specifications</td>
<td>Max loop impedance 1 K (24v)</td>
</tr>
<tr>
<td>Operating Temp Range</td>
<td>-10-40c</td>
</tr>
<tr>
<td>Humidity Range</td>
<td>0-99% non condensing</td>
</tr>
<tr>
<td>Accuracy of Reading</td>
<td>0.5% of reading + 1% FSD</td>
</tr>
<tr>
<td>Warm Up Time</td>
<td>30 seconds</td>
</tr>
<tr>
<td>Speed of Response</td>
<td>T90 = 45 seconds at STP</td>
</tr>
<tr>
<td>Zero Drift</td>
<td>&lt; 0.1 % / 30 days</td>
</tr>
<tr>
<td>Calibration Drift</td>
<td>&lt;0.25 % / 30 days at STP</td>
</tr>
<tr>
<td>Technology</td>
<td>Electrochemical sensor with SMT</td>
</tr>
</tbody>
</table>

Sensor output was recorded and stored in a computer as voltage using Labview software (National Instruments Labview (Version 7.2)) and a Labjack data acquisition card (U12, Labjack Corporation). The sensor was calibrated.
against a 100ppm Hydrogen Sulphide (H₂S) calibration gas cylinder with nitrogen balance (CALGAZ) and the data was converted to H₂S concentration by means of a calibration curve.

<table>
<thead>
<tr>
<th>H₂S concentration ppm</th>
<th>Voltage (V)</th>
<th>Average</th>
<th>SD</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Set 1</td>
<td>Set 2</td>
<td>Set 3</td>
</tr>
<tr>
<td>100.000</td>
<td>1.500</td>
<td>1.549</td>
<td>1.451</td>
</tr>
<tr>
<td>64.100</td>
<td>1.211</td>
<td>1.227</td>
<td>1.195</td>
</tr>
<tr>
<td>19.230</td>
<td>0.654</td>
<td>0.694</td>
<td>0.614</td>
</tr>
<tr>
<td>0.000</td>
<td>0.370</td>
<td>0.402</td>
<td>0.338</td>
</tr>
</tbody>
</table>

Standard curve of H₂S (g)

\[ y = 0.0114x + 0.4131 \]

\[ R^2 = 0.9878 \]