Use of activated carbon as biofiltration packing material

Tong, Dongjin

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USE OF ACTIVATED CARBON AS BIOFILTRATION PACKING MATERIAL

TONG DONGJIN

**SCHOOL OF CIVIL & ENVIRONMENTAL ENGINEERING
NANYANG TECHNOLOGICAL UNIVERSITY**

2005

Use of Activated Carbon as Biofiltration Packing Material

Tong Dongjin

School of Civil & Environmental Engineering

A Thesis Submitted to the Nanyang Technological University
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SUMMARY

This project aims to evaluate the feasibility of using biological activated carbon as a novel biofiltration packing material for H_2S removal. A special group of H_2S -degrading bacterium was isolated from a sample of returned activated sludge taken from a local wastewater reclamation plant. The isolated bacterium, identified as *Thiomonas sp.* was able to be immobilized on the surface of activated carbon (Calgon, AP3-60).

Pressure drop test showed that the activated carbon had a much higher pressure drop than that of conventional packing material used in chemical scrubbing systems. Nitrogen adsorption test showed that the average pore radius of the activated carbon was less than 10 nm, which was inaccessible to bacteria.

H_2S breakthrough test and H_2S adsorption test were conducted for the activated carbon. These two tests showed that both H_2S adsorption capacity and adsorption rate would decrease significantly for the water saturated and bacteria immobilized activated carbon because of the presence of the water film/biofilm.

Two biofiltration systems, i.e. biofilter and biotricking filter were adopted to investigate the performance of biological activated carbon for H_2S removal. High H_2S removal efficiency (99.9%) could be achieved by the biofilter at the gas retention time longer than 5s. The H_2S removal efficiency was 97% when the gas retention time was 4.1s with the inlet H_2S concentration controlled at 25 ppm.

Results from running the biotrickling filter showed that the startup time required to achieve a removal efficiency of 99% at a GRT of 12 s was only 2 days. A 99.9% H_2S removal efficiency could be achieved at GRT as low as 4 s. The maximum elimination capacity achieved by the biological activated carbon packed biotrickling filter was 115 g- H_2S / m³.hr when the GRT was 1.3s and inlet H_2S concentration was about 40 ppm.

The results also showed that the pH value inside biofiltration systems should be maintained above 1 in order not to inhibit the microorganism. The optimal bacterial concentration inside the liquid container should be maintained at the range of 10^9 CFU/ml in order to avoid clogging.

Based on the breakthrough test, the adsorption capacity of the non-biological activated GAC for H_2S was 5.4% by weight. Thus the H_2S adsorption capacity of the activated carbon would have been exhausted in 41 days under the operating conditions practiced in running biotrickling filter. Thus the removal mechanism was due to biological degradations.

From the above results, it can be seen that although both of the H_2S adsorption capacity and adsorption rate were affected by the biofilm, the activated carbon could still provide an attractive, nutrient-rich environment for bacteria growth because of its good water holding capacity, large external surface area and H_2S adsorption capacity. However, high pressure drop may be a potential problem when it is used as packing material for biofiltration.

NOMENCLATURE

A	Area
BAC	Biological Activated Carbon
BET	Brunauer-Emmett-Teller
BF	Biofitler
BTF	Biotrickling Filter
C _{in}	Inlet Concentration
Conc.	Concentration
C _{out}	Outlet Concentration
CFU	Colony Forming Unit
DAPI	4'6-Diamidino-2-Phenylindole
DO	Dissolved Oxygen
EC	Elimination Capcity
GAC	Granular Activated Carbon
GRT	Gas Retention Time
H	Henry's Law Constant
HAPs	Hazardous Air Pollutants
H ₂ S	Hydrogen Sulfide
IUPAC	International Union of Pure and Applied Chemistry
NTU	Nanyang Technological University
P	Pressure
PCR	Polymerase Chain Reaction
ppb	Parts Per Billion
ppm	Parts Per Million
Q	Flow Rate
RE	Removal Efficiency
SEM	Scanning Electron Microscope
SL	Surface Loading
SO ₄ ²⁻	Sulfate
S _s	Specific surface Area

S_t	Total Surface Area
T	Time
TS	Sodium Thiosulphate
UPW	Ultra Pure Water
V	Volume
VOC	Volatile Organic Compound
W	Weight
WWTP	Wastewater Treatment Plant

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CHAPTER 1 INTRODUCTION

1.1 Background

In the processing of wastewater, sewage odour is a major issue of concern to environmental engineers all over the world. At a typical wastewater treatment plant (WWTP), the principal sources of odours have been identified to be as follows (Metcalf and Eddy, 1979):

- Specific wastewater containing hydrogen sulfide and other odorous compounds on arrival at the plant;
- Industrial wastes discharged to the collection system;
- Unwashed grit;
- Scum on primary settling tanks;
- Organically overloaded biological-treatment process;
- Sludge-thickening tanks;
- Waste-gas-burning operations where lower-than-optimum temperatures are used;
- Chemical mixing operations;
- Sludge incinerators;
- Digested sludge in drying beds or sludge-holding basins.

The odours most associated with WWTPs are hydrogen sulfide and other reduced sulfide organic compounds such as mercaptans, dimethyl disulfide and dimethyl sulfide. These compounds are generated by the decomposition of a large amount of organic material contained in sewage water under anaerobic conditions. Table 1.1 lists the major odorous compounds identified, together with their normal ranges of concentrations detected near wastewater facilities (Koe, 1995). Although hydrogen sulfide is less odorous than mercaptans, it is still the major contributor of odour to sewage (Koe and Chew, 1998) and is often used as an indicator to the degree of odour of the sewage air by many researchers (Yang, 1999).

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Table 1.1 Major Odorous Compounds in Sewage (Koe, 1995)

Component	Reported Concentration		
	Minimum	Typical	Maximum
	(ppb)	(ppb)	(ppb)
Aldehydes	10	30	100
Ammonia	20	100	2000
Dimethylamine	10	20	50
Dimethyl Sulfide	10	20	50
Hydrogen Sulfide	200	1,000	30,000
Methylamine	10	20	50
Methyl Mercaptan	10	20	50
Skatole	-	50	-

Obnoxious sewage air at sewerage facilities in Singapore is currently treated by methods comprising of chemical scrubber, activated carbon adsorption, incineration and so on. These traditional methods could provide high odour removal efficiency, but they are also costly and may lead to the generation of secondary pollutants. One way to overcome these problems is to use biological control systems, which could be employed to control air emissions contaminated with low to moderate concentrations of biodegradable VOCs, hazardous air pollutants (HAPs), and odorous compounds (Davis, 2001). In recent years, biofiltration technology has gained acceptance worldwide as an economical and reliable air pollution control technology. Biological control systems include three types of process designs namely biofilter, biotrickling filter and bioscrubber.

Current research has shown that the existing biofiltration system implemented for sewage control require at least 30 seconds of gas retention time for a consortium of bacteria to effectively consume and degrade odorous compounds such as H_2S in the sewage air stream. Some new packing material such as the one recently trial tested at a local municipal wastewater treatment plant (Kranji Water Reclamation Plant, Singapore) have

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been demonstrated to reduce the gas retention time to about 8 seconds resulting in a significant reduction in volumetric space of the reactor. Whilst 8 seconds may be a significant improvement, it is still more than twice the size of a conventional chemical scrubber, which unfortunately uses hazardous chemicals.

On the other hand, activated carbon is known to effectively adsorb odorous compounds quickly and gas-carbon contact time designed for carbon systems is typical about 3 to 4 seconds. But once the activated carbon is exhausted, it must either be removed or land-filled, or, in the case of caustically impregnated carbon, re-impregnate with costly and hazardous high concentration caustic chemicals. After one or two reimpregnation operations, the impregnated carbon also required land-filling.

This project aims to utilize and combine the unique property of adsorption of odorous compounds by granular activated carbon with that of biodegradation of adsorbed odorous compounds by specific strain of bacteria so as to develop a new and novel biological carbon packing material for biofiltration system. Two benefits could be gained from using this biological activated carbon as biofiltration packing material.

1. Shortening the gas retention time and thus reducing the volumetric space of the bioreactor.
2. Overcoming and minimizing many problems commonly encountered in biofiltration systems such as poor performance during the start-up period and difficulty to control moisture content.

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1.2 Objective and Scope

The objective of this project is to evaluate the feasibility of using a new biological activated carbon as a novel biofiltration packing material. Laboratory experiments will be conducted to evaluate the performance in terms of removal efficiency and elimination rate of the biological activated carbon for the treatment of H₂S contaminated air. Effects of operating parameters such as gas retention time, H₂S loading rate, pH and SO₄²⁻ concentration inside the biofilter will also be investigated.

In order to achieve the above objective, the scope of this project will mainly cover the following areas:

- 1) The isolation of H₂S degrading bacteria from activated sludge;
- 2) The identification and characterization of the isolated bacteria;
- 3) The evaluation of the physical, chemical and biological properties of the biological activated carbon;
- 4) The assessment of performance of the biological activated carbon for H₂S treatment.

1.3 Outline of This Report

This thesis presents the study on the biofiltration process using biological activated carbon as packing material. The organization of this thesis is as follows. The literature review and some definitions related to biofiltration system are presented in Chapter Two. The methodologies adopted in the study are described in Chapter Three. Chapter Four gives the discussion on the experimental results. Chapter Five contains overall conclusions as well as recommendations for future research.

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CHAPTER 2

LITERATURE REVIEW

2.1 Biological Gas Treatment Technology

The traditional methods for treatment of sewage odour such as chemical scrubber, activated carbon adsorption, incineration could provide high odour removal efficiency, but they are also costly and may lead to the generation of secondary pollutants. One way to overcome these problems is to use biofiltration systems which have the ability to treat large gas flows economically without the production of secondary pollutants or the need to use hazardous chemicals.

Biofiltration is a biological air treatment technology. Waste gases are treated by passage through a biological active porous medium on which microorganisms are immobilized. The basic idea of biofiltration is to utilize these microorganisms to convert target pollutants to harmless products such as CO_2 , H_2O , and inorganic ions such as Cl^- , SO_4^{2-} , and NO_3^- . The schematic view of the sequence of processes leading to microbial degradation of pollutants is shown in Figure 2.1.

Biofiltration has been developed since the 1920's in Europe but up to the middle of the 70's, the proposed processes have remained partially empirical and mostly restrictive in their application. During the 1980s and 1990s, biofiltration progressed rapidly in Europe and slowly in North America. Over the past two decades, biofiltration have developed from systems abating odours to technically sophisticated and controlled units removing specific chemicals from industrial source (Swanson and Loehr, 1997). Today, biological treatment is seen as a mature technology (Groenestijn and Hesselink, 1993) and computer-operated, enclosed systems have been designed to treat odours, VOCs and mixtures (Devinny et al., 1999).

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Figure 2.1- Schematic View of the Sequence of Processes Leading to Microbial Degradation of Pollutants (Waweru et al., 2003)

2.1.1 Techniques for Biological Gas Treatment

Common techniques for biological gas treatment comprise biofilter, bioscrubber, biotrickling filter and membrane bioreactor. A short description of each of the four types of bioreactors for biological off-gas treatment currently in use is given below (see also Figure 2.2).

Biofilter

In a biofilter, the moist biofilm is attached to a porous medium in a packing column. Organic carriers such as compost, soil or wood bark are commonly used as support media, although synthetic media and a variety of mixed media are also used. The off-gas stream is passed through this biologically activated packing column, where the pollutants are degraded by the microorganism. In a conventional biofilter, the nutrients necessary for growth of the microorganisms are supplied by the organic matter. An important control parameter is the moisture content of the packing material at which optimum between 40% to 60% by wet weight, sustained performance is achieved (Lith et al., 1997). To avoid dehydration, the air is generally humidified before entering into the

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biofilter. The typical biofilter operation conditions for waste air treatment are shown in Table 2.1.

Table 2.1 Typical Biofilter Operating Conditions for Waste Air Treatment
(Devinny et al., 1999)

Parameter	Typical Value
Biofilter layer height	1 – 1.5 m
Biofilter area	1 – 3000 m ²
Waste air flow	50 – 300,000 m ³ /h
Biofilter surface loading	5 – 50 m ³ /(m ² .h)
Biofilter volumetric loading	5 – 50 m ³ /(m ³ .h)
Bed void volume	50%
Mean effective gas residence time	15 – 60 s
Pressure drop per meter bed height	0.2 – 1.0 cm water gauge (max. 10 cm)
Inlet pollutant and/or odour concentration	0.01 – 5 g/m ³ , 500 – 50000 OU/m ³
Operating temperature	15 – 30 °C
Inlet air relative humidity	> 98%
Water content of the support material	60% by mass
pH of the support material	pH 6 - 8
Typical removal efficiency	60 – 100%

Biotrickling Filter

A biotrickling filter is very similar to a biofilter. The principle difference between biofilter and biotrickling filter is that in biotrickling filter, the recirculation liquid moves through the packing material, whereas, the liquid phase is stationary in the biofilter. The pollutant gas is passed through a packing material on which a pollutant-degrading biofilm has established. Liquid medium is sprayed on the packing bed either continuously or intermittently so that there is no requirement for the gas to be pre-humidified prior to treatment. Gas flow can be any direction, although co-current, count-current and cross-current flow are by far the most common. The liquid medium usually

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consists of mineral nutrients such as nitrogen and phosphorous for microorganism growth. It should be noted that hydrogen sulfide degrading biotrickling filter host autotrophic organisms and have usually a low nutrient requirement (Cox and Deshusses, 2000). Secondary effluent from wastewater treatment plant could provide sufficient nutrients for H₂S removal in a biotrickling filter (Yang, 1999). Table 2.2 presents the typical characteristics of biotrickling filters.

Table 2.2 - Typical Characteristics of Biotrickling Filter (Cox and Deshusses, 2000)

Parameter	Typical Value
Biotrickling filter height	1 – 5 m
Biotrickling filter section area	1 – 3000 m ²
Air flow rate	100 –1000,000 m ³ /h
Packing void volume ^a	50-95%
Gas retention time	2 – 60 s
Pressure drop	< 1cm of water column per m bed depth
Operating temperatures	15-50 °C
Trickling rates ^b	0.01 –10 m/h
Liquid dilution rate ^c	0.1 –2 per day
Usual pH of the recycle liquid	About 7
-Removal of VOC or compounds difficult to degrade	
-Removal of H ₂ S	1 to 2
Inlet pollutant concentration	
-VOCs	0.010-10 g/m ³
- Odors	500 –50,000 odor units
Typical pollutant removal efficiencies	60-99.9%
^a Value at reactor startup; over time, biomass growth will decrease bed porosity, typical 10-30%	
^b Trickling flow rate / bed cross section area	
^c Liquid feed rate / recycle liquid volume	

Bioscrubber

In a bioscrubber system, absorption of the pollutants takes place in one unit such as a spray tower while biodegradation primarily takes places in a liquid-phase bioreactor, similar to an activated sludge reactor (Davis, 2001). In the latter, microorganisms growing in suspended flocs in the water, degrade the pollutants. The effluent of this unit

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is recirculated over the absorption tower in a co- or countercurrent manner in relation to the flow of the off-gas.

Membrane Bioreactor

In a membrane bioreactor, the waste gas stream is separated from the biofilm by a membrane which is selectively permeable to the pollutants. One side of the membrane is in contact with a liquid phase supplemented with nutrients while the other side is in contact with the waste gas stream. The nutrients rich liquid phase is inoculated with microorganisms capable of degrading the pollutant. These microorganisms organize themselves and form a layer of biofilm attached onto the membrane. As the pollutants migrate through the selectively permeable membrane, they enter the nutrient rich liquid phase and are consequently degraded. The liquid phase is maintained in a reservoir where the nutrients are refreshed, oxygen is supplied, and pH as well as temperature is controlled. Different types of membranes can be used, such as polar or hydrophobic ones. They can be installed in different configurations.

Distinctions between Biological Gas Treatment Techniques

The main distinctions between these four biological gas treatment techniques are summarized in Table 2.3.

Table 2.3 – Distinctions between Four Biological Gas Treatment Systems

Technology	Mobile Phase	Packing medium	Biomass
Biotrickling filter	Liquid and gas	Synthetic	Fixed
Bioscrubber	Liquid and gas	-	Dispersed
Biofilter	Gas	Organic	Fixed
Membrane Bioreactor	Liquid and gas	Membrane	Fixed

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Figure 2.2 - Biological Systems for Off-Gas Treatment (Waweru et al., 2003)

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Advantages and Disadvantages of Biofiltration System

Table 2.4 presents the advantages and disadvantages of the biofiltration technology for odour treatment.

Table 2.4 – Summary of Biofiltration for Odour Treatment

(Burgess et al., 2001)

Advantages	Disadvantages
<ul style="list-style-type: none"> ● Simple, flexible design with low capacity costs ● Good for treating high volumes of low concentration sulphurous odorants ● 99% removal efficiency in streams containing aldehydes, organic acids, sulfur dioxide, nitrous oxides and hydrogen sulfide ● 90% removal of methane, propane and isobutene ● Compounds with air/water partition coefficients of up to 10 can be treated in recirculating biofilters 	<ul style="list-style-type: none"> ● Design criteria still developing ● Large land area required ● Media requires regular replacement ● >15ppm H₂S can lead to rapid acidification of the filter media ● Dissolution of gas into liquid is the rate-limiting step, so long gas residence times are required ● Large media bed volumes are required to obtain such a long gas residence time

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2.1.2 Pollutants Amenable to Biological Treatment

Biological gas treatment has been shown to be efficient for the removal and degradation of many off-gas pollutants such as H_2S , NH_3 and some of VOCs. Several factors contribute to the overall removal efficiency. Since biofiltration functions via “diffusion-reaction” mechanisms (Tanyolac and Beyenal, 1997), contaminants that are amenable to treatment by biofiltration must have two characteristics, i.e. high water solubility and ready biodegradability (Adler, 2001).

High Water Solubility

This, together with low vapor pressure, results in a low Henry’s Law constant, and thus increases the rate at which compounds diffuse into the biofilm. The classes of compounds that tend to exhibit moderate to high water solubility include inorganic compounds, alcohols, aldehydes, ketones and some simple aromatics (Adler, 2001). Less soluble substrates, such as the hydrocarbons found in gasoline, do not accumulate in the liquid phase in significant quantities and the systems may be limited by mass transfer in some case (Schroeder, 2002). In order to enhance the water solubility of some poor water soluble substrates and thus to improve the removal efficiency, the effects of surfactants added to the biofilter on the removal of n-hexane was investigated by Budwill and Coleman (1999). Their results showed that the addition of surfactant (silicone oil) resulted in an enhanced removal of nearly twice the removal in an untreated control biofilter.

Ready Biodegradability

Once a molecule is absorbed on the packing material in a filter media or in the biofilm layer, the contaminant must then be degraded. Otherwise the filter bed concentration may increase to a level that is toxic to the microorganisms or detrimental to further mass transfer. Either of these conditions will result in decreased biofiltration efficiency or even complete failure of the system (Adler, 2001). More readily degradable organic compounds include those with lower molecular weights and those that are more water-soluble and polar. Some inorganic compounds such as H_2S and NH_3 can be biologically treated easily. Biofiltration was effective in removing hydrogen sulfide, VOCs and other

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toxic air emissions. In terms of degradability, experimental results from Webster and Devinny (1996) suggest that the order of removal efficiency appears to be hydrogen sulfide > aromatics > aldehydes and ketones > chlorinated hydrocarbons.

Mass Transfer vs. Biological Reaction

In biofilm, mass transfer (by diffusion) and biological reaction (biodegradation) occurs together. In most cases, biofiltration systems are applied for the removal of low-concentration malodor ingredient, such as sewage air containing sulfur and nitrogen substances, and the inlet loading of the gas does not exceed the microbial activity which the packing media can hold. In these conditions, the performances of the biofiltration system are restricted by the mass transfer of the target pollutant from the gas-phase to microorganisms with first order kinetics (Higuchi et al., 2000). However, a particular emphasis also should be placed on the analysis of the rate-limiting step for treating pollutants such as MTBE, where it was established that the process was mostly limited by the biological reaction rather than by mass transfer (Fortin and Deshusses, 1999a,b).

2.1.3 Summary of Pollutants Removal in Biofiltration Systems as Reported in the Literature

Experimental results with biofiltration have been reported by various investigators, and a summary review is given in Table 2.5. This table gives information on the pollutant treated, the type of biofiltration system used, the type of packing material and microorganism employed, as well as the maximum elimination capacity achieved.

In this literature review, a special interest is given to the treatment of H_2S which is the major contributor of sewage odour. Table 2.6 summarizes the study of H_2S treatment using biological techniques by different researchers. The maximum elimination capacity varied from 7 to 140 $\text{g-H}_2\text{S} / \text{m}^3 \cdot \text{hr}$. Koe and Yang (2000) treated H_2S in a biotrickling filter operated at a GRT of 5-15s. Significant breakthrough of H_2S was observed at 5 and 7 s GRT for loadings of 40-50 $\text{g-H}_2\text{S} / \text{m}^3 \cdot \text{hr}$. The minimum GRT for achieving 99% removal efficiency was 5 seconds. While in Gabriel and Deshusses's study (Gabriel and

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Deshusses, 2003), 98% removal efficiency was reportedly achieved at the GRT as low as 1.6s.

From Table 2.5 and Table 2.6, it can be seen that parameters related to the mass transfer, the microbiology (e.g., type of bacteria), the design (e.g., type of bioreactor and type of packing material) and the operating parameters of the bioreactor (e.g., GRT and inlet concentration) affected the performance of biofiltration systems.

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Table 2.5 - Elimination Capacities of Various Odorous Compounds in a Biofiltration System.

Pollutant	Treatment System	Packing Material	Inoculum	Max. EC (g/m ³ .hr)	Reference
Ammonia	BF	Compost /GAC	Activated Sludge	13.5	Liang et al., 2000
Dichloromethane	BTF	Super Torus Saddles	<i>Hyphomicrobium GJ21</i>	52	Okkerse et al., 1999
Diethyl ether	BTF	Ceramic Pellets	Activated Sludge	60	Zhu et al., 1996
DMS	BF	Peat	NA	19.21	Budwill and Coleman
Heptane	BTF	Pall ring	NA	24	Schindler and Friedl, 1995
Hydrogen Sulfide + Carbon Disulfide	BF	Peat	<i>Thiobacillus</i> strain	187 (Sulfur)	Hartikainen, et al., 2001
Methyl ethyl ketone	BTF	Plastic Packing	<i>Bacillus thuringiensis</i>	40	Chou and Huang, 1997
Mono-Chlorobenzene	BTF	ceramic particles	NA	60	Mpanias and Baltzis, 1998
Methanol	BF	Inert material	Sludge	120	Yang et al., 2002
MTBE	BTF	Pall ring	NA	45.4	Fortin and Deshusses, 1999
MTBE	BTF	Lava rock (1-3cm)	NA	37.1	Fortin and Deshusses, 1999
n-butanol	BTF	Granular Clay	NA	102	Heinze and Friedrich, 1997
Nitric Oxide	BTF	Blast-Furnace Slag	NA	37	Chou and Liu, 2000
Nitrobenzene	BTF	Perlite	<i>Agrobacterium sp</i> <i>Sphingomonas sp</i> <i>Achromobacter sp</i>	50	Oh and Bartha, 1997
Styrene	BTF	Jeager Pack®	Mixture of Microbes	35	Webster et al., 1999
Styrene	BTF	Blast-Furnace Slag	Activated Sludge	44.2	Chou and Hsiao, 1998
Toluene	BTF	Pall ring	<i>Pseudomonas sp.</i>	125	Wu, 2000a
Toluene	BF	Compost	NA	55	Delhomenie el al., 2002
Sulfur Dioxide	BTF	Polyurethane foam	NA	944	Deshusses and Philip, 2003
Volatile Fatty Acids	BTF	Ceramic Beads (SiO ₂)	<i>Rhodococcus sp</i>	642	Yun and Ohta, 2002
Hydrogen Sulfide			Refer to Table 2.6		

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Table 2.6 - Summary of Studies of H₂S Treatment Using Biological Techniques by Different Researchers

Treatment System	Packing Material	Micro-Organism	Removal Efficiency	Max. EC (g-H ₂ S/m ³ .hr)	Reference
BF	Compost	N.A	> 99% at GRT = 23s; 93% at GRT = 7s	130	Yang and Allen, 1994
BTF	3 mm glass bead	<i>T. thiooxidans</i>	GRT = 60s	30	Lizama and Sankey, 1993
BTF	Pall ring	<i>Thiobacillus sp</i>	99% at GRT=5s; 78% at GRT=3s	-	Koe and Yang, 1999
Fibrous Bed Bioreactor		NA	92% at GRT > 22s	65	Li et al., 1998
			96.5 % at GRT> 50s		
BTF	polyurethane foam	activated sludge	98% at GRT= 1.6-2.3s (C _{in} = 30ppm)	140	Gabriel and Deshusses, 2003
BF	peat	<i>T.thioparus</i>	100% at GRT = 120s 90% at GRT = 51s; 60% at GRT =26s (C _{in} = 355ppm)	55	Oyarzun et al., 2003
BTF	Pall rings	<i>T.thiooxidans</i>	92% at GRT = 7s (C _{in} = 100ppm)		Wu et al., 2001
BF	Biosorbens TM	N.A	97% at GRT = 30s (C _{in} = 39ppm)	6.32	Shareefdeen, 2002
BTF	Polyurethane foam + activated Carbon	Activated sludge	93% at GRT = 3s (C _{in} = 16.2 ppm)	25	Highchi et al., 2000
BF	Lava Rock	NA	99% at GRT =15s (C _{in} = 300 ppm)	100	Yang et al., 1999
BTF	Pall ring	<i>T.thiooxidans</i>	90% at GRT=3s (C _{in} = 100 ppm) 99% at GRT=5s (C _{in} = 20 ppm)	88.3	Wu, 2000a
BTF	Pall ring	<i>T.thiooxidans</i>	40% at GRT=3s (C _{in} = 100 ppm) 99% at GRT=30s (C _{in} = 5 ppm)	82	Zhou, 2000
BF	Beads (3mm Dia)	<i>T. novellus</i>	96 .5% at GRT= 50s 98% at GRT= 100s	29.2	Chung et al., 1998

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2.1.4 Bacteria for H₂S Biodegradation

The presence of microorganisms is necessary for effective removal of H₂S gas. Although activated sludge (mixed culture) has been used in biofiltration system, acclimation times of at least 1-3 weeks are required. Recently, the use of pure cultures is gaining a lot of attention because it shortens start-up time and enhances removal efficiencies and capacities (Chung et al., 1998).

Several species of microorganisms can oxidize H₂S to form SO₄²⁻ such as *Thiobacillus*, *Thiomicrospira* and *Thiosphrera*. Nearly all of them are able to grow autotrophically and one-half can also grow organotrophically (Madigan et al., 1997). *Thiobacillus sp.* is the most frequently used one in the biotreatment of gaseous H₂S (Jensen and Webb, 1995) among others. Lizama and Sankey (1993) also pointed out that *T. thiooxidans* is most suitable for the oxidation of H₂S in an industrial process because CO₂ fixation is a high-energy-requiring process, it must oxidize large amounts of sulfide for growth, producing very low levels of biomass. The standard oxidation reactions for H₂S by the aerobic species in standard conditions are as follows (Oh et al., 1998).

Thiobacillus sp.

Thiobacillus sp. has been defined by its main feature, its ability to generate energy from oxidation of inorganic sulfur compounds (Mitchell, 1974). They are gram-negative, non-spore-forming rod-shaped cells and motile by means of a single polar flagellum. Altogether there are eight species of *Thiobacillus sp.* in the natural environment. The optimum temperature for *Thiobacillus sp.* is about 28-30°C. Table 2.7 shows the different pH ranges for all *Thiobacillus sp.*

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Table 2.7 – pH range for the *Thiobacillus* sp.

Species	Growth range	Optimum pH range
<i>Thiobacillus novellas</i>	5.0-9.2	7.8-9.0
<i>Thiobacillus thioparus</i>	4.5-10	6.6-7.2
<i>Thiobacillus neapolitanus</i>	3.0-8.5	6.2-7.2
<i>Thiobacillus perometabolis</i>	2.8-6.8	N.A
<i>Thiobacillus intermedius</i>	1.9-7.0	6.0-7.0
<i>Thiobacillus ferroxidans</i>	1.4-6.0	2.5-5.8
<i>Thiobacillus thiooxidans</i>	0.5-6.0	2.0-3.5
<i>Thiobacillus denitrificans</i>	N.A	N.A

The *Thiobacillus* species are differentiated on the basis of the sulfur compound they use as an energy source (Mitchell, 1974). The best known sulfur bacterium is *Thiobacillus thiooxidans*. It is a highly aerobic strict autotroph and converts H₂S to sulfuric acid. It has the ability to grow and metabolize in highly acidic condition. It grows well at pH 2 as shown in Table 2.7. Jaworska and Urbanek (1998) reported that the optimum temperature for *Thiobacillus thiooxidans* was 33°C. *Thiobacillus novellus* utilizes thiosulfate as its energy source. It is more sensitive to acidity and dies below pH 4. *Thiobacillus denitrificans* can grow anaerobically. It uses nitrate as the terminal electron acceptor and sulfur as the energy source to produce sulfates and nitrogen gas. In biological system, *Thiobacillus thiooxidans* is commonly used. According to the eighth edition of Bergey's Manual of Determinative Bacteriology (Holt and Bergey, 1989), the shape of *Thiobacillus thiooxidans* is short rod, 0.5 by 1-2 µm, occurring singly, in pairs or in short chains. Colonies on thiosulfate agar are minute (usually less than 1.0 mm), transparent or whitish yellow which clears on prolonged growth.

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Thiomonas sp.

Although most of *Thiobacillus sp* are autotrophic, many species also can grow under organotrophic conditions, exhibiting variable patterns of utilization of organic compounds as carbon or/and energy sources. Recently, it is found that some sulfide oxidizing microorganisms have more versatile physiologies and can grow autotrophically, heterotrophically and mixotrophically. Extensive characterization of some thiobacilli has allowed different physiological groups to be defined. As a result, mixotrophic thiobacilli have recently been reassigned to a new genus, *Thiomonas* (Amils et al., 1998).

2.1.5 Packing Material

The selection of an appropriate packing media for biofiltration systems is essential to overall bioreactor performance because packing material not only supplies the surface for the biomass to grow, but also plays an important role in air and water distribution, as well as mass transfer (Yang et al., 2000). Therefore, it is generally believed that the odour removal performance of a bioreactor system depends primarily on the type of packing medium. However, few examples were methodically reported about the relationship between the characteristics of packing material and bioreactor performance (Higuchi et al., 2000).

Organic material such as compost, soil and wood bark are commonly used in biofilters while random-packed polypropylene pall rings are one common type of packing material for biotrickling filter. This kind of packing material was used by Yang (1999), Wu (2000a) and Zhou (2000).

The packing media used in biofiltration systems should have appropriate capacities of ventilation, moisture retention and microorganism holding capacities. Effective specific surface area, which in most cases is approximated by the outer packing surface area per unit volume, is also important because nearly all of the surface area of highly porous materials such as activated carbon is inaccessible to the

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microorganisms (Schroeder, 2002). The desirable properties for packing material used in biofiltration systems are summarized as follows: (Davis, 2001):

1. High surface area per unit volume of packing material. A high available surface area is necessary to support biofilm growth, minimize packing column volume and achieve high pollutant-elimination capacities.
2. High void ratio. A high void ratio is desirable in biotrickling filter to maintain low pressure drops and minimize clogging as biomass accumulates in the system.
3. Chemical resistance. The selected packing material should be resistant to degradation by the gas stream contaminants, microbial by-degradation generated within the biofilm and the nutrient solution that is trickled over the packing material.
4. Lightweight. In general, it is advantageous to use lightweight packing material for ease of handling and avoid reinforcing the biotrickling filter.
5. Inexpensive. The packing material can represent a significant fraction of the total system cost; so it is important to use inexpensive packing material.

2.2 Definitions and Performance Parameters

Operation and performance of biotrickling filter for air pollution control is generally reported in terms of removal efficiency (RE) or pollutant elimination capacity (EC) as a function of the pollutant loading (L) and gas retention time (GRT). These terms are defined as follows:

$$RE = \frac{C_{in} - C_{out}}{C_{in}} \times 100\% \quad (2.4)$$

$$L = \frac{C_{in} \times M.W}{24521 \times V} \times Q \times 60 \quad (2.5)$$

$$GRT = \frac{V}{Q} \quad (2.6)$$

$$EC = L \times RE \quad (2.7)$$

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Where

C_{in} = Inlet pollutant concentrations (ppmv)

C_{out} = Outlet pollutant concentrations (ppmv)

V = Volume of packing bed (Liter)

Q = Gas stream flow rate (L/min)

$M.W$ = Molecular weight of pollutant (g/mole)

Another parameter that will affect the performance is surface loading (SL) which is defined in equation (2.5). Surface loading is a measure of the volumetric gas loading applied to a bioreactor. Although often expressed in units of meters per hour (m/h) and referred to as “face velocity”, it is really a loading parameter (Swanson et al., 1997). For a specific bioreactor, higher surface loading means higher flow, shorter GRT and lower RE. Upper limits on surface loading exist due to pressure drop concerns and GRT requirements.

$$SL = \frac{Q}{A} \quad (2.8)$$

Where A is the cross-sectional area of the bioreactor.

The elimination capacity and the loading are calculated based on the volume of the packing material and not on the total volume of the reactor. Also, the GRT is calculated based on the total volume of packing material and not the void space in the packing material. Thus the actual gas retention time will be lower depending on the void ratio of the packing material, the dynamic liquid hold-up and the amount of biomass attached on the packing material.

The relationship between elimination capacity and pollutant loading in a biotrickling filter is shown in Figure 2.3. It is a common practice to report the performance as a function of the pollutant loading, rather than the concentration. One underlying assumption is that the performance depends on the pollutant loading, hence, that low concentration-high flow rate conditions lead to similar elimination capacities to high-concentration-low flow rate conditions. This

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assumption is generally valid because the pollutant concentrations commonly encountered in biotrickling filters are high enough for the micro-kinetic to be zero order (Cox and Deshusses, 2003). However, this is no longer true when the pollutant concentrations are very low level because first order kinetics (mass transfer kinetics) will prevail in the biofilm resulting in a reduction of the maximum elimination capacity.

Figure 2.3 Typical Elimination Capacity vs. Load Curve for a Biotrickling Filter

Examination of Figure 2.3 reveals that there are essentially three operating regimes:

1. Low loading, also called first order regime. The elimination capacity and the loading are identical and the pollutant is completely removed. The performance increase proportionally with the loading;
2. Intermediate range. Breakthrough of the pollutant occurs. With higher inlet concentration or higher air flow rates, the elimination capacity increases, but to a lesser extent than the loading;
3. High loading, also called zero order regime. The biotrickling filter is operated at its maximum elimination capacity. Increases in loading do not result in further increases in elimination capacity, the removal efficiency

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decrease. As indicated on the figure, if the concentration is very low, the maximum elimination capacity is reduced accordingly.

For the evaluation of biotrickling filter performance, one should consider both the maximum elimination capacity and the removal efficiency (Cox and Deshusses, 2003).

2.3 Activated Carbon

2.3.1 Activated Carbon as Adsorbent an Adsorption System

Activated carbons are widely used as adsorbents of gas and vapors. They are manufactured in granular form, usually between 4x6 to 4x10 mesh in size (Davis, 2000). The usefulness of activated carbon results from their remarkable surface and structural properties, which in turn arise from the presence of significant amount of micropores. According to International Union of Pure and Applied Chemistry (IUPAC) recommendations (Kruk et al., 1997), it is expedient to characterize pores according to their size.

1. Pores with opening exceeding 500 Å in diameter are called “macropores”.
2. The term “micropores” describes pores with diameters less than 20 Å.
3. Pores of intermediated size are called “mesopores”.

Activated carbons can remove many odours, but will always have a slight residual odour (Koe, 1999). The performance of the activated carbons is governed by the unique features of their surface such as developed microporosity, high pore volume and large specific surface area. Experiment conducted by Adib et al. (1999) showed that the surface areas and volumes of micropores decrease in the same order as H₂S breakthrough capacity. Another fact that seems to play an important role in removal of H₂S is the average pH of the carbon surface or the pH resulting from the local environment (Adib et al., 1999). Bandosz (2002) reported that when the acidity is

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expressed as pH, its value of activated carbon should be higher than 5 to ensure the effective removal of H_2S .

Unimpregnated virgin (or unreactivated) carbon and carbon impregnated with various chemicals such as NaOH and KOH are both commonly employed in the adsorption system. In both activated carbon systems, a saturation point will be reached where no further adsorption can take place. In most cases, the carbon is taken off line and regenerated, after which, the carbon is placed back until the saturation point re-occurs.

The spent activated carbon could be regenerated by two means, i.e. thermal treatment and cold water washing. Study conducted by Bagreev et al. (2002) showed that thermal treatment is more efficient than cold water washing. The latter process was able to remove only a small percentage of sulfur species in the form of sulfuric acid, leaving the deposit of elemental sulfur intact. However, treatment at 300°C resulted in the removal of a significant amount of deposited sulfur species. The hydrogen sulfide adsorption capacity of regenerated samples was low due to the alternations in surface chemistry, which occurred during the treatment.

Both impregnated and unimpregnated activated carbons provide some degree of odour removal capacity, but all have drawbacks (Daniel and Leo, 2003). For unimpregnated activated carbons, they have very poor H_2S removal capacities and once the carbons are exhausted, they must be regenerated, removed or land filled. For impregnated activated carbons, although they can remove H_2S odour very effectively, they associated with a few significant disadvantages (Bagreev et al., 2001). Among these disadvantages are:

- 1 Lower temperature of self-ignition due to exothermic reaction of caustics with CO_2 present in the air;

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- 2 Limited capacity for physical sorption due to filling of the pore system with impregnate;
- 3 Special precautions have to be observed due to the presence of corrosive materials;
- 4 Costs of caustic impregnated materials are usually higher than as-received unimpregnated carbons.

2.3.2 Biological Activated Carbon

The term biological activated carbon (BAC) was suggested by Rice and Robson, (1982) for water and wastewater treatment. BAC processing in water and wastewater treatment is defined as a simultaneous combination of GAC adsorption of dissolved organic materials coupled with aerobic biological oxidation of organic material. Similarly, the idea of biological activated carbon (Biocarbon) proposed to use in biological gas treatment system is to buffer the fluctuations in the concentration of contaminants in waste gases so that a constant supply of contaminants to the bioreactor can be achieved (Weber and Hartmans, 1995).

There are two main component steps namely, GAC adsorption and biological degradation involved in biological activated carbon system. When the pollutant gas passes through a biocarbon packed reactor, its concentration will be reduced by two means, i.e. GAC adsorption and biological degradation. This can occur because GAC media operating in biologically enhanced modes contain bacterial colonies on the external surface layer and their “exoenzymes” in the micropores (Scholz and Martin, 1997). Figure 2.4 (Rice and Robson, 1982) schematically shows the relationships between micropores, macropores and bacteria located in the macropores.

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Figure 2.4 Relationships between Micropores, Macropores and Bacteria
(Rice and Robson, 1982)

Macropores are the large openings on the outer surface of GAC where the bacteria are immobilized. The pollutant gas molecules must pass the macropores into the much smaller micropores where it is adsorbed. Thus the pollutant gas molecules are exposed to the bacterial action as they pass on their way into the micropores. If and when the adsorbed pollutant molecules are later desorbed from the micropores and diffuses back out into the main solution stream, they must again pass the bacterial colonies located in the macropores (Rice and Robson, 1982). As a result, a microorganism on the surface or in the macropores might benefit because the GAC increases transport of molecules on the cell over what is available from the water phase only (Hodge et al., 1992). Besides this, granular activated carbon has excellent structural properties, with uniform particle size and good resistance to crushing. It also has substantial water-holding capacity and provides a good surface for microbial attachment (Devinny et al., 1999).

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Because of the above advantages, the uses of biological activated carbon for off-gas treatment have been investigated extensively. Biological deodorization of methyl mercaptan using activated carbon as packing material was studied by Lee and Shoda (1989). Their results showed that activated carbon was the best tested packing material compared with other carriers or peat. Activated carbon also had worked quite well in biofiltration of hydrocarbon fuel and ethanol vapors (Devinny et al., 1999). Granular activated carbon packed biofilters have been operated successfully at a wastewater treatment plant for simultaneously removal of low concentration of hydrogen sulfide and VOCs (Webster and Devinny., 1996). A three phase fluidized bed bioreactor in which *Thiobacillus sp.* was immobilized on activated carbon has been run by Oh et al.(1998). Their results showed that the system could remove 94% of the hydrogen sulfide in the concentration range of 100-200 ppm; from the upset and recovery test, the system was proved stable within the moderate inlet concentration changes.

Activated carbon also can be mixed with other packing material in a biofilter treating pollutant such as toluene vapor. Weber and Hartmans (1995) found that the buffer capacity of the activated carbon depended on the desired concentration range of the toluene vapor entering the bioreactor and on the time available for desorption.

Alternatively, some researchers have proposed the application of suspended activated carbon in bioscrubbers to improve mass transfer of hydrophobic volatile compounds in the scrubber and to buffer fluctuations in the supply of contaminants (Groenestijn and Hesselink, 1993).

Although activated carbon based packing materials have adsorbing properties that are not encountered in other conventional packing materials, the presence of a bacterial population on the surface of the GAC rapidly leads to the formation of a biofilm over the entire surface on the GAC particle. This increases the resistance to

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mass transfer for the pollutants from the aqueous phase onto the GAC surface (Mason et al., 2000).

Zhao et al. (1999) reported that the toluene adsorption capacity of biofilm coated activated carbon remained at 70% of initial levels during the first two month and after 6 months, the remaining capacity was only about 50%. There was no direct relation between the amount of biomass or the thickness of the biofilm on the carbon and the remaining adsorptive capacity. The loss of adsorption capacity over an extended period of operation appears to result directly from bioactivity, rather than from toluene loading. Based on this result, if the adsorption removal mechanism is used to provide a buffer during the transient conditions, this remaining capacity may be sufficient without carbon replacement.

Another drawback using GAC as packing material was that the addition of an alkaline solution to control the pH in GAC packed biofilter was less effective in compost packed biofilter for treating H₂S (Webster et al., 1996a).

2.4 Gaps in Research

While much work has been done on the biological activated carbon for water and wastewater treatment, little information is available on biofiltration system packed with biological activated carbon for odour, especially H₂S treatment.

This project aims to utilize and combine the unique property of adsorption of odorous compounds by granular activated carbon with that of biodegradation of adsorbed odorous compounds by a specific strain of bacteria so as to develop a new and novel biological carbon packing material for biofiltration systems. This biological activated carbon is supposed to help to shorten the gas retention time and thus to reduce the volumetric space of the bioreactor.

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CHAPTER 3 METHODOLOGY

3.1 Bacteria

3.1.1 Bacteria Isolation and Cultivation

Preparation of Liquid Culture Medium

The medium derived from the component in Table 3.1 was used in the preparation for cultivation of H₂S degrading bacteria.

Table 3.1 Chemical Composition for Isolating H₂S Degrading Bacteria

Components	Chemical Formula	Weight	Function
Sodium Thiosulphate	Na ₂ S ₂ O ₃ .5H ₂ O	10 g/L	Energy Source
Potassium Dihydrogen Phosphate	KH ₂ PO ₄	1 g/L	P Source & Buffer
Ammonium Chloride	NH ₄ Cl	1 g/L	N Source
Magnesium Chloride Hexahydrate	MgCl ₂ .6H ₂ O	0.46 g/L	Mg Source
Cyclohexi-mide		50 mg/L	Anti fungus

The above components (excluding sodium thiosulphate) were added to distilled water in a 1 L beaker and the volume was brought to about 880 ml. The solution was mixed thoroughly and pH of around 4.8 at room temperature was recorded. This pH was slowly adjusted to 6.8 ± 0.2 at 25°C using 0.1 M NaOH solution. After the final volume of liquid medium was brought to 900 ml by topping up with distilled water, the liquid medium was then poured into 1 liter autoclave bottle and autoclaved for 15 minutes at 15 psi and at 121°C.

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Under a laminar flow chamber, 100 ml of 10% $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ solution was added to the autoclaved liquid medium while filtering through the $0.2\mu\text{m}$ sterile microfilter. The mouth of the autoclave bottle was flamed before and after each addition.

Preparation of Solid Medium

A mass of 20 gram of Bacto™ agar was added into 900 ml liquid culture medium mentioned above (excluding Sodium Thiosulphate) in a 1 L autoclave bottle. The mixture was then autoclaved for 15 minutes at 15 psi and at 121°C .

The autoclaved agar salt solution was then cooled in a water bath to 60°C prior to adding 10% $\text{Na}_2\text{S}_2\text{O}_3$ solution. This will prevent instability of $\text{Na}_2\text{S}_2\text{O}_3$ at high temperature and solidification of agar at low temperature. A volume of 100 ml 10% $\text{Na}_2\text{S}_2\text{O}_3$ was added to the agar salt solution while filtering through the $0.2\mu\text{m}$ microfilter and swirled to mix. The mouth of the autoclave bottle was flamed before and after adding $\text{Na}_2\text{S}_2\text{O}_3$ solution and the cap was flamed before covering the bottle.

The agar was left to solidify in the agar plates under a laminar flow chamber. Once cooled and solidified, the agar plates were stored in a refrigerator at 4°C prior to use with the covers facing down.

Flask Culturing

A volume of 10 ml activated sludge from the secondary sedimentation tank at a local Water Reclamation Plant was added to 90 ml of liquid medium in a 250 ml glass flask. This process was done in a laminar flow chamber. The flask was sealed with cotton and then shaken continuously on a shaker at 100 – 120 r/min at room temperature.

5 ml sample of the above bacteria liquid was taken everyday for measurement of pH value and SO_4^{2-} concentration. The sodium thiosulphate (TS) concentration was

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also measured by Iodometric method according to Standard Method for the Examination of Water and Wastewater (1998).

The bacterial liquid was transferred to fresh medium once the pH reached 2 and the final pH of the newly transferred bacterial liquid was adjusted to 5 to 6 using 0.1 M NaOH solution.

Culturing on Agar Plate

After 4 to 5 times of transformation of the flask cultures, a volume of 0.1 ml bacteria seed was taken from the flask and then plated onto the agar plate. A blue spreader was used to spread the bacteria seed evenly on the agar (solid medium) surface.

About 3 to 4 days later, bacteria colonies began to appear on the agar plates. A loopful of the colonies was selected using a sample loop and streaked onto a fresh agar plate. The above step was repeated for 4 to 5 times to obtain the pure culture of the bacterium.

Mass Culture

After obtaining the pure culture, a loopful of the colonies selected was added to 100 ml of liquid medium in a 250 ml flask. The cotton-sealed flask was then shaken continuously on a shaker at 100 – 120 r/min for about two weeks at room temperature until pH dropped to 2.

Figure 3.1 shows the process of isolating H₂S degrading bacteria.

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Figure 3.1 - Processes of Isolating H_2S -Degrading Bacteria

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3.1.2 Morphological Characterization

Gram Staining of Bacterial Smear

Under a laminar hood, a drop of ultra pure water (UPW) was placed onto the centre of a clean microscope slide. Samples were grabbed using a sample loop and mixed into the water droplet on the microscope slide (Sample loop was flamed and cooled before and after grabbing the cultures). Once air dried, the microbes were fixed on the slide by flaming.

The fixed sample was allowed to cool and gram staining procedure was carried out. The crystal violet was applied onto the visible sample stain and left for 1 min to react. The slide was then flooded with iodine solution for 2 minutes. After that, the slide was then washed under distilled water and decoloriser to remove excess crystal violet and iodine. Once dried, the smear was counter stained using red staining for 30 seconds. To remove the excess stain, the smear was washed again with water and then dried before examination under the microscope.

Scanning Electron Microscopy (SEM)

Bacteria sample was fixed on a 0.2 μm polycarbonate (Millipore, USA) filter paper and the filter paper on which the bacteria sample was retained was soaked in a breaker of 2% (v/v) glutaraldehyde for about 2 hours. The sample was then washed 20 minutes for three times with 0.1 M sodium cacodylate buffer. After that, the washed sample was dehydrated in 50, 70, 85, 95, 100% ethanol each for 15 minutes. Followed by dehydration, the sample was dried using a critical point drying equipment (E3000 Serious). The dried sample was sputter-coated with gold at 20 mA in a high vacuum and low temperature cryo-chamber for 60 seconds, and then viewed with a scanning electron microscope (Stereoscan 420, Leica, Cambridge Instruments) at 15 kV.

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3.1.3 Bacterial Counting

Direct count method and indirect count method are two main methods for determining bacteria numbers. Compared to other direct count methods, Epifluorescence direct counting is one of the best methods for enumeration of bacteria counts in natural environmental samples (Kuwae and Hosokawa, 1999). In this counting method, DAPI (4'-6-diamidino-2-phenylindole) was employed as fluorescent. For indirect count method, spread plate method was used since it is in favour of other indirect count method such as pour plate method.

4'-6-diamidino-2-phenylindole (DAPI) Stain and Total Cells Counting

Before DAPI stain, a DAPI stock solution of 1 mg/ml concentration was prepared and stored in a refrigerator at 4°C when not in use. Bacterial samples were diluted with sterilized Ultra Pure Water (UPW) to reach a final concentration of 10^5 to 10^6 cells per ml. 10 µl DAPI solution was mixed with 1ml diluted bacterial sample. The mixture was gently vortexed and kept in dark for 30 minutes. The DAPI-stained cell suspension was filtered through 0.2 µm polycarbonate (Millipore, USA) filter paper which was then fixed on a clean microscope slide. Bacteria retained in the filter paper was observed and counted under fluorescent microscopy (Olympus BX-FLA-3 Epifluorescence microscope, Japan) equipped with a 100X oil immersion objective. Bacterial cells that fluoresce appeared as blue or green in color.

This method usually provides numbers that are higher than culturable counts because direct counts include viable, dead and viable but nonculturable organisms.

Plating Counting Method

In this counting method, it is assumed that each viable cell can yield one colony. A volume of 0.1 ml appropriately diluted culture was spread over the surface of the agar plate using a sterile spreader. The plate was then incubated at 30°C for 3 to 5 days when the colonies appeared. The number of colonies was counted on plates

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that had 30 to 300 colonies as it gave the most valid counts statistically. Viable count is expressed as the number of colony-forming units (CFU).

3.1.4 Bacteria Identification

Polymerase Chain Reaction (PCR)

After bacterial cells were cultured on agar plate for 5 days, colonies were collected using a sterile pipette tip and smeared onto the bottom of a PCR tube.

Thermal cycling was carried for 30 cycles. Each cycle consists of denaturation at 94°C for 1.5 minutes, primer annealing at 57°C for 1.5 minutes and extension at 72°C for 2 minutes. The last step of the last cycle was continued for 10 minutes and followed by cooling at 4°C.

Agarose Gel Electrophoresis

Agarose gel was prepared by dissolving 0.5 g agarose (Promega, USA) and 1 ml 50X TAE buffer in 50 ml of distilled water. The mixture was boiled in a microwave oven for 1.5 minutes. 2.5 µl of 10 mg/ml ethidium bromide solution (BioRad, England) was added to the molten agarose del which was cooled down to 50°C. The gel was cast in a horizontal gel slab. The set gel was immersed in a mini-subcell GT (BioRad, England) containing 250 ml 1X TAE buffer (5 ml 50XTEA diluted in distilled water at a final volume of 250 ml). 5 µl of PCR product sample was mixed with 2 µl gel loading dye and loaded onto the agarose gel. The gel was run at 90 mV for 45 minutes. Once the run was completed, the gel was viewed and photograph was taken with a Kodak Digital Image Station 440CF (NEN Life Science Product)

After purification, PCR Product was send to the Biolab, at the School of Civil and Environmental Engineering, Nanyang Technological University, Singapore, for identification.

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3.2 Bacterial Immobilization

Two common techniques namely continuous-circulation method and immersion method are normally used to immobilize bacteria onto packing materials (Yap, 1999). The first method is used for biotrickling filter and the second technique is usually used for the purpose of regular monitoring of viable cell attachments. In this study, immersion method was adopted to create biological activated carbon. In the method, a volume of 400 ml of autoclaved activated carbon (Calgon, AP3-60) was immersed in a 3 L flask containing 1.5 L nutrient medium inoculated with the isolated H₂S degrading bacteria.

The flask was continuously shaken at 100-120 r/min at room temperature. The viable cell adhesion onto activated carbon (Calgon, AP3-60) was monitored weekly. This was done using the Centrifuge Method as used by Yap (1999). In this method, about one gram of carbon sample was extracted from the bacteria-carbon mixture and placed in 10 ml of 0.8% NaCl solution in a centrifuge tube. The bottle was then centrifuged at 10,000 r.p.m for 5 minutes to dislodge the bacteria from the carbon surface. A bacteria count of the NaCl solution was then conducted using direct counting (DAPI stain) method.

3.3 Characterization of Packing Material

In this project, activated carbon (plain and immobilized with bacteria), was studied.

3.3.1 pH of Carbon Surface

The pH of the carbon suspension, which provides some information about the average acidity/basicity of sorbents, was evaluated according to ASTM standard procedure D3838. Briefly, 10 gram of activated carbon was placed in 100 ml of hot water and boiled gently for 15 minutes. Then the flask content was filtered, the filtrate was cooled, and its pH was measured.

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3.3.2 Pressure Drop Test

Pressure drop is the major factor that determines the amount of energy needed to force the contaminated gas through a bioreactor system. In order to investigate the effect of liquid recirculation and flow direction on the pressure drop for the activated carbon, pressure drop tests were conducted under three gas-liquid flow conditions, i.e. count-current, co-current and cross-current gas-liquid conditions. For each gas-liquid flow condition, pressure drop tests for water saturated activated carbon with and without recycle liquid were conducted.

Pressure Drop under Co- and Count-current Flow Conditions

Figures 3.2 (a) and 3.2 (b) show the set-ups used for pressure drop test under co- and count-current gas-liquid flow conditions. The packing height was 43 cm and the internal diameter of the column was 10 cm. The pressure drop was measured using a manometer filled with water.

Pressure Drop under Cross-current Flow Conditions

Figure 3.2 (c) presents the set-up for pressure drop test under cross-current flow conditions. The total packing length was 30 cm and the cross-sectional area of the packing bed was 0.0225 m^2 (15 cm x 15 cm). The pressure drop was measured using a manometer filled with water.

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Figure 3.2 - Schematic Diagram for Pressure Drop Test

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3.3.3 Nitrogen Adsorption Test

Different packing materials are expected to differ in surface features such as surface area, pore volume and micro pore diameter. These surface features which provide the key information to understand the adsorption performance were calculated from nitrogen adsorption/desorption isotherms. The nitrogen adsorption/desorption isotherm for the activated carbon was measured using Autosorb 1C-MS (Refer to Figure 3.3).

After the isotherm was obtained, the parameters describing the surface features of the carbon was calculated based on the theories presented in Appendix D.

Figure 3.3 - Quantachrome Autosorb 1C-MS

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3.3.4 Activated Carbon Breakthrough Test

The purpose of this test is to determine the capacity of activated carbon (Calgon, AP3-60) for treating a 1% H_2S stream to a 50 ppm breakthrough. Three batches of activated carbon samples, as-received (Sample I), water saturated (Sample II) and bacteria immobilized (Sample III) were tested.

The breakthrough test was conducted according to modified ASTM D28, which is intended to evaluate the performance of activated carbon against H_2S . The breakthrough test setup is given in Figure 3.5. In this method, the carbon sample was packed in a glass column with the internal diameter of 4.8 cm. The packing height was fixed at 22.9 cm. Glass beads were packed at the bottom and top of the carbon bed to ensure good mixing of H_2S gas stream.

The 1% H_2S (5% H_2S at 0.5 L/min + moist compressive air at 2 L/min) gas stream was introduced into the bottom of the carbon packed column. The H_2S concentration was monitored at the outlet of the carbon packed column by a Jerome 631-X Hydrogen Sulfide Analyzer (Arizona Instruments, Tempe, AZ) until a breakthrough at 50 ppm concentration was reached. The time taken for breakthrough was recorded, and carbon breakthrough capacity in terms of weight (grams of H_2S per gram activated carbon sample) was calculated.

Figure 3.4 - Jerome 631-X Hydrogen Sulfide Analyzer

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Figure 3.5 - Schematics of Activated Carbon Breakthrough Test

3.3.5 Activated Carbon H₂S Adsorption Test

This test was carried out to evaluate the low concentration H₂S adsorption capacity of the activated carbon saturated with water at the acidic condition.

Prior to the test, 200 ml activated carbon sample and 600 ml distilled water were placed into a 1.5 L glass flask. Taken into consideration the fact that the optimum pH range in the bioreactor system is 2 to 3, the final pH of the sample was thus adjusted to about 2 with sulfuric acid. To ensure that no microbes were involved in the test, the sample was sterilized by autoclaving at 121°C for 15 minutes.

After autoclaving, the water saturated activated carbon sample was packed into a Perspex column at a fixed height of 20 cm (refer to Figure 3.6). The air diluted H₂S air stream was allowed to pass through the column bed at different flow rates at a series of inlet H₂S concentration. At each flow rate, the inlet and the corresponding outlet H₂S concentration were measured and recorded. Again, the H₂S concentration was measured using a 631-X Hydrogen Sulfide Analyzer.

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Figure 3.6 - Schematic Diagram for Carbon Adsorption Test

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3.4 Preliminary Assessment of Biological Activated Carbon Performance in a Biofilter

After the isolated H_2S degrading bacteria had successfully immobilized on the activated carbon, the biological activated carbon was packed into a Perspex column to create a biofilter. The biofilter was set at Temperature Room II, CEE ENV Lab, NTU, Singapore, where the temperature was controlled at 25°C . This part of the work is the preliminary study of the biological activated carbon for treating H_2S without any pH, nutrient and SO_4^{2-} monitoring throughout the study. Removal efficiency at different GRTs, pressure drop across the packing bed, shocking loading as well as upset and recovery ability of bioreactor were investigated.

3.4.1 Experimental Setup

The experimental setup for this study is shown in Figure 3.7. The internal diameter of the packing column is 3.5 cm. The packing height was varied from 5 cm to 20 cm in order to achieve different GRTs (refer to Table 3.2). The H_2S gas used in the experiment was supplied from a 5% H_2S gas cylinder (Manufactured by Linde Gas Singapore Pte Ltd) and diluted to the expected inlet concentration using ambient air supplied by an air blower. The gas flow rate was controlled and measured by an air flow meter with a built-in valve. The air diluted H_2S gas stream was humidified by bubbling through a water bottle before entering the biofilter. The exhaust H_2S gas was absorbed by 0.1 M NaOH solution prior to discharge to the ambient environment.

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Figure 3.7 - Schematic Diagram for Assessment of Biological Carbon in a Biofilter

3.4.2 Operating Conditions

A total of nine stages according to different operating conditions were conducted to:

- 1 Investigate the performance of the biological activated carbon for the treatment of H₂S at different gas retention time;
- 2 Determine the ability of the bioreactor to adapt to fluctuations in the H₂S loading rate;

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- 3 Evaluate the upset and recovery ability of bioreactor when shut down for 48 hours.

The operating parameters of each stage for this preliminary phase (Phase I) are shown in Table 3.2.

Table 3.2 - Operating Parameters of the Biofilter

	Bed Depth	Packing Volume	Flow Rate	GRT	Intended Inlet Con.	Running days
Stage 1	20 cm	0.192 L	0.35 L/min	33 s	25 ppm	1 to 7
Stage 2	12 cm	0.115 L	0.35 L/min	20 s	25 ppm	7 to 14
Stage 3	5 cm	0.048 L	0.35 L/min	8.2 s	25 ppm	14 to 17
Stage 4	5 cm	0.048 L	0.51 L/min	5.6 s	25 ppm	17 to 20
Stage 5	5 cm	0.048 L	0.56 L/min	5.1 s	25 ppm	20 to 23
Stage 6	5 cm	0.048 l	0.70 l/min	4.1 s	25 ppm	23 to 30
Stage 7	5 cm	0.048 L	0.56 L/min	5.1 s	25 ppm	30 to 32
Stage 8	5 cm	0.048 L	0.56 L/min	5.1 s	Varied from 1 to 40 ppm	32 and 33
Stage 9	5 cm	0.048 L	0.56 L/min	5.1 s	25 ppm	32 to 35 Shut down for 48 hrs and then restarted
Nutrient and pH control: No control						

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3.4.3 Gas Sampling and Measurement

A volume of about 5 liters of inlet and outlet air samples were collected over a 24-hour period (in Stage 7 and Stage 8, the sampling period is about 2 hours) in Nalophan Air Sampling Bags (40 L) supplied by Aromatrix Pte Ltd (Singapore). The H_2S concentration of the collected air samples was measured immediately after sampling to avoid the deterioration of the sample by the 631-X Hydrogen Sulfide Analyzer as shown in Figure 3.8. To eliminate all the residual H_2S in the air sampling bags, all the bags were flushed by clean ambient air immediately after each analysis.

Figure 3.8 - H_2S Concentration Measurement by Jerome 631-X H_2S Analyzer

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3.5 Assessment of Biological Activated Carbon Performance in a Biotrickling Filter

Compared to biofilters, biotrickling filters usually exhibit high pollutant elimination capacities over a broader range of pollutants. This is because of the presence of a free trickling liquid phase, which allows the better control of the operating conditions.

After the preliminary study of the biological activated carbon for treating H_2S in a biofilter, a biotrickling filter was designed to investigate performance of the biological activated carbon in terms of H_2S removal efficiency and elimination capacity. The effects of GRT, pH and bacterial concentration on the performance of the reactor were also studied. The physical, chemical and biological properties of the packing material were also tested at the end of this run.

3.5.1 Experimental Setup

Figure 3.9 shows the set-up of the biotrickling filter used in the study. The size of the packing bed is 15 cm x 15 cm x 30 cm (Width x Height x Length). The total packing volume is 13.5 L and the volume of the liquid container is 14 L. Detailed dimension of the reactor body is shown in Figure 3.10. This biotrickling filter consists of six segments (Segment A to F, each with a volume of 2.25 liter). Segment A, C and F will be empty; segment B, D and F will be packed with GAC with trickling liquid passing perpendicular to the air flow.

The H_2S used in the experiment was supplied from a 5% H_2S gas cylinder (Manufactured by Linde Gas Pte Ltd, Singapore) and diluted to the expected inlet concentration using ambient air supplied by an air blower. The recirculating liquid used was either artificial liquid medium (Composition: KH_2PO_4 1 g/L, NH_4Cl 1 g/L and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ 0.46 g/L) or tap water depending on run objectives. Liquid recirculated continuously (by a liquid pump) from day 0 to day 116. From day 117 to day 135, the bioreactor was operated under intermittent trickling condition

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(trickling for 30mins every 12 hours). The flow rate of the recirculating liquid was controlled by three liquid flow meters. The untreated exhaust H_2S gas was absorbed by 0.1 M NaOH solution before emitting to the ambient environment. The biotrickling filter was set at Temperature Room II, Environment Lab, NTU, Singapore, where the temperature was maintained at 25°C.

Figure 3.9 - Schematic Diagram for Assessment of Biological Activated Carbon in a Biotrickling Filter

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Figure 3.10 - Detailed Dimension of the Biotrickling Filter Reactor Body

3.5.2 Operating Parameters and Events

The H₂S influent concentration in this study was fixed around 40 ppm. The GRTs were varied between 1.3 s to 12 s by adjustments of the gas flow rate. The flow rate of the trickling liquid was maintained at 1 L/min for each liquid flow meter. Because of leakage and evaporation, 1 to 2 L of fresh trickling liquid was topped up into the liquid container of the reactor everyday to maintained the trickling liquid at a level of 10 L.

A short summary of the activities is presented in Table 3.3.

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Table 3.3 –Operating Events of Biotrickling Filter

Days	GRTs (s)	Trickling Liquid	Events and Remarks
0-4	4/8/12	10 L L.M. without bacterial	Without bacteria; the mechanism for H ₂ S removal was carbon adsorption only
4-18	4/8/12	6 L L.M. with 4 liter bacterial seed at day 18	Started bacteria immobilization
18	4/8/12	L.M.	Effect of pH on the performance was determined by adding H ₂ SO ₄ /NaOH into the liquid container
19-42	2/4/6	L.M.	GRTs were reduced to 2/4/6 s
31	2/4/6	10 L 0.5 M NaOH.	Clogging occurred, 10 L 0.5 M NaOH was used to wash
31-42	2/4/6	L.M.	GRTs were maintained at 2/4/6s
42-58	4/8/12	L.M.	GRTs was increased to 4/8/12s
53	4/8/12	10 L 0.5 M NaOH.	Clogging occurred, 10 L 0.5 M NaOH was used to wash
58-76	4/8/12	T.W.	Tap water was use as trickling liquid to control the growth of biomass
77 – 86	4/8/12	L.M.	Liquid Medium was used as trickling liquid again because of nutrient limitation
86	1.3/2.7/4	L.M.	GRTs were reduced to 1.3/2.7/4 s
87 – 92	1.3/2.7/4	T.W	Tap water was use as trickling liquid to control the growth of biomass
92 – 97	1.3/2.7/4	L.M.	Liquid Medium was used as trickling liquid again because of nutrient limitation
98 – 100	1.3/2.7/4	-	Reactor was shut down for 48 hours
100	1.3/2.7/4	L.M	Restarted the reactor.
100 – 116	1.3/2.7/4	L.M	GRTs were maintained at 1.3/2.7/4 s
117 – 135	1.3/2.7/4	L.M.	Stopped continuously trickling; the packing material was trickled 30 minutes per 12 hours
129	1.3/2.7/4	L.M.	Shock loading test was conducted

L.M = Liquid medium; T.W = Tap water

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3.5.3 Gas Sampling and Measurement

A volume of about 5 liter air samples were collected in Nalophan Air Sampling Bags (40 L) supplied by Aromatrix Pte Ltd (Singapore). The inlet and corresponding outlet H_2S concentrations were measured by Infitron Finch Com II gas monitor (Maximum Range 100 ppm) equipped with a battery-operated motorized pump as shown in Figure 3.11. A plot of Jerome 631-X vs. Infitron Finch Com II gas monitor measuring data for Hydrogen Sulfide is given in Appendix B. The air sampling bags were flushed by clean ambient air immediately after each analysis.

Figure 3.11 - H_2S Concentration Measurement by Infitron Finch Com II Gas Monitor

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3.5.4 Pressure Drop

The pressure drop of the biotrickling filter was measured by a water manometer. The experimental result would be compared with the predicted value based on the pressure drop test.

3.5.5 pH Measurement

H^+ and sulfate are the main final product of biological degradation of H_2S . In order to monitor the H^+ concentration inside the bioreactor, the trickling liquid was collected for pH measurement. The pH was measured by a pH meter (Corning pH Meter 145). Measurement was not conducted for sulfate concentration as it correlates with the pH.

3.5.6 Bacteria and Biofilm

SEM was used to examine the structure of the biofilm coating on the surface of the activated carbon at the end of this study. Before SEM observation, the biological activated carbon samples were dried using a freeze dryer (EDWARDS).

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CHAPTER 4

RESULTS AND DISCUSSION

4.1 Bacteria

4.1.1 Bacterial Isolation

Flask Culturing

In order to monitor the microbial activity, pH, SO_4^{2-} concentration and Sodium Thiosulphate (TS) concentration of bacterial liquid were measured everyday for each transformation. Figure 4.1 gives the pH variation with time. The changes of SO_4^{2-} concentration and TS concentration with time are shown in Figure 4.2. After 2 to 3 days, the pH of the bacterial liquid dropped significantly from about 6.5 to 2.5 (refer to Figure 4.1). Figure 4.2 shows that the maximum rate of the change of the SO_4^{2-} concentration occurred on the day 3, which was consistent with the pH variation. At the same time, the TS concentration reduced dramatically from 8 g/L to 0.1 g/L, which was mainly caused by the dissociation of TS when pH dropped below 4.67 although microbial activity also had some contribution.

Figure 4.1 - pH Variation with Time of Bacterial Liquid

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Figure 4.2 - TS and Sulfate Concentration Variation with Time of Bacterial Liquid

To monitor the bacterial growth, DAPI-stained bacteria were examined under fluorescent microscopy (See Figure 4.3). This was just to gauge the growth of the bacteria. Actual bacteria counting was not taken.

Figure 4.3 - DAPI-Stained Bacteria under Fluorescent Microscopy

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Culturing on Agar plate

Bacteria colonies were formed on the agar plate after 3 to 4 days of incubation. The white colony is rounded in shape that is about 0.5 – 1.5 mm in diameter. Upon prolong incubation for 10 days, it was observed that the colony turned yellowish in colour, possibly due to the precipitated sulfur element.

4.1.2 Morphological Characterization

Gram Staining of Bacterial Smear

After gram staining, the bacterial cell was observed under a phase-contrast microscope. Figure 4.4 shows the thin, rod-shape microorganisms.

Figure 4.4 - Photograph of the Isolated Bacteria (x2500) after Gram-Straining

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Scanning Electron Microscopy (SEM)

Photographs of the bacteria observed under SEM (Figure 4.5) also revealed thin, rod-shaped micro-organisms, each typically measuring 0.5 by 1.0 μm . This is also in line with the description given by Wu (2000) and Yang (1999).

Figure 4.5 - SEM Photograph Showing the Isolated Bacteria

4.1.3 Bacterial Identification

Table 4.1 presents the 800R partial sequencing of the isolated bacteria. By using the BLAST searching engine, the bacterium was identified as *Thiomonas* sp. This genus was defined as *Thiobacillus* sp. at the early age. Later, it was found that although most of the *Thiobacillus* sp are autotrophic, some of them can grow under

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organotrophic condition. Phylogenetic analysis confirmed the need for a taxonomic revision of the *Thiobacillus* genus and the mixotrophic *Thiobacilli* have been reassigned to a new genus, *Thiomonas* (Amile et al, 1998).

Table 4.1 - 16S rDNA 800R Partial Sequence for Isolated Bacteria

(Length: 748 Base Pair)					
001	TCCNNAANNA	AAAAGNGNNG	TTCTCCCAAG	NAGAAAANTN	CGGATCGGTG
051	TTCTCCGCA	TATCTACNTT	TTNCCCTGNT	ACACNANGAA	NNCCACTCCC
101	CTCTGCCACA	CTCTAGTCGA	GCAGTCACAA	ATGCAGTTCC	CAGGTTGAGC
151	CCGGGAATTT	CACATCTGTC	TTACCCAACC	GCCTGNGCAC	GCTTTACGCC
201	CAGTAATTCC	GATTAACGCT	CGCACCTAC	GTATTACCGC	GGCTGCTGTT
251	TNNGTAGTTA	GCCGNGCTT	ATTCTGCGGG	TACCGTCATC	ACCGAATGGT
301	ATTAGCACTC	GATATTTTCG	CCCCGCCAAA	AGNGGTTTAC	AACCCGAAGG
351	CCTTCATCCC	ACACGCGGCA	TTGCTGGATC	AGGGTTGCCC	CCATTGTCCA
401	AGATTCCCCA	CTGCTGCCTC	CCGTAGGAGT	CTGGGCCGTG	TCTCAGTCCC
451	AGTGTGGCTG	GTCGTCCTCT	CNGACCAGNT	ACGGGATCGT	CGCCTTG GTA
501	ACCTTTACCC	TCCCAACTAG	CTAAATCCGC	CATCGGCCGC	TCCTATGAAC
551	GGTGGAGGTC	TTGCNGATCC	CCCACTTTTC	ACCCGTNAGG	TCNGTATGCG
601	GGTATTNAGC	TACGCTTTCN	CGTAANTNTA	TCCCCCNACC	AAAGGGGNAC
651	GCTTCCGGAT	GGTAATTACT	CACCCGTNCG	CCNCTCGNCG	CNAGGTTGCC
701	CCNGNNTGTC	CGGTTCNANT	TGNNTGCGNT	AAANAATGCC	NCNTANCN

4.2 Bacterial Immobilization

Sample of bacterial immobilized activated carbon culture were checked for viable cell attachment and pH value during the bacterial immobilization phase. Results of bacteria attaching to the carbon surface and pH of the bacterial immobilized activated carbon culture with the immobilization time were obtained and shown in Table 4.2. The bacteria attaching to the carbon surface was a conservative estimation since not all the immobilized bacteria could be detached from the carbon surface by centrifugation. From Table 4.2, it can be seen that the number of bacteria attaching the carbon surface increased with the immobilization time; after four weeks, there were about 2×10^5 bacterial cells immobilizing on the surface of 1 gram of activated carbon. Figure 4.6(a) shows the SEM image of the surface of the activated carbon sample taken from the bacteria-carbon mixture. From this

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Figure, it could be seen that there were rod-shaped bacteria on the surface of the activated carbon. For comparison, the SEM image of the surface of the as-received carbon sample was shown in Figure 4.6(b). These results indicated that the H_2S degrading bacterial was able to grow on the surface of the activated carbon.

Table 4.2 – Variation of Bacteria Attaching to the Carbon Surface and pH with the Immobilization Time

Time (Days)	0	6	14	28
Bacterial Counting (CFU/g.GAC)	0	8.0×10^4	1.4×10^5	2.0×10^5
pH	4.8	2.6	2.3	1.8

Figure 4.6 –SEM Images of Surfaces of Activated Carbon

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4.3 Packing Material

The technical description of the activated carbon (Calgon AP3-60) given by the supplier is shown in Table 4.3.

Table 4.3 - Technical Description of Activated Carbon (Calgon AP3-60)

Specifi- cations	Hardness Number	Mesh Size	Water Content	Ash Content	Dia- meter	Apparent Density
Value	90	95% > US Mesh 6	5%	5%	3.25 mm	490 kg/m ³

The average length of the cylindrical activated carbon measured was 6.2mm. The specific area was 1553 m²/m³ or 0.02 m²/g.

The pH of the as-received GAC was 9.9 measured according to ASTM standard procedure D3838 as described in section 3.3.1.

4.3.1 Pressure Drop Test

Pressure Drop Test Results

Pressure drop for the activated carbon was tested under four water flow conditions, i.e. dry, counter-current, cross-current and co-current for the activated carbon (Calgon, AP3-60). Figures 4.7 to 4.10 illustrate the test results under each recirculation liquid flow condition. The water content for the activated carbon was 73%.

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Figure 4.7 - Pressure Drop per Unit Length of Dry Activated Carbon as a Function of Gas Velocity

Figure 4.8- Pressure Drop per Unit Length of Activated Carbon with Cross-Current Water Flow as a Function of Gas Velocity

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Figure 4.9 - Pressure Drop per Unit Length of Activated Carbon with Co-Current Water Flow as a Function of Gas Velocity

Figure 4.10 - Pressure Drop per Unit Length of Activated Carbon with Counter-Current Water Flow as a Function of Gas Velocity

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Darcy's Law

According to Darcy's law, the pressure drop per unit depth of the packing material can be determined by:

$$\frac{\Delta P}{Z} = v \frac{\mu}{k} \quad (4.1)$$

Where ΔP is the pressure drop across the packing media, z is the height of the packing media, v is the gas velocity, μ is the dynamic viscosity of the fluid and k is the permeability. Permeability is a function the size distribution and void ratio of the particles and the water content of the packing media. For given packing material and fluid, the values of μ and k are constants. So the pressure drop per unit length has a linear relationship with the gas entering velocity with a slope of μ/k . By applying the least square method to the test results, the μ/k value for each packing material under different flow condition could be found as shown in Table 4.4.

Table 4.4 - μ/k Value for the Activated Carbon

Flow Direction	Dry	Cross-Current	Count-Current	Co-Current
Liquid Flow Rate		(1 L/min)	(0.16 L/min)	(0.16 L/min)
μ/k	515(0.98)	611(0.98)	2752 (0.97)	902(0.99)

Note: Numbers in the bracket are the R-squared values

Side Wall Effect

In considering the side wall effects, the following relation could be used to determine the pressure drop (Cloirec et al., 2001).

$$\frac{\Delta P}{Z} = Mv^2 + Nv \quad (4.2)$$

M and N are defined by the following Equations.

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$$M = \{0.0413[1 - (1 - \frac{d_p}{a})^2 + 0.0968(1 - \frac{d_p}{a})^2]\tau^3 \rho a_{vd} \frac{1 - \varepsilon}{\varepsilon^2} \quad (4.3)$$

$$N = 2\eta\tau^2 a_{vd} [1 + \frac{4}{a_{vd}a(1 - \varepsilon)}]^2 \frac{(1 - \varepsilon)^2}{\varepsilon^3} \quad (4.4)$$

Where: a is side of reactor

d_p is the equivalent particle diameter

a_{vd} is the specific surface area of the packing material

τ is the tortuosity of the reactor

ε is the bed void fraction

Ignore the first term of right hand side of equation (4.2) if the equivalent particle diameter (d_p) is far less than the side of the reactor (a), it becomes:

$$\frac{\Delta P}{Z} = Nv \quad (4.5)$$

The relationship between pressure drop and velocity in equation (4.5) is similar as which described by Darcy's law, but taking the side wall effect into account.

4.3.2 Nitrogen Adsorption Test

As indicated in Chapter Three, the objective of this analysis is to identify the surface features of the packing material. The nitrogen adsorption isotherm of the activated carbon is shown in Figure 4.11. According to the classification mentioned in Appendix D, nitrogen adsorption isotherms of activated carbon (Calgon AP3-60) was of type I, from which it could be concluded that the activated carbon was a microporous material having relatively small external surface area.

From the nitrogen adsorption isotherms, the specific surface area, pore volume and pore size could be calculated using the theories introduced in Appendix D and they

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were summarized in Table 4.5, from which, it could be concluded that activated carbon (Calgon AP3-60) has much more internal surface area and micro pore volume than two another types of packing material such as *Decoton* and *Hydroton* (These are material used in existing biotrickling filter by a local company). However, as packing material in biotrickling filters, it is the external surface area that is important because nearly all of the internal surface area of highly porous material such as activated carbon is inaccessible to the microorganisms (Schroeder, 2002). Normally the size of the microorganisms such as bacteria is in the order of 1 μm which is much larger than the micropore size of packing material as shown in Table 4.5.

Figure 4.11 - Nitrogen Isotherm of AP3-60

Table 4.5 - Surface Area, Micro Pore Volume and Pore Size of Packing Material

Packing material	Surface area	Micro pore volume	Average Pore Diameter
AP-360	912 m ² /g	0.2865 cc/g	6.472 nm
<i>Hydroton</i>	2.49 m ² /g	0.009 cc/g	3.74 nm
<i>Decoton</i>	1.58 m ² /g	0.005 cc/g	3.74 nm

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4.3.3 Activated Carbon Breakthrough Test

The test was carried out for 3 batches of carbon, as-received (Sample I), water saturated (Sample II) and bacteria immobilized (Sample III). Both Sample II and III broke through almost immediately after the start of the experiment. In case of sample I, the weight of activated carbon sample was 235 gram and the breakthrough concentration of 50 ppm was reached after 364 minutes. Based on the above information, the hydrogen sulfide adsorption capacity of AP3-60 was 5.4%, which was calculated using the following equation:

$$\frac{\text{g H}_2\text{S}}{\text{gGAC}} = \frac{\frac{C}{100} \times Q \times T \times \frac{1\text{L}}{1000\text{cm}^3} \times \left(\frac{1\text{ mole}}{24.5\text{ L}}\right) \times \frac{34\text{ g H}_2\text{S}}{\text{mole}}}{W} \quad (4.6)$$

Where

C = Concentration of hydrogen sulfide in air stream, volume %

Q = Total H₂S/air flow rate, cm³/min

T = Time to 50 ppm breakthrough, minutes

V = Actual weight of the carbon sample in the adsorption tube, g

The breakthrough test result shows that the presence of an excess amount of water on the carbon surface and in the carbon micro pore would decrease the H₂S adsorptive capacity and H₂S adsorption rate dramatically. It was reported by Bandosz (2002) that to reach the maximum H₂S adsorption capacity, the water content of the carbon should not be greater than 5% and surface pH of the carbon surface should be controlled higher than 5.

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4.3.4 Activated Carbon H₂S Adsorption Test

Figure 4.12 (a) to (d) presents the performance of water saturated activated carbon for removing hydrogen sulfide at different gas retention time. From the figure, it could be seen that the outlet H₂S concentration was proportional to the inlet H₂S concentration, i.e. the removal efficiency was a constant at a specific gas retention time. With increase of gas retention time, the ratio of outlet concentration to inlet concentration decreased and thus the removal efficiency increased.

Figure 4.12 (a) - Performance of Water Saturated Activated Carbon for H₂S
Treatment at GRT = 16.5 s

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Figure 4.12 (b) - Performance of Water Saturated Activated Carbon for H₂S
Treatment at GRT = 11.5 s

Figure 4.12 (c) - Performance of Water Saturated Activated Carbon for H₂S
Treatment at GRT = 9.6 s

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Figure 4.12 (d) - Performance of Water Saturated Activated Carbon for H₂S
Treatment at GRT = 7.2 s

In an ideal plug-flow system, the gas flows through the column at a uniform rate without intermixing. The concentration of the hydrogen sulfide decreases along the direction of flow. For steady-state conditions the relationship between retention time and concentration, applying first-order kinetics, is given in Equation 4.7.

$$\frac{C_{\text{Outlet}}}{C_{\text{Inlet}}} = e^{-GRT \times k} \quad (4.7)$$

Where C_{inlet} = Inlet H₂S concentration

C_{outlet} = Outlet H₂S concentration

GRT = Gas retention time

k = Rate constant for first-order kinetics

Knowing the ratio of the outlet concentration to the inlet concentration as well as the gas retention time, the rate constant for first-order kinetics could be determined

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by best curve fitting as shown in Figure 4.13 , from which $k = 0.061$ per second was obtained.

Figure 4.13– Variation of $C_{\text{outlet}}/C_{\text{inlet}}$ with GRT

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4.4 Preliminary Study of Biological Activated Carbon in a Biofilter

4.4.1 System Performance

Figure 4.14 presents the performance curve of the biofilter packed with the biological activated carbon in the preliminary study phase (Phase I). It shows that it took 7 days for the biofilter to achieve a 99.9% H₂S removal efficiency at a GRT of 33 seconds. The H₂S removal efficiency decreased from 99.9% to about 88% when the GRT was reduced from 33 s to 20 s at day 8. However, it only took 2 days for the H₂S removal efficiency to reach back to 99%. The biofilter could achieve 99% removal efficiency as long as the GRTs were longer than 5 seconds. The H₂S removal efficiency dropped to 97% when the GRT was set to 4.1 seconds. Further decrease in GRT would reduce the H₂S removal efficiency accordingly.

Figure 4.14 - Performance Curve of the Biofilter Packed with AP-360

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4.4.2 Upset and Recovery

As shown in Figure 4.14, after the termination of the H₂S air stream for 48 hours, the bioreactor still could perform well with H₂S removal efficiency higher than 99%. However, early experiments done by other researcher (Koe and Yang, 1999) showed that the activity of the microorganism would be seriously inhibited after the termination of recirculation solution for 24 hours. Examining the difference between these two results, it seems that the activated carbon had a much stronger water holding capacity compared to other conventional packing material. The other reason which might keep the bioreactor system active was that the bacteria could utilise the H₂S adsorbed by activated carbon, as an energy source.

4.4.3 Shock Loading Test

In this experimental run, the gas retention time was set at 5.1 seconds, for which the H₂S removal efficiency had been reasonably high (99%) as shown in the early stage of the experimental run. Figure 4.15(a) and Figure 4.15(b) give the performance of the bioreactor under shock loading where sudden change to the inlet H₂S concentration was imposed. The inlet H₂S concentration was varied from 3 ppm to 45 ppm. It was shown that the bioreactor reacted well to achieve a removal efficiency of higher than 99%. The result indicates that the biological activated carbon had an excellent H₂S buffering capacity.

4.4.4 Limitations of the Preliminary Study

Nutrient level, pH and bacterial concentration, which are critical factors that will affect the performance of biofiltration, inside the biofilter were not monitored and controlled during this preliminary study. This was due to the difficulties in sampling and analyzing of liquid phase inside the biofilter. A biotrickling filter, which has recirculating liquid moving through the packing material, should be able to offer more flexible means to control pH, nutrient level and bacterial concentration than a biofilter.

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Figure 4.15(a) – Performance Curve of the Biofilter under Fluctuating Loading on Day 32

Figure 4.15(b) – Performance Curve of the Biofilter under Fluctuating Loading on Day 33

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4.5 Study of Biological Activated Carbon in a Biotrickling Filter

4.5.1 Performance without Bacterial Inoculation

In order to test the H_2S adsorption capacity of the activated carbon in the trickling reactor, the reactor was run without addition of bacterial seed into the reactor container from day 0 to day 4. Figure 4.16 presents the performance curve of the trickling filter. The best curve fitting profile for the outlet H_2S concentration at different GRTs showed that adsorption of H_2S by activated carbon followed the first order kinetics. The carbon adsorption capacity decreased gradually with the time as show in Figure 4.16.

Figure 4.16 – Removal of H_2S by Carbon Adsorption in Biotrickling Filter

During this test, the H_2S was removed by carbon adsorption. Therefore, there was no production on H^+ from bioconversion and the pH value of the recirculation solution (without bacteria) remained at about 8.5.

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4.5.2 Startup Period

After 2 liter bacterial seed (pH=1.5, Conc. = 1.3×10^8 CFU/ml) was added into the liquid container at day 4, the removal efficiency increased suddenly from 51% to 67% at the GRT of 4 s as shown in Figure 4.17. This indicated that the free-floating bacterial cells could removal 12% of the H_2S at a GRT of 4 s (at this stage, there were no biofilm developed around the carbon surface).

The start-up removal efficiency was 67%, 91% and 97% under GRT corresponding to 4s, 8s and 12s respectively. The removal efficiency increased with the development of biofilm at the startup period as shown in Figure 4.18. It took only 2 days for the reactor to achieve a 99% removal efficiency at a GRT of 12 s. This startup period was much shorter than about one month as reported by researchers such as Koe and Yang (1999), Chung et al.(1998), and Wu (2000).

Figure 4.19 illustrates the pH variation of the trickling liquid during the startup period. After the bacterial seed was added into the liquid container at day 4, the pH value of the trickling liquid dropped from 8.2 to 3. However, it increased to 5.6 at day 5 because the as-received activated carbon was alkaline (pH=9.9). In order to prevent further increase of pH value, a volume of 100 ml 98% H_2SO_4 was added into the liquid tank to bring the pH value to about 2. The pH continuously increased from day 5 to day 7 because of the remaining alkalinity of the activated carbon. It started to decline at day 8 as all the alkalinity of the activated carbon had been neutralized by the H^+ produced from the biodegradation of H_2S by bacteria. The pH reached a value of 2 at day 16 as shown in Figure 4.19.

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Figure 4.17 – Comparison of the Performance of the Reactor before and after Bacterial Inoculation at Day 4

Figure 4.18 – The Performance of the Bioreactor during the Startup Period

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Figure 4.19 – pH Variation with Time during Startup Period

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4.5.3 Overall Performance

The overall performance curve of the biotrickling filter is reported in Figure 4.20. The results showed that the bioreactor perform well during the first four weeks. During the startup period, the removal efficiency increased gradually and reached 99.9% for the gas retention time as low as 4 s. The H_2S removal efficiency was 70% when the gas retention time was 2 s with corresponding inlet H_2S concentration as high as 40 ppm. The maximum elimination capacity of the biotrickling filter achieved at the inlet H_2S inlet concentration of 40 ppm during the first four weeks was $75 \text{ g-H}_2\text{S/m}^3\cdot\text{hr}$ and it increased with inlet H_2S concentration.

After 30 days' operation, clogging by microbial growth was observed during the course of the experiment. The excess biomass would fill up the void space of the packing material and decreased the contact time between the gas stream and the biofilm, which subsequently caused the removal efficiencies to drop. This problem may be alleviated however, by using tap water as trickling liquid instead of artificial nutrient liquid medium to control the bacterial growth.

From day 117, the reactor was operated under intermittent trickling condition (trickling 30 minutes every 12 hours). Under this operation condition, the reactor could achieve a removal efficiency of 99.9% when the system was operated at GRT as low as 4 s. The H_2S removal efficiency was 85% and 70% when the gas retention times were 2.7 s and 1.3 s respectively with the corresponding inlet H_2S concentration as high as 40 ppm. This performance was better than the one achieved under the continuously trickling model. The maximum elimination capacity of the biotrickling filter achieved at this stage was $115 \text{ g-H}_2\text{S/m}^3\cdot\text{hr}$ (Refer to Appendix C) when the GRT was 1.3 s and the inlet H_2S concentration was 40 ppm.

Overall, the results demonstrate that H_2S can be effectively removed under carefully controlled environmental conditions.

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Figure 4.20- Overall Performance of Biotrickling Filter

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4.5.4 Factors Affecting the Performance of the Biotrickling Filter

Effect of Gas Retention Time

A major objective of this research was to investigate the biotrickling filter response to the reduction of gas retention time (GRT). The effect of gas retention time on H_2S removal efficiency was studied by changing the gas flow rate through the packing bed. During this scenario, the inlet H_2S concentration was controlled at about 40 ppm. Figure 4.21(a) and (b) presents the plots of R.E. vs. GRT of the bioreactor operated under continuously trickling model and intermittent trickling model respectively.

As can be observed in the Figure 4.21, there were no apparent effects on H_2S removal efficiency as long as the GRTs were longer than about 4s for both trickling model. When the GRTs were less than 4s, the bioreactor performed better under the intermittent trickling model than under the continuously trickling model. When the GRTs were reduced from 4 s to 2.7 s and 1.3 s, the H_2S removal efficiency decreased from 100% to 85% and 70% respectively under intermittent trickling model. Yang (1992) reported that the H_2S could be metabolized by H_2S -degrading bacteria within 1-2 seconds and therefore they suggested that the reduction of H_2S removal efficiencies under shorter GRT was not due to insufficient reaction time between the H_2S molecules and the biomass, but was possibly due to the slower step of H_2S diffusion from the gas into the liquid phase.

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Figure 4.21(a) - The variation of R.E. with GRT under Continuous Trickling Condition (H_2S Inlet Concentration = 40 ppm)

Figure 4.21(b) - The variation of R.E. with GRT under Intermittent Trickling Condition (H_2S Inlet Concentration = 40 ppm)

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Effect of Bacterial Concentration

Bacterial concentration in the liquid container reflects the amount of biomass present in the bioreactor. Too little biomass would cause the treatment process to be limited by biological reaction, which means that there would be not enough bacteria to degrade the H_2S in the gas stream. On the other hand, too much biomass would cause clogging inside the reactor, which in turn would reduce the removal efficiency and increase the pressure drop across the packing bed.

Figure 4.22 shows the relationship between the bacterial concentration inside the liquid container and the H_2S removal efficiency of the bioreactor. From the figure, it could be concluded that the optimal bacterial concentration inside the liquid container should be maintained at the range of 10^9 CFU/ml.

Figure 4.22 – The Variation of R.E. with the Bacterial Concentration
(Inlet H_2S Con. = 40 ppm, GRT= 4 s)

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Effect of pH

The effect of pH on the performance of the reactor was determined by adding $\text{H}_2\text{SO}_4/\text{NaOH}$ into the liquid container at day 18. The time interval for each change was set at two hour. Figure 4.23 shows the variation of H_2S removal efficiency with pH value of the tricking liquid. It can be observed from the figure that the pH has no apparent effect on H_2S removal efficiency as long as it was maintained above a value of 1.0. When the pH values reduced to 0.6 and 0.2, the H_2S removal efficiency decreased slightly from 99.9% to 97.6% and 96.7% respectively at a GRT of 4 s. Therefore, it could be concluded that control of pH value above 1 was necessary as below this value, H^+ probably was present at a toxic level and the activity of the microorganisms was reduced.

Figure 4.23 – The Variation of R.E. with pH (GRT=4 s, H_2S Inlet Con. = 40 ppm)

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4.5.5 Bacteria and Biofilm

Figure 4.24 (a) to (c) are the images of the biofilm coating on the activated carbon surface obtained from SEM and show a typical bacterial population. Microorganisms are found to be scattered over the surface area, with heavier concentration in the areas of the macropores. Bacteria were not observed to form a uniform biofilm over the entire surface area of the GAC particles. Figure 4.24 also show that packing bed closer to the H_2S inlet would have a much higher bacterial concentration and therefore most of the incoming H_2S would be biodegraded there.

The SEM images indicated that the H_2S degrading bacteria were able to form the biofilm structure by using H_2S as energy source.

Figure 4.24(a) - Biofilm (Sample from the 1st 10cm Packing Bed)

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Figure 4.24(b) - Biofilm (Sample from the 2nd 10cm Packing Bed)

Figure 4.24(c) - Biofilm (Sample from the 3rd 10cm Packing Bed)

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4.5.6 Pressure Drop

As mentioned earlier, the pressure drop across the packing bed determines the amount of energy needed by the blower to force the air stream through the packing material. It is dependent on the geometry of the packing, the gas and liquid load, the liquid hold-up on the packing material, and biomass accumulation, etc. During the course of the experiment, the pressure drop was measured by a water manometer. The result is shown in Figure 4.25. The measured pressure drops across the BAC bed were higher than the predicted results based on the pressure drop test on the as-received GAC. This was due to the presence of the biofilm which would reduce the porosity of the packing material. The amount of pressure drop measured is high. How to overcome this problem will be a critical issue if activated carbon is to be used as a packing material in a biofiltration system.

Figure 4.25- Pressure Drop across the Biological Activated Carbon Bed

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4.5.7 Shock Loading

Shock loading test were conducted to evaluate the performance of the biotrickling filter under a simulated sinusoidal fluctuating influent H_2S loading condition in the order of 55ppm→15ppm→60ppm→15ppm→60ppm→15ppm→60ppm→35ppm. The time interval prior to change was set at one hour. Figure 4.26 gives the performance of the biotrickling filter in terms of H_2S removal efficiency under the shock loading simulation. It was found that the reactor could achieve almost constant removal efficiency regardless of the inlet H_2S concentration at varied GRTs. This result indicated that the biological activated carbon had excellent buffering capacity.

Figure 4.26 – Performance of the Biotrickling Filter under Shock Loading

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4.6 Improvements Achieved

4.6.1 Maximum Elimination Capacity

Experimental results of biofiltration system for treatment of H_2S have been reported by various researchers. The maximum H_2S elimination capacity varied from 7 to $140 \text{ g-H}_2\text{S/m}^3\cdot\text{hr}$. The maximum elimination capacity achieved in this work was $115 \text{ g-H}_2\text{S/m}^3\cdot\text{hr}$ when the GRT was 1.3s and the inlet H_2S concentration was 40 ppm. This maximum elimination capacity was higher than most of those reported in the literature, but it was lower than $140 \text{ g-H}_2\text{S/m}^3$ as reported by Gabriel and Deshusses (2003). One of the possible reasons for Gabriel and Deshusses (2003) achieving such a high maximum elimination capacity was that the air velocity imposed on their bioreactor was as high as 1.75 m/s, which was about 20 times than that of the current system. A higher air velocity implies a more turbulent regime and higher gas-film mass transfer coefficients (Gabriel and Deshusses, 2003), which in turn, could improve the performance of biofiltration systems.

4.6.2 Gas Retention Time

The shortest GRT to achieve a 99% H_2S removal efficiency by a biofiltration system reported in the literature was 5 s (Yang and Allen, 1994; Koe and Yang, 1999; Oyarzun et al., 2003; Shardeefdeen, 2002; Yang et al., 2000; Wu, 2000a; Zhou, 2000 and Chung et al., 1998). However, in current work, the activated carbon packed biotrickling filter operated under intermittent trickling condition could achieve a 99% removal efficiency at a GRT as low as 3 s. This was because the activated carbon could provide a nutrient-rich environment for biofilm development as activate carbon has good nutrient adsorption and strong water holding capacity.

4.6.3 Startup Period

It took only 2 days for the current BAC packed bioreactor to achieve a 99% removal efficiency at a GRT of 12 s. This startup period was much shorter than

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about one month as reported by researchers such as Koe and Yang (1999), Chung et al. (1998) and Wu (2000). In a biofiltration system packed with conventional packing material, the H_2S removal is contributed by suspended bacterial biodegradation only during the startup period as there is no biofilm developed at this stage. However, in a biofiltration system packed activated carbon, not only the suspended bacterial biodegradation but also the activated carbon adsorption could remove H_2S during the startup period.

4.7 Advantages and Disadvantages of BAC Packed Biofiltration System

As mentioned in Chapter 2, both impregnated and unimpregnated activated carbon adsorption systems provide some odour removal capacity, but they need to be regenerated and finally land filled. For chemical scrubber, corrosive and hazardous chemicals have to be added to the system. So both activated carbon and chemical scrubber are costly to operate. In addition, both of these two systems will produce secondary pollutant. On the other hand, BAC packed biofiltration system utilizes non-pathogenic microorganisms for H_2S treatment. It is cheap to operate and will not produce any hazardous by-products. The H_2S removal efficiency by the BAC packed biofiltration system can be as high as 99% at a GRT as low as 4 second when the H_2S inlet concentration is less than 40 ppm.

However, compared to chemical scrubber and activated carbon tower, BAC packed biofiltration system has its own drawbacks. Firstly, the design criteria are still under development as it is a relatively new technology. Secondly, larger area is required as the BAC packed biofiltration system need longer GRT for H_2S removal than that needed by chemical scrubber or activated carbon tower. Thirdly, the pressure inside the BAC packed biofiltration system might be higher due to the over growth of the biomass.

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CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

It was found that H₂S-degrading bacteria could be isolated from returned activated sludge. Photographs of the bacteria observed under SEM revealed thin, rod-shaped micro-organisms, each typically measuring 0.5 by 1.0 µm. The isolated bacteria has been identified as *Thiomonas sp.*, which was defined as *Thiobacillus sp.* at the early age and later, it was found that it could growth under mixtrophic condition, while most of the *Thiobacillus sp.* are autotrophic. In this study, it was also shown that the isolated H₂S-degrading bacterium was able to be immobilized on the surface of granular activated carbon (Calgon, AP3-60).

Experiments including pressure drop test and nitrogen adsorption test have been conducted to determine the physical properties of the packing material. It was found that activated carbon (Calgon, AP3-60) had a very high pressure drop. Nitrogen adsorption test showed that the pore size of the activated carbon was less than 10nm, which was inaccessible to the microorganism.

H₂S breakthrough test and H₂S adsorption test was conducted for the activated carbon (Calgon, AP3-60). From H₂S breakthrough test, it was shown that both H₂S adsorption capacity and adsorption rate would decrease significantly for the water saturated and bacteria immobilized activated carbon because of the presence of the water film/biofilm. The results of H₂S adsorption test revealed that about 50% of the H₂S could be removed by the water saturated activated carbon. The removal efficiency increased with the gas retention time and it followed a first order kinetic equation.

Preliminary study of using biological activated carbon as biofiltration packing material was conducted in two phases. In phase I, a biofilter was created by packing

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the bacteria immobilized activated carbon into a 3.5 cm diameter Perspex column to evaluate the performance of biological activated carbon for H₂S treatment. It was found that high H₂S removal efficiency (99.9%) could be achieved by the biofilter at the gas retention time longer than 5s. The H₂S removal efficiency was 97% when the gas retention time was 4.1 s with the inlet H₂S concentration maintained at 25ppm. The performance of the biofilter under shock loading scenario was also studied by rapidly changing the inlet H₂S concentration from 3 ppm to 45 ppm. The result showed that the biofilter was still able to react well to achieve a removal efficiency higher than 99% when the gas retention time was 5.1 s. Nutrient level, pH and SO₄²⁻, which are critical factors that will affect the performance of biofiltration, inside the biofilter were not monitored and controlled during this preliminary study.

Phase II was designed to investigate the performance of biological activated carbon using a biotrickling filter. The effect of pH, bacterial concentration and GRT on the H₂S removal efficiency was studied in this phase. The startup time required to achieve a removal efficiency of 99% at a GRT of 12 s was only 2 days. A 99.9% H₂S removal efficiency could be achieved at GRT as low as 4 s. The maximum elimination capacity achieved in Phase II was 115 g-H₂S/ m³.hr when the GRT was 1.3 s and inlet H₂S concentration was about 40 ppm. This maximum elimination capacity was higher than most of those reported in the literature. The maximum value was 140 g-H₂S/ (m³.hr) as report by Gabriel and Deshusses (2003).

The results in Phase II also showed that the pH of the trickling liquid was a critical factor affecting the performance of the bioreactor. The pH value inside biofiltration systems should be maintained above 1 in order not to inhibit the microorganism. The bacterial concentration inside the liquid tank should be maintained at the range of 10⁹ CFU/ml in order to avoid clogging.

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Results from both Phase I and Phase II indicated that a short period of temporary (48 hours) shut down would not affect the performance of the bioreactor. The system could recover immediately. Two reasons might keep the bioreactor system active. The first one was that the bacteria could utilise the H_2S adsorbed by activated carbon as an energy source; the second one was the strong water holding capacity of the activated carbon.

Based on the breakthrough test, the adsorption capacity of the GAC for H_2S was 5.4%. Thus the H_2S adsorption capacity of the activated carbon would have been exhausted in 41 days under the conditions practiced in Phase II. It can hence be concluded that the removal mechanism obtained during Phase II was due to biological degradations.

From the above results, it can be seen that although both of the H_2S adsorption capacity and adsorption rate were affected by the biofilm, the activated carbon could still provide an attractive, nutrient-rich environment for bacteria growth because of its good water holding capacity, large external surface area and H_2S adsorption capacity. However, high pressure drop may be a potential problem when it is used as packing material for biofiltration.

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5.2 Recommendations

5.2.1 Improvement of the Existing Biotrickling Filter System

One of the major problems that was encountered in the existing biotrickling filter was the trickling liquid distribution problem. The trickling liquid was not able to distribute evenly on the top of the packing bed. In the future design, more liquid distribution nozzle shall be used to overcome this problem. Another major problem was the clogging which would increase the pressure drop and decrease the H_2S removal efficiency of the reactor. The clogging problem can partially be solved by using granular activated carbons that are larger in size than the current one.

5.2.2 Spent Activated Carbon

In view of the spent carbon generated, there appears to be a possibility of using spent activated carbon as a biofiltration packing material. There are two advantages of using spent activated carbon.

The first advantage is the resource recovery of costly activated carbon. This will reduce the total cost of a biofiltration system as the packing material can represent a significant fraction of the total system cost. Another advantage is that spent activated carbon could offer additional food source for bacteria assimilation because the spent activated carbon has already adsorbed large amount of H_2S . This should be able to help to reduce the startup time.

5.2.3 Field Evaluation

The results obtained in this study were based on the laboratory experiments using standard hydrogen sulfide gas as the surrogate sewage air. However, in real swage air, not only H_2S but also other odour compounds such as VOCs and ammonia are present. Field experiments should be conducted to determine the influence of these co-existing substances on the removal of H_2S by biofiltration system.

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5.2.4 Mathematical Model

Mathematical model should be built up in order to have a better understanding of the H₂S biodegradation mechanism. Mathematical equation describing the biomass growth kinetics and mass transfer should be developed based on the theoretical equations such as Monod equation as well as experimental data.

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APPENDIX A PROPERTIES OF HYDROGEN SULFIDE

Hydrogen sulfide (H_2S) is a colorless, flammable and poisonous gas that is heavier than air. The physicochemical properties of H_2S are listed in Table A.1. The Henry Coefficient for H_2S soluble in water is shown in Table A.2. Table A.3 presents solubility data for H_2S at various temperature at a pressure of 1 standard atmosphere.

Table A.1 - Physicochemical Properties of H_2S

http://www.who.int/water_sanitation_health/GDWQ/Chemicals/hydrsulphidefull.htm#Environmental

Property	Value
Physical appearance	Colorless gas
Melting point	-85.5 °C
Boiling point	-60.7 °C
Density	1.54 g/L at 0 °C
Water solubility	4370 mL/L at 0 °C; 1860 mL/L at 40 °C
Vapour pressure	1875 kPa at 20 °C

Table A.2 - Henry Coefficient for H_2S Soluble in Water

Temperature (°C)	0	10	20	30	40
Henry Coefficient	0.027	0.037	0.048	0.061	0.075

Table A.3 - Solubility of H_2S in Water at a Pressure of 1 Standard Atmosphere

Temperature (°C)	0	5	10	15	20
Solubility (mg/l as S)	6648	5646	4810	4150	3618
Temperature (°C)	25	30	35	40	
Solubility (mg/l as S)	3175	2806	2491	2221	

Dissolved hydrogen sulfide dissociates in accordance with the following reversible ionization reaction:

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Figure A.1- Effect of pH on H₂S Equilibrium

Figure A.1 shows the effect of pH on H₂S equilibrium. It is apparent that the concentration of HS⁻ is insignificant in a biotrickling filter system where the pH value is less than 4.

H₂S can be accumulated in poorly ventilated areas and become a safety risk. The odor threshold of H₂S is about 0.00047ppm. The characteristic smell is that of rotten egg. Hydrogen sulfide is toxic at higher concentrations and will cause rapid death at levels of 0.2%. The effect of H₂S gas on human is summarized in Table A.4

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Table A.4 - Effect of H₂S Gas on Human

Concentration (ppm)	Effect
0.0005	Olfactory detection threshold
0.0047	Olfactory recognition threshold
0.5-30	Strong odour
10-50	Headache, nausea and eye, nose irritation
50-100	Eye and respiratory injury
300-500	Life threatening
Above 700	Immediate death

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APPENDIX B
PLOT OF JEROME 631-X VS. INFITRON FINCH COM II GAS MONITOR
MEASURING DATA FOR HYDROGEN SULFIDE

Plot of Jerome 631-x vs. Infatron Finch Com II Gas Monitor Measuring Data for Hydrogen Sulfide

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APPENDIX C

LOADING RATE AND ELIMINATION CAPACITY CALCULATIONS

$$L = \frac{C_{in} \times M.W}{24521 \times V} \times Q \times 60 \quad (C.1)$$

$$EC = L \times RE \quad (C.2)$$

Where

L = Loading (g/ (m³.hr))

EC = Elimination capacity

C_{in} = Inlet pollutant concentration (ppmv)

V = Volume of packing bed (L)

Q = Gas flow rate (L/min)

RE = Removal Efficiency

M.W = Molecular Weight of Pollutant

Given

C_{in} = 41 ppmv; V = 2.18 L; Q = 96 L/min; RE=70%

So:

$$L = \frac{41 \times 34}{24521 \times 2.18} \times 96 \times 60 = 150 gH_2S / (m^3 hr)$$

$$EC = 150 \times 70\% = 105 gH_2S / (m^3 hr)$$

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APPENDIX D

THEORIES FOR NITROGEN ADSORPTION TEST FOR ACTIVATED CARBON

Carbon Surface Area by BET Method

The Brunauer-Emmett-Teller (BET) method is the most widely used procedure for determination of the surface area of solid materials and involves the use of the BET equation.

$$\frac{1}{W((P_0/P)-1)} = \frac{1}{W_m C} + \frac{C-1}{W_m C} \left(\frac{P}{P_0}\right) \quad (D.1)$$

In which W is the weight of gas adsorbed at a relative pressure P_0 and W_m is the weight of the adsorbate constituting a monolayer of surface coverage. The term C , the BET constant, is related to energy of adsorption in the first adsorbed layer and consequently is an indication of the magnitude of the adsorbent/adsorbate interactions.

The BET equation requires a linear plot of $1/[W(P_0/P)-1]$ vs P/P_0 which for most solids, using nitrogen as the adsorbate, is restricted to a limited region of the adsorption isotherm, usually in the P/P_0 range of 0.05 to 0.35. This linear region is shifted to lower relative pressures for microporous materials. The standard multipoint BET procedures require a minimum of three points in the appropriate relative pressure range. The weight of a monolayer of adsorbate W_m can then be calculated from the slope s and intercept i of the BET plot. From the BET equation:

$$s = \frac{C-1}{W_m C} \quad (D.2)$$

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$$i = \frac{1}{W_m C} \quad (D.3)$$

Thus the weight of a monolayer W_m can be obtained by combining equations (D.2) and (D.3).

$$W_m = \frac{1}{s + i} \quad (D.4)$$

The second step in the application of the BET method is the calculation of the surface area. The total surface area S_t of the sample can be expressed as:

$$S_t = \frac{W_m N_A A_{cs}}{M.W} \quad (D.5)$$

Where N_A is Avogadro's number (6.023×10^{23} molecules/mole) and $M.W$ is the molecular weight of the adsorbate. Nitrogen is the most widely used gas for surface area determinations since it exhibits the intermediate values for the D constant (50-250) on most solid surface, precluding either localized adsorption or behavior as a two dimensional gas. For the hexagonal close-packed monolayer at 77K, the cross-sectional area A_{cs} for nitrogen is $16.2 \text{ \AA}^2$.

The specific surface area S_s of the solid can be calculated from the total surface area S_t and the sample weight W according to equation D.6

$$S_s = \frac{S_t}{W} \quad (D.6)$$

Isotherms

An understanding of the surface area and porosity of an adsorbent can be achieved by the construction of an adsorption isotherm. When the quantity of adsorbate on a

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surface is measured over a wide range of relative pressures at constant temperature, the result is an isotherm. Similarly, desorption isotherms can be obtained by measuring the quantities of gas removed from the sample as the relative pressure is lowered. All adsorption isotherms may be grouped into one of the five types shown in Figure D.1.

Type I isotherms are concave to the relative pressure and the amount of adsorbate approached a limiting value as the relative pressure approaches 1. Type 1 physisorption isotherms are exhibited by microporous solids having relatively small external surface, for example, activated carbons. The limiting uptake of adsorbates is governed by the accessible micropore volume rather than the internal surface area.

Type II isotherms are the normal form of isotherm obtained with a nonporous or macroporous adsorbent. This type of isotherm represents unrestricted monolayer-multilayer adsorption.

Type III isotherms are convex to the relative axis over its entire range. Type III isotherms are rarely encountered. A well-known example is the adsorption of water vapor on nonporous material.

Type IV isotherms are associated with capillary condensation in mesopores, indicated by steep slope at higher relative pressures. The initial part of the type IV isotherm follows the same path as the type II.

Type V isotherm are uncommon, corresponding to the type III, except that pores in the mesopore range are present.

Types I, II and III adsorption isotherms are generally reversible, but microporous material having type I isotherms can exhibit hysteresis. Type IV and V, associated

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with mesoporosity, usually exhibit hysteresis between the adsorption and desorption isotherms.

Figure D.1 Isotherm Types

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Pore Volume and Average Pore Radius

The total pore volume is derived from the amount of vapor adsorbed at a relative pressure close to unity, by assuming that the pores are then filled with liquid adsorbate. If the solid contains no macropores the isotherm will remain nearly horizontal over a range of relative pressure approaching unity and the pore volume is well defined. However, in the presence of macropores the isotherm rises rapidly near relative pressure equal to 1 and in the limit of large macropores may exhibit an essentially vertical rise. In this case, the limiting adsorption can be identified reliably with the total pore volume assuming careful temperature control of the sample. The volume of nitrogen adsorbed (V_{ads}) can be converted to the volume of liquid nitrogen (V_{liq}) contained in the pores using equation (D.7).

$$V_{liq} = \frac{P_a V_{ads} V_m}{RT} \quad (D.7)$$

In which P and T are ambient pressure and temperature, respectively, and V_m is the molar volume of the liquid adsorbate (34.7 cm³/mole for nitrogen).

Since pores which would not be filled below a relative pressure of 1 have a negligible contribution to the total pore volume and the surface area of the sample, the average pore size can be estimated from the pore volume. Assuming cylindrical pore geometry, the average pore radius r_p can be expressed as

$$r_p = \frac{2V_{liq}}{S} \quad (D.8)$$

Where S is the BET surface area.