

A  
Project Report on

# **Removal of Hydrogen Sulfide using bio filters**

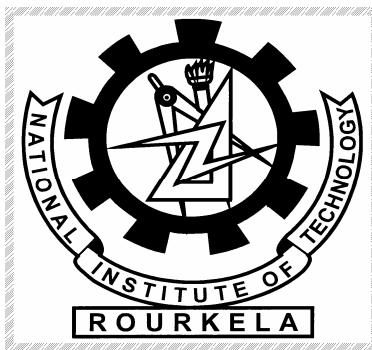
In partial fulfillment of the requirements of  
Bachelor of Technology (Chemical Engineering)

Submitted By

**Devesh Pandey (Roll No.10300046)**  
**Samudrala Prasanth (Roll No.10200030)**  
**Session: 2006-07**

Under the guidance of

**Prof. G.K.Roy**



**Department of Chemical Engineering**  
**National Institute of Technology**  
**Rourkela-769008**  
**Orissa**



**National Institute of Technology  
Rourkela**

**CERTIFICATE**

This is to certify that that the work in this thesis report entitled “Removal of Hydrogen sulfide using Bio filter” submitted by Devesh Pandey and Samudrala Prasanth in partial fulfillment of the requirements for the degree of Bachelor of Technology in Chemical Engineering Session 2003-2007 in the department of Chemical Engineering, National Institute of Technology Rourkela, Rourkela is an authentic work carried out by them under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University/Institute for the award of any degree.

Date:

Prof .G.K.Roy  
Professor  
Department of Chemical Engineering  
National Institute of Technology  
Rourkela - 769008

## ACKNOWLEDGEMENTS

We express our deep sense of sincere gratitude to our project guide Prof. G.K.Roy, Professor for his kind support, guidance and constructive criticism in the completion of project. We are thankful to Prof. R.K.singh for providing us with this opportunity to complete the present work.

We are also thankful to Prof. Pradip Rath, Head of the Department, for providing us the necessary opportunities in the course of our project.

Devesh Pandey (Roll No. 10300046)

Samudrala Prasanth (Roll No. 10200030)

B.Tech. Final Yr. Chem. Engg.

## CONTENTS

Figures and Tables		vii,viii
Abstract		ix
		Page No
Chapter 1	INTRODUCTION	1-9
1.1	Bio filtration, an Introduction	2
1.1.1	Compounds amenable to bio filtration	4
1.2	Bio filter Design and Specifications	5
1.2.1	Bio filter Scale up and design	7
Chapter 2	Analysis of Different Techniques and methods	10-28
2.1	Exploring the gas-phase anaerobic bio removal of H <sub>2</sub> S for coal gasification fuel cell feed streams	11
2.1.1.	Bacterial strain and medium	12
2.1.2.	Analysis of results	14
2.2	Biological Deodorization of Hydrogen Sulfide using porous lava as a carrier of <i>Thiobacillus thiooxidans</i>	16
2.2.1.	Results and discussion	17
2.3	Hydrogen sulfide adsorption on a waste material used in bioreactors	20
2.3.1.	Adsorption models	21
2.3.2.	Mass transfer coefficient in the bio filter	24
2.3.3.	Conclusion	24
2.4.	Hydrogen sulfide removal by compost biofiltration: Effect of mixing the filter media on operational factors	25

	2.4.1 methods	26
Chapter 3	Removal Of Hydrogen Sulfide	29-50
3.1	Conventional methods for the removal of Hydrogen Sulfide	31
3.1.1.	By using a biogas Scrubber	31
3.1.2	Activated Sludge Diffusion	32
3.1.3.	USING SULPHA-TREAT PROCESS	33
3.1.4.	By sulphidation of hydrous ions (iii) oxides	33
3.2	Removal of H <sub>2</sub> S using a Bio trickling filter	34
3.2.1.	Bio trickling filtration principle	35
3.2.2.	Bio trickling filter performance	38
3.2.3.	Examples of Bio trickling Filter Performance	40
3.2.4.	Biomass growth in bio trickling Filter	41
3.3	Mathematical modeling of a Bio filter	43
3.3.1.	Model Development	43
3.3.2.	Model Equations	45
3.4	Mass balance of Off-gas coming from refineries (IOCL Haldia):	49
Chapter 4	Design of Hydrogen sulfide scrubber	51-61
4.1	Data and Assumptions:	52
Chapter 5	Assessment of Operation and Cost	63-68
5.1	Bio trickling filtration costs	64

5.2	Operating costs	65
5.3	Technology assessment, design, and operation	66
5.3.1	Flow rate and composition variability	67
5.3.2.	Cost	67
5.3.3.	Enclosed Biofilter	67
5.4	Bio filtration equipment manufactures.	67
5.4.1	Future Developments	67
REFERENCES		69

### **List of Figures and Tables**

<b><u>Figure / Table</u></b>	<b><u>Title</u></b>	<b><u>Page Number</u></b>
Figure-1	Experimental setup of anaerobic removal of Hydrogen sulfide	12
Figure-2	Anaerobic biological removal of H <sub>2</sub> S as a function of process parameters	14
Figure-3	H <sub>2</sub> S removal rate as a function of mass loading and residence time	15
Figure-4	Physicochemical removal of H <sub>2</sub> S by lava filters without inoculation of T.thiooxidans	19
Figure-5	Experimental setup for adsorption test	23
Figure-6	Layout of the adsorption/absorption phenomena in a bio filter	24
Figure-7	A Biogas Scrubber	31
Figure-8	Schematic of a Biogas scrubber process	32
Figure-9	Applicability of various air pollution control technologies	34
Figure-10	Schematic principle of bio trickling filtration	35
Figure-11	Mechanism of pollutant removal	36
Figure-12	Schematic of a typical elimination capacity vs. load characteristic	39
Figure-13	Schematic of the model structure with wetted and non-wetted bio films	43
Figure-14,15	Result of Model	48

Table-1	Test Matrix	13
Table-2	Physical properties and buffering capacities of the lava samples	18
Table-3	Chemical compositions of the lava samples	19
Table-4	Typical characteristics of a bio trickling filter	37
Table-5	summary of main parameter values for main simulation	47
Table-6	Results, Summary	60
Figure-16	A plot of total Power Vs Solvent rate ( $L_M$ )	61
Figure-17,18	Gas Scrubber	62



## ABSTRACT

Malodorous gases emitted from many environmental and industrial facilities are not a nuisance, but also cause significant health problems for workers and even nearby residents it can be treated using physical, chemical, and biological methods, but among these, biological treatment surpasses the physicochemical methods in that it costs the least and is easy to maintain. The gases are passed through biofilters packed with carriers into which deodorizing microorganisms are immobilized. Such techniques have been developed and are commonly used in various countries. In our present work, various biofilters such as in the gas-phase anaerobic bio removal of  $H_2S$  for coal gasification fuel cell feed streams, removal of  $H_2S$  by sulfate resistant *Acidithiobacillus thiooxidans* AZ11, Deodorization of  $H_2S$  using porous lava as a carrier of *Thiobacillus thiooxidans*,  $H_2S$  adsorption on a waste material used in bioreactors etc are analyzed. Based on the analysis of these biofilters, a design of horizontal bio trickling filter based on biological activated carbon is advocated. The bio trickling filter performance and its modeling is then discussed. The design of the filter is made on the basis of effluent gases in the IOCL Haldia refinery.

A design of conventional  $H_2S$  scrubber is designed next and the operating conditions and cost of filter and scrubber are compared.



# CHAPTER 1

## **INTRODUCTION**

## 1.1 BIO FILTRATION: AN INTRODUCTION

Bio filtration is an emerging energy efficient technology for the control of volatile organic compounds (VOCs). It has been used extensively for over 40 years in the U.S and Europe for the control of odors from the waste water treatment facilities , rendering plants , composite facilities , and other odor-producing operations .they are used for treating high volume .low concentration air streams.

In bio filtration, off-gases containing biodegradable VOCs and other toxic or odorous compounds are passed through a biologically active bed of peat, soil, or other media .containment compounds diffuse from the gas phase to the liquids or solid phase in the media bed, transfer to the bio film layer where microbial growth occurs, and subsequently are biodegraded.

Bio filtration is a general term applied to the conversion of gas-phase chemical compounds to the common biological degradation products of carbon dioxide, water, and inorganic salts. It relies on two primary fundamental mechanisms –sorption and biodegradation.

Technologies considered being forms of bio filtration include soil beds, bio filters, bio scrubbers, bio trickling filters and engineered bio filters. While all of these operate based on the same fundamental mechanisms of contaminant sorption and biodegradation, they have different design and control parameters, operational flexibility and performance characteristics. It is noted that the conventional trickling filter used for waste water treatment is sometimes referred to as a bio filters, but the technology is very different.

A typical bio filter configuration is shown in the figure -1 the contaminated off-gas is passed through a pre conditioner for particulate removal and humidification. The conditioned gas stream is then sent into the bottom of a filter bed of soil, peat, composted organic material (such as wood or lawn waste), activated carbon, ceramic or plastic packing, or other inert or semi inert media. The media provides a surface for the micro organism's attachment and growth. The off-gas stream is typically either forced or included through the system with a blower. A vent stack is employed when necessary to meet monitoring or discharge requirements.

A mixture of media types are sometimes used to provide operational advantages. In a soil, peat, or composite bed, the media itself may provide some or overall of the essential nutrients required for microbial growth. Bulking agents and/or minerals can be incorporated into the media, depending on the pH control requirements.

As the contaminated gas streams pass through the bed, contaminants are transferred from the gaseous phase to the media. Three primary mechanisms are responsible for this transfer and the subsequent biodegradation in organic media bio filters:

- Gas streams- adsorption on organic media – desorption / dissolution in aqueous phase – biodegradation.
- Gas streams-direct adsorption in bio film –biodegradation.
- Gas streams- dissolution in aqueous phase- biodegradation.

Once adsorbed in the bio film layer or dissolved in the water layer surrounding the bio film, the contaminants are available to the micro organisms as a food source to support microbial life and growth. Air that is free, or, nearly free, of contaminants is then exhausted from the bio filters.

There are many variations to this basic approach, Biological activity in a filter will eventually lead to degradation of a soil or compost media as organic matter is mineralized and the media particles are compacted. Degradable filter materials typically require replacement every three to five years.

Proper media selection affects bio filters performances with respect to its compaction and useful life. In addition, the media largely determines environmental conditions for the resident microorganisms. These micro organisms are the most critical component of the bio filters, since they produce the actual transformation or destruction of contaminants. Microorganisms can vary significantly in metabolic capabilities and preferences. Naturally occurring microbes are usually suitable and most desirable for treating most gas-phase contaminants. However, some of the more unusual anthropogenic chemicals may require specialized microorganisms. Sometimes these organisms can simply be taken from sewage and acclimated to the specific contaminants that are present; in a few cases, specially grown pure, mixed or genetically engineered cultures may be preferred.

Microbial cultures require a carefully controlled environment for optimal contaminant degradation. The most important environmental factor for microbial function is the moisture in the contaminated air stream entering the bio filters. Most industrial or remediation off-gases have less than 100% relative humidity, so supplemental humidification is needed to minimize bed drying. This can be achieved with an upstream humidifier (commonly a spray drier), spray nozzle humidifiers mounted within the bio filters, or steam injection built into the bio filters...(Bio scrubbers and bio trickling filters, which rely on a recycled aqueous-phase solution, do not need pre humidification.) Humidification is generally the single most influential parameters affecting the sorptive capacity of bio filters, especially at lower inlet concentrations, where Henry's Law controls mass-transfer rates within the bio filters.

Bio filters were commonly constructed as open, single-bed systems. Recently fully enclosed bio filters have become more popular. These are frequently required to comply with emission monitoring requirements. Enclosed systems usually contain separate stacked beds in parallel or in series. This allows for a greater containment loading over a given foot print area. Fully enclosed systems also provide more precise control of bio filter moisture, thereby reducing the potential for failure due to moisture level fluctuations.

#### **1.1.1. *Compounds amenable to bio filtration***

Bio filtration has been found to be efficient not only for the removal or destruction of many off-gas pollutants, particularly organic compounds, but also some inorganic compounds such as  $H_2S$  and  $NH_3$ . Several factors contribute to the overall removal efficiency. Since bio filtration functions via contaminant that are amenable to treatment by bio filtration must have two characteristics:

*High water solubility:* This coupled with low vapor pressure, results in a low Henry's law constant, and thus increases the rate at which compounds diffuse into the microbial film that develops on the media surface. The classes of compounds that tend to exhibit moderate to high water solubility include organics, alcohols, aldehydes, ketones, and some simple aromatics (BTEX compounds); compounds that are more highly oxygenated are generally removed more efficiently than simpler hydrocarbons. However some biofilter designs have been developed for some less water soluble compounds such as petroleum hydrocarbons and chlorinated hydrocarbons.

*Ready biodegradability:* Once a molecule is adsorbed on the organic material in filter media or in a bio film layer, the contaminant must then be degraded. Otherwise, the filter bed concentration may increase to levels that are toxic to micro organism or detrimental to further mass transfer (sorption and dissolution). Either of these conditions will result in decreased biofilters efficiency or even complete failure. More readily degradable organic components include those with lower molecular weights and those are more water soluble and polar. Some inorganic compounds such as  $H_2S$  and  $NH_3$  can also be oxidized biologically.

Research now under way aims to identify methods of treating contaminants that were previously considered to be untreatable by biofiltration such as chlorinated hydro carbons. Use of innovative reactor designs, specialized or anaerobic microbes, or supplemental substrates can help to accomplish this result.

To maximize the efficiency of bio filtration, it is most important to select excellent carriers onto which microorganisms are immobilized. The criteria for the choice of an optimal bio filter media are as follows: (i) high water holding capacity; (ii) high porosity; (iii) large surface area; (iv) low degree of clogging; (v) low pressure drop in broad ranges of water content; (vi) high persistence; (vii) low cost; (viii) light; (ix) ability to absorb odor gases to some extent. From the perspective of the activities of microorganisms, criteria (i) to (iii) are the most important, but from the perspective of construction and maintenance of the bio filter, criteria (IV) to (viii) are most important. Criterion (ix) becomes significant when the concentration of malodorous gases is fluctuated.

## 1.2. Bio filter Design and Specifications

Bio filter vessels are typically larger than the reactors of other air pollution control devices. The relationship between off gas flow rate, required residence time and the corresponding reactor volume is the most crucial aspect in bio filter design since it strongly affects space requirements and capital cost of a biofilter.

The figure 2 summarizes the most commonly used bio filter design parameters.

The elimination of a single pollutant in a well functioning bio filter follows the concentration profile in which the rate of removal is linear with the distance into the media or with the empty bed resistance time(EBRT) at higher concentrations. At the lower concentrations, the rate of

removal decreases and follows the power function. Lowering the off gas velocity by increasing the filter bed area increases the effective residence time and improves performance per unit of bed height, thus causing a steeper concentration profile. However it also requires more filter volume per unit of air flow.

EBRT is generally considered the primary design parameter for a biofilters reactor. Consequently the main objective of a pilot test for scale up purposes is the determination of EBRT.

For a given set of off-gas composition and filter conditions, the pollutant removal efficiency or the maximum outlet concentration allowed by regulations dictates a minimum EBRT. In modern biofilters applications, EBRT typically ranges from 15 to 60 seconds. This corresponds to a filter volume of 0.25-1ft<sup>3</sup> of filter medium per cfm of off-gas flow rate (4.2-16.7m<sup>3</sup> filter media/1,000m<sup>3</sup> per hr). To avoid media compaction and uneven moisture distribution, individual bio filters beds are typically no higher than 3 to 5 ft (90 to 150 cm). The actual appropriate bed height depends on media type and expected pressure drop. The required reactor footprint is calculated by:

$$A = Q/v$$

$$= Q [EBRT / (h \times 60)]$$

Where A= cross sectional area or footprint (m<sup>2</sup>), Q= volumetric flow rate (m<sup>3</sup>/hr), v=surface loading rate or face velocity (m/hr), h=filter bed height(m) and EBRT=Empty bed resistance time in minutes.

Thus if treatment of a 20,000 cfm off- gas stream requires an EBRT of one minute and the bio filter has a single bed 1.5m high, the required reactor foot print is about 380 m<sup>2</sup>.

Stacking of beds reduces the biofilters food print area. However in addition to doubling the media height, stacking also increases off-gas space velocity and the total off-gas pressure drop increases by at least four fold. Thus to limit power consumption and risk of off-gas channeling and because stacked beds are more expensive to build, total media height in modern bio filters rarely exceed 10ft.

Another quantity commonly used in biofilter engineering is the system bulk elimination capacity (EC) for the target compound per media volume. It is measured in grams of pollutant removed per cubic meter of media per hour ( gram/m<sup>3</sup> hr) and is defined as:

$$\begin{aligned}
 EC &= (C_m - C_{out}) (Q/v) \\
 &= C_{in} (RE) (Q/v) \\
 &= \Delta C (60/EBRT)
 \end{aligned}$$

Where EC= elimination capacity (g/m<sup>3</sup>.h), C<sub>in</sub> = inlet concentration(gm/m<sup>3</sup>) ,C<sub>out</sub> = outlet concentration(gm/m<sup>3</sup>) ,v= media volume(m<sup>3</sup>) , RE=Removal efficiency(%), C = Concentration difference=C<sub>in</sub>-C<sub>out</sub>

The pollutant loading L(gm/m<sup>3</sup>.h) is defined as:

$$\begin{aligned}
 L &= C_{in} (Q/v) \\
 &= (C_{in} * 60)/EBRT
 \end{aligned}$$

and relates the elimination capacity and the removal efficiency by :

$$EC = RE * L$$

### ***1.2.1 Bio filter Scale up and Design***

Numerous biofilters have generally achieved reliable performance at low operating costs. Yet a number of installations have experienced poor performance and required significant maintenance and repair and repeated replacement of filter media.

The most frequent problems were caused by changes in the media characteristics: dry out, rapid degradation, or particulate clogging, resulting in excessive pressure drops and gradual accumulation of acidic bi-products. Clogging of air distribution systems, rapid corrosion of duct work and concrete parts, emissions of odorous bi-products, over heating and flooding of media have also occurred. These problems usually result from one or more of the following factors-

- unsuitable off-gases
- improper sizing of filter bed
- design flaws

These experiences emphasize the need of a careful scale up and design procedure (assuming that the off-gas has been deemed suitable for biofiltration). Such a procedure should include the following elements

*Compound screening:* With the available database, determine for the evidence that the compound is treatable using a bio filter.



*Vent stream characterization:* Determine the gas flow rate, temperature and humidity, particulate levels and component VOC concentration (estimated from the mass and energy balances or from actual data).

*Review of regulatory requirements:* Consult regulatory experts to determine how regulations may relate to biofilters performance. For example regulation may require either very high levels of contaminant removal or very consistent levels of removal .Either of these may be more difficult for bio filtration to achieve specially for refractory compounds like aromatic molecules

*Experimental considerations:* access the time available for testing (period up to one year is most helpful for predicting performance), plan for proper disposal of leach ate from the test unit identify the proper analysis's of the inlet and outlet gases, access the need for additional air or oxygen, consider the value of working with a vendor as a partner, prepare for a downtime and “cold starts” and be ready for the eventuality of drying out and over saturation of media beds.

A key element of the scale up process is testing for the technical and economic suitability of biofiltration. Types of testing include shake flasks, bench scale testing and pilot testing

Shake flasks are used to access the biodegradability and micro kinetics of a compound not previously treated in a bio filter, to identify inhibitor effects between compounds in mixtures, and to help isolate suitable micro organisms for target compounds. They are performed for novel application or where performance problems have occurred.

Bench scale test allow for over accurate observation of the interaction between a target compound, other co –pollutants and the filter media. They are also useful for explaining potential performance problems encountered during a pilot test. However because of the limitation inherent in using a synthetic stream and given the increasing body of knowledge on the treatable of volatile compounds, bench scale test is rarely performed.

Pilot test are routinely conducted for any new application involving large flows (greater than 10,000 cfm) and requiring quantifiable removal of VOCs and HAPs unless prior bio filter experience exist for a similar off-gas. The main objectives of a pilot test are: Accurate determination of EBRT required meeting a regulatory control objective; identification of incompatibilities, such as the presence of poorly removed compounds and excessive temperatures and establishment of design parameters.

Once it has been determined that a stream is suitable for bio filtration and small scale evaluation have been completed, a full scale design must be chosen, most full scale bio filters include following four elements;

*Off-gas pretreatment:* Maintenance of greater than 95% relative humidity with wet bulb temperatures between 70<sup>0</sup>f and 100<sup>0</sup>f, and maintain particulate concentration below 10mg per m<sup>3</sup> to minimize blood clogging

*Biofilter reactor:* For the target range of EBRTs between 0.15 and 60 sec, medium volume of cfm off-gas flow should be in the range of 0.25 to 1 ft<sup>3</sup>; media volume is typically in the range of 100 to 2000 yd<sup>3</sup>, for flow rates from 2000 to 150,000 scfm;and media bed heights are about 3 ft with pressure drops of 0.5 to 8 inch(wg).

*Air handling:* biofilters can operate with blowers either upstream or down stream.

*Monitoring and control:* in addition to controlling moisture, the off-gas temperature, pressure drop and flow rate of air must be monitored for proper control and to assist in future failure analysis. If the total organic carbon (TOC) is needed for regulatory purposes, flame ionization detection is the analytical method of choice.

The volume and type of media must be determined. The required EBRT as determined by pilot testing is typically the primary parameter used for calculating the media volume. Other consideration include planning for channeling within the media, reactor heat loss or gain, changed pollutant concentration, interference between the compounds and other operational factors.



# CHAPTER 2

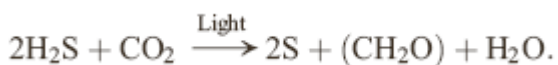
**Analysis of different Techniques and Methods**

## 2.0. Different bio filtration techniques: Media and Micro organisms

### 2.1. Exploring the gas-phase anaerobic bio removal of H<sub>2</sub>S for coal gasification fuel cell feed streams

The use of syngas generated by coal gasification in fuel cells is one of the advanced coal utilization technologies currently being developed for coal-based power generation. An area of concern is the impact that contaminants in the syngas have upon the operation and durability of the fuel cell. An important contaminant is sulfur which exists as hydrogen sulfide (H<sub>2</sub>S) in coal gasification syngas. The removal of H<sub>2</sub>S from these gas streams is essential to prevent poisoning of fuel cell catalysts such as the anode catalyst and the fuel processing catalyst in a proton exchange membrane fuel cell. For most fuel cell applications, H<sub>2</sub>S levels must be lowered below 1 ppm to avoid degradation of fuel cell components. The greatest concern is for low-temperature proton exchange membrane fuel cells as even trace amounts of hydrogen sulfide can greatly decrease the power output. This is because H<sub>2</sub>S causes blockage of the active sites of Platinum catalysts. The removal of trace quantities of H<sub>2</sub>S from a syngas stream is a challenging problem. Processing must avoid degrading the quality of the syngas during remediation. As such, the method must avoid the addition of oxygen or water vapor to the gas stream and maintain H<sub>2</sub> and CO concentrations while removing H<sub>2</sub>S to very low levels. Traditional physico-chemical methods of H<sub>2</sub>S removal require oxygen for treating the gas stream and face the problem of regeneration of catalyst or absorbent/adsorbent. High temperature absorption offers an energy-efficient route for dry fuel streams, but the regeneration of metal-oxide sorbent is expensive and difficult.

Microorganisms that use H<sub>2</sub>S as a source of reducing equivalents under anaerobic conditions in the absence of oxidants are known as photoautotrophs (i.e., organisms that are capable of obtaining their energy directly from a light source). Photoautotrophs utilize an overall photosynthetic process mechanism similar to that of photosynthesis in plants where H<sub>2</sub>O is replaced with H<sub>2</sub>S:



During this process, carbon dioxide is fixed in the form of cell biomass and H<sub>2</sub>S is oxidized to elemental sulfur in the presence of light. Hydrogen sulfide serves as an electron

donor for the process. Henshaw and Zhu have shown that photoautotrophic bacteria provide nearly 100% efficient removal of sulfide from liquid media at loadings of up to  $100\text{--}280\text{ g h}^{-1}\text{ m}^{-3}$ . It is of note that photoautotrophic bacteria, unlike chemoautotrophs, tend to convert sulfide to the non-corrosive elemental sulfur rather than to sulfate. It is evident that none of the previously studied bioreactor systems will adequately address the needs of coal-derived syngas for fuel cells. However, these results do indicate that anaerobic bacteria have the potential to achieve the removal levels and efficiencies required for a commercial process. Thus the question remains, can an anaerobic bioprocess be developed that will remove trace quantities of  $\text{H}_2\text{S}$  from a syngas stream without adding an oxidant and without saturating the gas stream with water? The objective of the present study was to determine if such a process is worthy of.

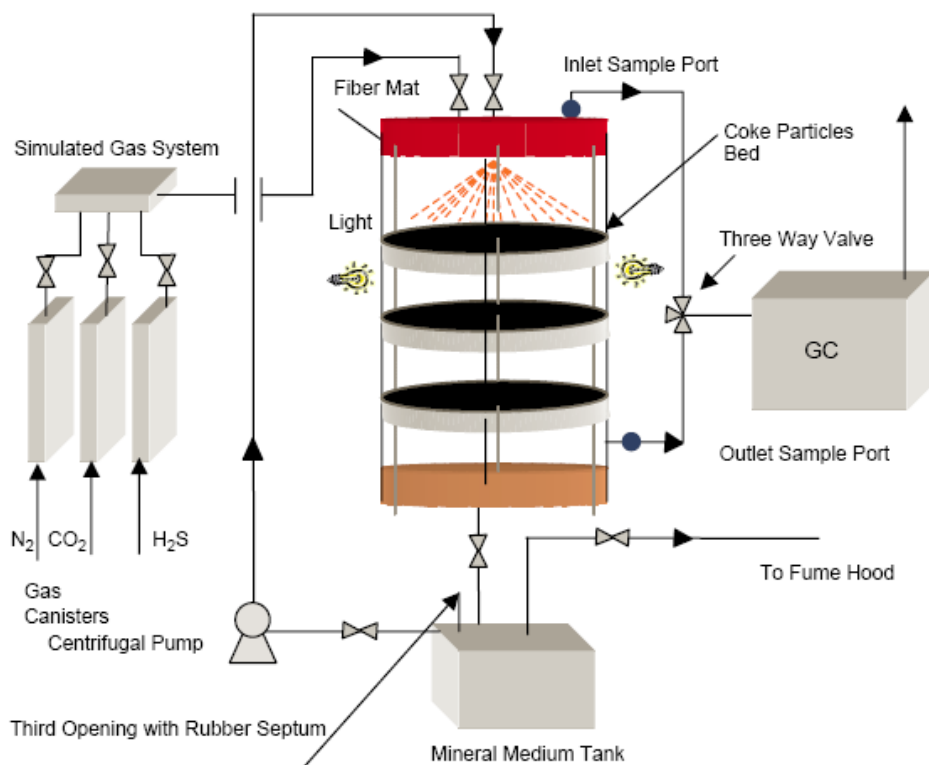


Fig. 1. Experimental setup for the anaerobic bioremoval of hydrogen sulfide.

### 2.1.1. Bacterial strain and medium

The strain *Heliobacterium chlorum* [DSMZ-3682, DSMZ bacterial collection, Germany] was used for these experiments. The maximum growth for this strain occurred in a

period of 7 days. The medium for this strain consisted of  $K_2HPO_4$ ,  $MgSO_4 \cdot 7H_2O$ , yeast extracts, distilled water, and sodium ascorbate and was prepared under strict anaerobic conditions. The pH of the final medium before inoculation was 7.0. 10-ml test tubes fitted with a screw cap and rubber septum were filled with the medium leaving just enough space in the test tube for the bacterial inoculation. The bacteria were transferred to the test tubes through the rubber septum under a continuous stream of nitrogen. The tubes with cultures were then incubated in a shaker bath in low light. Optimum growth was determined from the maximum change in density as measured using a spectrophotometer.

After successful growth in the test tube, the strain was reinoculated in fresh medium in a test tube. After successful reinoculation of the strain on the test tube scale, approximately 5 ml of bacterial culture were transferred to a one-liter flask against a stream of nitrogen and carbon dioxide which was also used to inert the flask. The growth of the cultures was observed by measuring the density of the medium by periodical sampling. If necessary, the bacteria from the flask were reinoculated in a new flask after a period of 4 weeks and the old medium was discarded.

Table 1: **Test matrix**

Test #	Nominal inlet $H_2S$ conc. (ppmv)	Residence time (min) <sup>a</sup>	pH of the medium at start	Medium sprinkling interval (min) <sup>b</sup>
1	1000	5	7.0	20
2	1000	10	7.0	20
3	1000	15	7.0	20
4	1500	10	7.0	20
5	1000	10	7.0	60
6	1000	10	7.0	120
7	1000	10	7.0	180

<sup>a</sup> Empty bed residence time, independent of biomass loading.

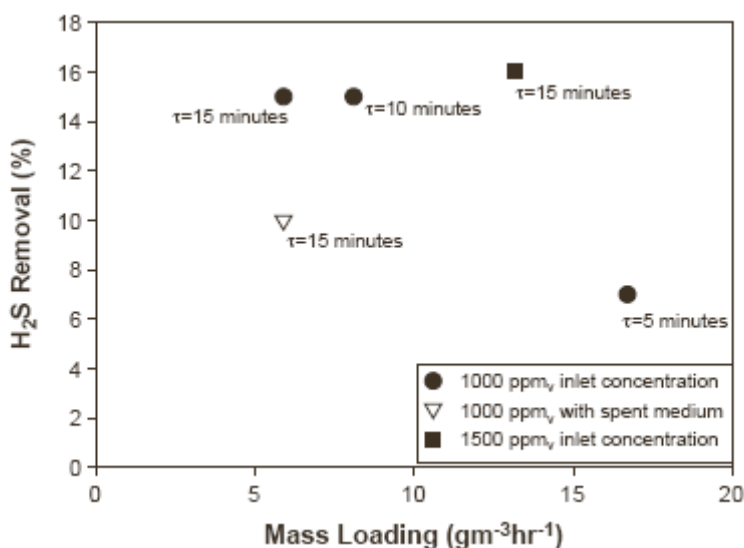
<sup>b</sup> Interval between start times, medium was sprinkled onto the top biomass bed for 9 s for each test. Each sprinkling provided 365 ml of the mineral medium.

After 28 days of growth, the bacterial culture was immobilized on coke particles to form the biocatalyst. This was accomplished by sprinkling medium containing actively growing bacteria onto the beds continuously for a period of 20 min; completely soaking the coke particles in bacteria-laden medium. After this initial inoculation, the lab controller was programmed to pump mineral medium into the bioreactor at an interval of 15 min and duration

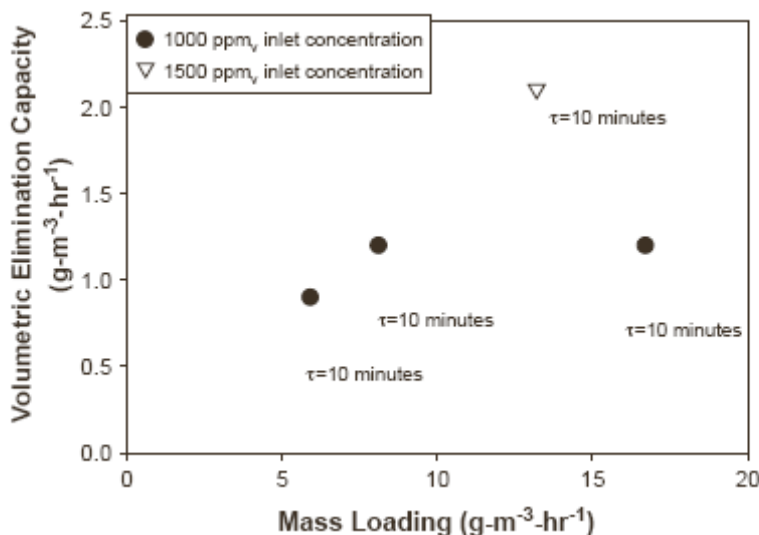
of 20 s. This was carried out at a gas residence time of two minutes for a period of 12 h with a hydrogen sulfide concentration of 2000 ppmv.

Next, an adaptation time of three weeks was given to the bacteria. During this period, the gas flow rate was adjusted such that the gas residence time in the bioreactor was five minutes and the concentration of H<sub>2</sub>S in the gas stream was 1000 ppmv. During the adaptation period, the medium containing bacteria was sprinkled onto the bed at intervals of 20 min with a sprinkling time of 9 s. The inlet and outlet H<sub>2</sub>S concentrations were monitored during this time to verify that the bacteria reached stabilization, i.e., no change was observed for at least 10 days.

### 2.1.2. Analysis of results:



**Fig 2: Anaerobic biological removal of H<sub>2</sub>S as a function of process parameters: mass loading, inlet H<sub>2</sub>S concentration, age/quality of the mineral medium, and residence time.**



**Fig 3: H<sub>2</sub>S removal rate (volumetric elimination capacity) as a function of mass loading and residence time**

In Fig. 2, H<sub>2</sub>S removal is plotted versus mass loading, which is a normalized mass flow rate (inlet concentration per empty bed residence time). The steady-state value of 15–16% net H<sub>2</sub>S removal is achieved unless the process parameters are even more suboptimal, i.e., the residence time is below the threshold of 10 min or the mineral medium is old. Fig. 3 displays the results in a slightly different manner — volumetric elimination capacity vs. mass loading. Volumetric elimination capacity is a normalized removal rate (the difference between inlet and outlet H<sub>2</sub>S concentrations divided by the empty bed residence time).

When the results in Figs. 2 and 3 are compared to previous published data for aerobic bio filtration, one significant difference can be seen. In aerobic biofiltration, near-100% removal efficiency is observed at sufficient residence time and optimum mass loading. This translates into a straight line with a slope of one on graphs of the parameters displayed in Fig. 2. Therefore, based on the low removal rates observed and a lower slope of 0.15 in Fig. 3, our anaerobic photo bioreactor exhibits severe limitations related to the delivery of essential components to bacterial cells, either hydrogen sulfide or light.

From Figs. 2 and 3 it can be seen that as the residence time of the gas in the bioreactor decreases from 10 to 5 min, the removal of H<sub>2</sub>S decreases drastically and the



volumetric elimination capacity reaches saturation. However, if the mass loading is increased in an alternate way, by increasing the H<sub>2</sub>S inlet concentration from 1000 to 1500 ppm, the volumetric elimination capacity follows a straight line that originates at the origin. This indicates that pollutant mass transfer limitations become more severe if the biocatalyst/gas contact time is decreased. The minimum residence time essential for the efficient H<sub>2</sub>S removal under optimum mass transfer conditions was estimated as 1–2 s. The comparison of this value to that obtained in our study (10 min) indicates severe transport limitations in our anaerobic photo bio filter. It should be noted though, that the nutrient (H<sub>2</sub>S) transport through the aqueous medium does not appear to be rate limiting because the same removal efficiency was maintained within a rather broad range of aqueous medium renewal rates, including the case when the biocatalyst functioned without addition of any water for up to 6 h (data not shown).

Other factors such as changes in the liquid medium composition also appear to contribute to the low values of pollutant removal. If the mineral medium is not exchanged weekly, the H<sub>2</sub>S removal efficiency drops significantly around 10 days after its last exchange (see Fig. 2 data point for “spent medium”). The values of volumetric elimination capacities (Fig. 3) are lower, by 1–2 orders of magnitude, than those obtained in liquid cultures under optimal conditions, 25–90 g m<sup>-3</sup> h<sup>-1</sup>. This, combined with high residence times essential for noticeable H<sub>2</sub>S removal may be due to the fact that the light cannot penetrate into the bulk of coke and only the surface located bacteria can convert H<sub>2</sub>S.

The challenge for future development is in designing an anaerobic biological photo reactor with a significantly greater actual biomass surface area to volume ratio than traditional bio filtration reactors, such as the reactor utilized in these experiments while maintaining the relatively dry conditions of the biocatalyst during operation.

## **2.2. Biological Deodorization of Hydrogen Sulfide using porous lava as a carrier of *Thiobacillus thiooxidans***

Biological residues such as compost, peat, soil, and wood bark have been used as carriers for bio filtration. However, peat, fiber, compost, and wood bark are not durable, and the pressure drop increases after a long period of use. When compost is used as a carrier, it must be

replaced every 2-4 years (18). Therefore, it is essential to develop excellent carriers which are easy to replace, can be used for long periods of time, and have a high microorganism adhesion capacity. Various synthetic carriers such as porous ceramics, granulated activated carbon, activated carbon fabrics, polystyrene spheres, and perlite have been developed. However, these synthetic carriers are more expensive than natural carriers.

To maximize the efficiency of bio filtration, it is most important to select excellent carriers onto which microorganisms are immobilized. The criteria for the choice of an optimal bio filter media are as follows: (i) high water holding capacity; (ii) high porosity; (iii) large surface area; (iv) low degree of clogging; (v) low pressure drop in broad ranges of water content; (vi) high persistence; (vii) low cost; (viii) light; (ix) ability to absorb odor gases to some extent. From the perspective of the activities of microorganisms, criteria (i) to (iii) are the most important, but from the perspective of construction and maintenance of the bio filter, criteria (IV) to (viii) are most important. Criterion (ix) becomes significant when the concentration of malodorous gases is fluctuated.

In this study, the possibility of using natural, porous lava as a carrier for bio filtration was investigated. They used three different kinds of porous lava samples, A, B, and C, and compared their physical properties such as water-holding capacity (WHC), pH, density, surface area, and average pore size. The buffering capacities and chemical compositions of the samples were also measured and compared. In addition, determining the removal efficiencies of  $H_2S$  by immobilizing *T. thiooxidans* on these carriers and tested the possibility of using these samples as carriers for bio filtration.

### **2.2.1. Results and discussion**

Physicochemical properties of lava samples the physical properties of lava samples such as color, WHC, pH, density, surface area, and average pore size are listed in Table1. The WHC of samples A, B, and C were 0.38, 0.25, and 0.47 g  $H_2O$ .g-lava<sup>-1</sup>, respectively. Sample C exhibited a particularly high WHC, and was able to hold water up to 50% of its dry weight. Moisture plays a major role in microbial activities, and most microorganisms are able to live in environments with a water activity of over 0.9. In bio filtration, malodorous gases such as  $H_2S$  and  $NH_3$  are dissolved in water and are biologically degraded. Therefore, the

higher the WHC, the easier it is to achieve high deodorization efficiencies. pH is also an important factor in bio filtration applications. When the pH is either too high or too low, the growth of microorganisms decreases. The pH of the lava samples used as in the range of 8.25 to 9.24. The densities of samples A, B, and C were in the range of 920 to 1190kg.m<sup>-3</sup>, and were in the order of B>A>C.

Malodorous gases such as H<sub>2</sub>S, methanthiol, dimethyl sulfide, and ammonia are degraded to strong acids such as those of sulfate and nitrate by deodorizing microorganisms.

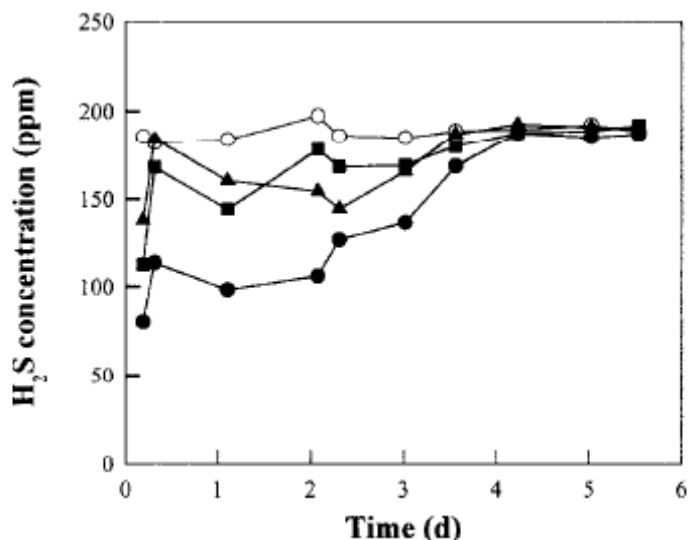
**Table 2: Physical properties and buffering capacities of the lava samples**

Property	Lava A	Lava B	Lava C
Color	Dark brown	Reddish brown	Light brown
WHC (g-H <sub>2</sub> O · g-dry lava <sup>-1</sup> )	0.38	0.25	0.47
pH	8.25	9.24	8.64
Density (kg · m <sup>-3</sup> )	1040	1190	920
Specific surface area (m <sup>2</sup> · g <sup>-1</sup> )	1.41	2.68	3.47
Pore size (Å)	85.24	123.75	116.59
Buffering capacity (g-SO <sub>4</sub> <sup>2-</sup> · kg-lava <sup>-1</sup> )	60	50	90

**Table 3: Chemical compositions of the lava samples**

Sample	Chemical content (wt %)								
	O	Na	Mg	Al	Si	K	Ca	Ti	Fe
Lava A	40.70	3.90	4.40	9.89	24.88	1.68	5.33	1.59	8.63
Lava B	37.49	2.60	5.15	9.47	24.72	1.43	6.59	1.66	10.88
Lava C	40.60	3.43	2.60	10.55	25.39	1.51	5.68	1.51	9.27

**Fig 4: Physicochemical removal of H<sub>2</sub>S by lava filters without inoculation of T.thiooxidans AZ1 1. H<sub>2</sub>S was supplied to filters at a SV of 200 h-l. Symbols: ○, inlet H<sub>2</sub>S cont.; ●, outlet H<sub>2</sub>S cont. of lava bio filter A; ▲, outlet H<sub>2</sub>S cont. of lava biofilter B; □, outlet H<sub>2</sub>S concentration of lava Biofilter c.**



When the strong acids accumulate in the bio filter, the pH of the bio filter decreases. When the pH was lowered to the point where the activity of the deodorizing microorganisms was inhibited, it was reported that the deodorization efficiency significantly decreased. Therefore, buffering capacity of a carrier, which is the ability of the carrier to resist pH change, is very important in maintaining microorganism activity for long-term bio filter operation. The amount of sulfuric acid added to lower the pH to 4 for all the lava samples is listed in Table 2. The buffering capacity of sample C was 90 g-SO<sub>4</sub><sup>2-</sup> · Kg lava-l, and was the highest among the three. The buffering capacities of samples A and B Were 60 and 50 g-SO<sub>4</sub><sup>2-</sup> · Kg-lava al, respectively. The buffering capacities of the lava samples were lower than those of other carriers such as compost and porous ceramics. The compositions of each lava sample are listed in Table 3. Each lava carrier is composed of O, Na, Mg, Al, Si, K, Ca, Ti, and Fe, and the percentages of these elements in each sample did not differ significantly. The major components were and Si. The Fe content was also high at 8.63 to 10.88 wt%. The lava samples contain essential elements such as Na, Mg, K, Ca, and Fe which microorganisms need for growth. Most H<sub>2</sub>S deodorizing microorganisms are chemo autotrophs. They can obtain carbon source and energy source from CO<sub>2</sub> and malodorous gases, respectively. However, other essential elements such as Na, Mg, K, Ca, and Fe should be supplemented. Therefore, to evaluate the possibility of

lava as an essential element source, leaching of these elements from lava was performed. The amounts of the essential elements in the leachate as measured by ion chromatography were negligible. This result indicated that the lava is not suitable as a source of essential elements and another source of the elements needs to be provided. Therefore, in this study, a mineral salt medium was supplied to the lava bio filter every 10 days. Removal characteristics of  $H_2S$  using lava as a Biofilter carrier before the use of the lava samples as potential bio filter carriers, the physicochemical removal of  $H_2S$  by lava samples without inoculation of *T. thiooxidans* AZ11 was investigated. There was poor  $H_2S$  removal in the lava alone, and the lava reached breakthrough point within only 4 d. The quantity of  $H_2S$  removed per unit gram of samples A, B, and C was 2.6, 0.81, and 1.2 g- $S_2$ /Kg-lava respectively. Compared with other carriers such as activated carbon, activated carbon fiber, and zeo carbon (I), the  $H_2S$  removal capacities by the lava samples is very low. *T. thiooxidans* AZ11, a  $H_2S$ -degrading microorganism was immobilized in lava samples, A, B, and C, and packed into a bio filter made using a glass column to investigate the removal rate of  $H_2S$ . The SV was set at 200 h-l and the inlet  $H_2S$  concentrations were varied from 200 ppm to 900 ppm during the initial 14 d. When the SV was set at 200 h-l, less than 0.01 ppm of  $H_2S$  was detected in the outlet for all three bio filters regardless of the inlet concentrations. These results indicate that  $H_2S$  in lava bio filters is mainly removed by the biological activity of *T. thiooxidans*.

### **2.3. Hydrogen sulfide adsorption on a waste material used in bioreactors**

Unlike activated carbons, where surface properties and oxidation products have been studied intensively, a high adsorptive capacity of the packing material is not a target property for bio filtration purposes. Nevertheless, by combining the biological action of microorganisms with the adsorption capacity of the filtering media, the pollutant removal or retaining performance of the bio filter can be significantly improved. In fact, Kowal et al provided evidence to suggest that the removal of hydrogen sulphide ( $H_2S$ ) in a bio filter occurs following three distinct phases: (1) absorption into the water present in the bed; (2) adsorption onto the solid phase and (3) biodegradation. McNevin et al. concluded that the prediction of adsorption and biological degradation of sulphide in an aerobic environment is complicated by the chemical oxidation of sulfide by dissolved oxygen in the liquid phase. These authors also

concluded that when sulfide is depleted from the aqueous phase, it is replaced by ions desorbed from the organic surface of the carrier material (peat in their study) until a new adsorptive equilibrium is achieved. This means that a sudden surge in inlet concentration would mostly be adsorbed onto the surface of the organic carrier material. McNevin and Barford proposed a dynamic mathematical and numerical model to predict the extent of adsorption and biodegradation of nutrients in an organic perfusion column with recycling. Other models have been augmented to include data as speciation in order for the model to accurately predict qualitative aspects of dynamic transients observed in a peat bioreactor assuming an adsorption mechanism simply by cation exchange

The bare surface of the packing material particles is a focus for contaminant adsorption. Adsorption can be defined as a process in which molecules diffuse from the bulk of a fluid (gas) to the surface of a solid adsorbent forming a distinct adsorbed phase. Finding the equations that best agree with the experimentally obtained isotherm is necessary for modeling purposes and for predicting the performance of adsorption beds

### 2.3.1. Adsorption models

The adsorption of single components may follow a Langmuir adsorption isotherm. According to this model, at the same time as molecules are being adsorbed, other molecules will be desorbed from the surface if they have sufficient activation energy. When the rates of adsorption and desorption are equal, the dynamic equilibrium may be expressed as follows:

$$k_0 a_0 C = k_1 (1 - a_1) C = k_{-1} a_1 \text{ or } a_1 = \frac{B_0 C}{1 + B_0 C}$$

Where  $a_0$  is the fraction of empty surface;  $a_1$  is the fraction of surface occupied by a monolayer of adsorbed molecules;  $B_0$  is the ratio  $k_0/k_{-1}$ ;  $k_0$  is the rate constant for adsorption on the empty surface and  $k_{-1}$  is the rate constant for desorption from a monolayer. When considering gas adsorption (i.e. hydrogen sulphide), the former equation can be expressed in terms of pressure, Whereby:

$$C_s/C_{sm} = \frac{B_1 P}{1 + B_1 P}$$

With  $C_s$  being the concentration of  $H_2S$  adsorbed on the solid;  $C_{sm}$  is the concentration of  $H_2S$  adsorbed when the monolayer is complete;  $B_1 = B_0/RT$ ;  $P$  is the partial pressure of  $H_2S$  in the gas flow fed into the bioreactor;  $R$  is the ideal gas constant; and  $T$  is the absolute temperature.

The linear expression of the former equation when using concentrations is:

$$C_{in}/C_s = C_{in}/C_{sm} + 1/B_1 C_{sm}$$

Where  $C_{in}$  is the inlet concentration.

When plotting  $C_{in}/C_s$  against  $C_{in}$ , a straight line should be obtained; otherwise, the system does not fit this model. Nevertheless, the application of this model is based on the following three assumptions: (i) that there is no interaction between adjacent molecules on the surface; (ii) the adsorption energy is constant all over the surface; and (iii) molecules adsorbed at fixed sites do not migrate to other sites. The Freundlich isotherm is an empirical expression used to describe adsorption isotherms and it is represented as :

$$C_s = K_F C_{in}^n \quad (4)$$

Where  $K_F$  and  $n$  are the Freundlich empirical constants. By taking logarithms, the former expression is expressed as follows:

$$\ln C_s = \ln K_F + n \ln C_{in} \quad (5)$$

And by representing  $\ln C_s$  versus  $\ln C_{in}$ , the Freundlich constants can be calculated.

In 1938, Brunauer, Emmett and Teller and Emmet and De Witt developed what is known as the BET theory. The BET theory is also based on the concept of an adsorbed molecule that is not free to move over the surface and which does not interact with other adjacent molecules. Moreover, this theory allows different numbers of layers to be built up at the surface although it assumes that the net amount of surface which is empty or which is associated with a monolayer, bi layer and so on is constant for any particular equilibrium condition. The equation based on the BET theory is called the BET isotherm and its deduction is described in literature.

The final expression is:

$$\frac{V_s}{V_s^1} = \frac{P}{P^0} \frac{[1 - (n+1)(P/P^0)^n + n(P/P^0)^{n+1}]}{[1 + (B_2 - 1)(P/P^0) - B_2(P/P^0)^{n+1}]} \frac{B_2}{(1 - P/P^0)} \quad (6)$$

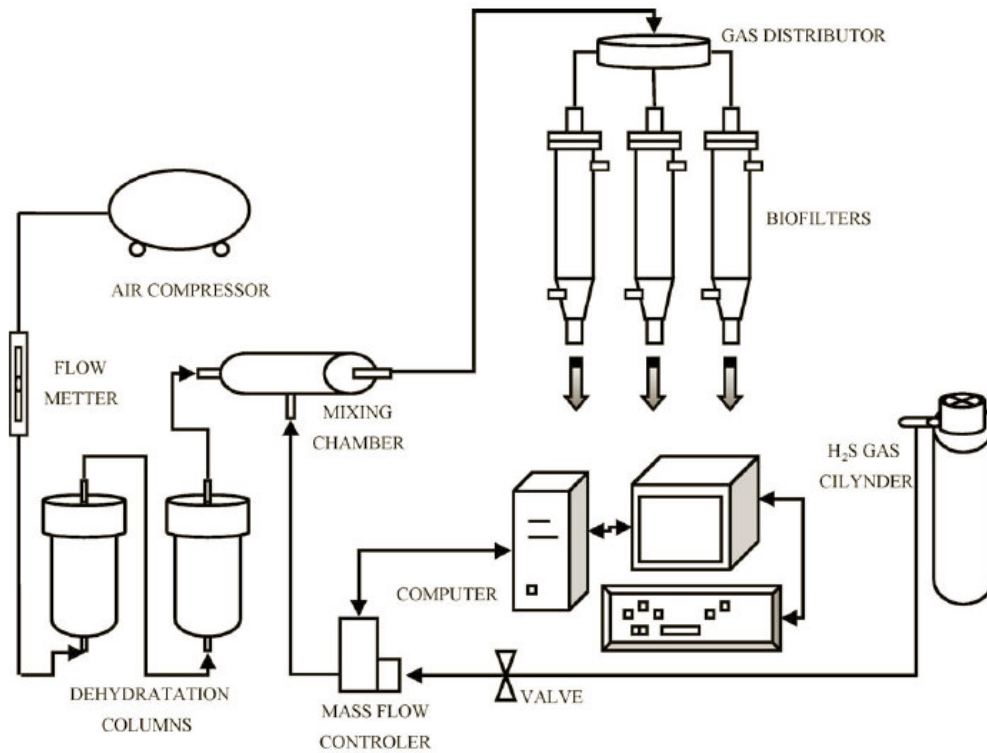
where  $V_s$  is the volume of contaminant contained in the monolayer over the surface area per unit mass of adsorbent which does not depend on the number of layers;  $P_0$  is the vapour pressure at  $T$

temperature;  $P$  is the partial pressure of the component;  $n$  is the number of layers;  $B_2$  is a constant related to the heat of adsorption; and  $V_s$  is the total volume of contaminant associated.

When  $n \rightarrow \infty$ , and  $P_0 \gg P$ ,  $(P/P_0)^n$  approaches zero, Eq.(6) becomes:

$$\frac{P/P^0}{V(1 - P/P^0)} = \frac{1}{V^1 B_2} + \frac{B_2 - 1}{V^1 B_2} \left( \frac{P}{P^0} \right) \quad (7)$$

Where  $V$  and  $V_1$  are the equivalent gas phase volume of  $V_s$  and  $V'_s$ . Based on Eq. (6), in 1938, a classification of isotherms was proposed which consisted of five characteristic shapes (from type I to type V). In some gas-solid systems, certain adsorption stages may be discerned in the characteristic shapes and they consist of concave and convex regions appearing in the same shape.

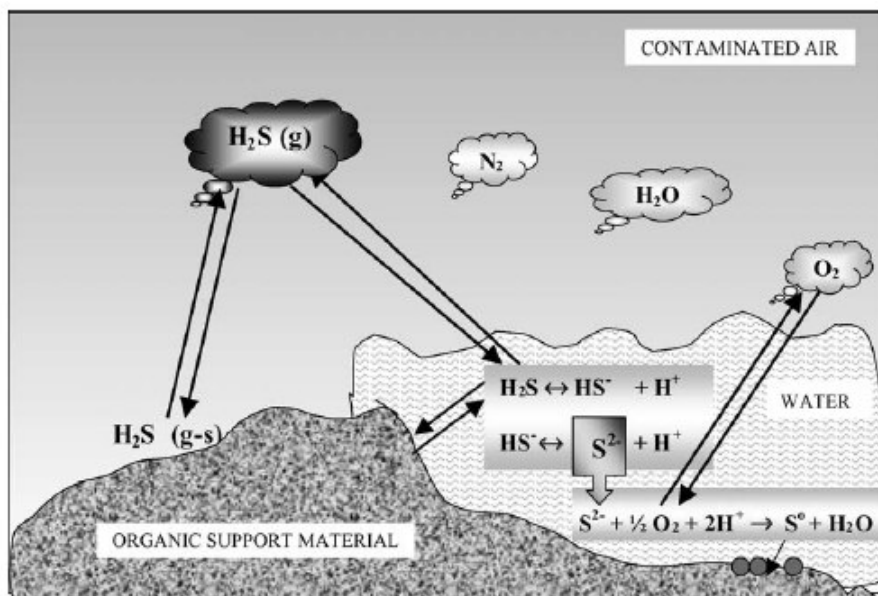


**Fig 5: Experimental setup for adsorption test**

### 2.3.2. Mass transfer coefficient in the biofilter



The particle Reynolds number ( $Re_p$ ) was calculated considering that the viscosity of the air- $H_2S$  mixture at 298K was  $170.5 \times 10^{-7} \text{ kgm}^{-1} \text{ s}^{-1}$ . The particle equivalent radius was calculated by taking 42-pellet average volume and by considering the approach to the volume of a spherical particle. According to the low particle Reynolds number, the fluid dynamics are that of laminar flow and the mass transfer coefficient was  $7.93 \times 10^{-3} \text{ ms}^{-1}$ , which suggests that mass transfer from the gas phase to the solid surface takes place slowly under operating conditions. This mass transfer coefficient is low enough for the contaminant to diffuse into the solid surface. Only external diffusion was considered, as the contribution of micro pore area to the surface area is about 2.63% (considering micro pores as all those pores with a diameter smaller than  $20 \text{ \AA}$ ).



**Fig 6: Layout of the adsorption/absorption phenomena in a bio filter treating  $H_2S$  in absence of microorganisms.**

### 2.3.3. Conclusions

Although contaminant biodegradation is the main purpose of biofiltration, the contribution of other physical phenomena to the retention of the pollutant in the bed material is an additional advantage when biomass activity is suppressed or when operating problems eventually arise. The adsorption capacity of a sterilized bed material has been studied by determining the adsorption equilibrium isotherm at room temperature and by comparing the results with the equilibrium isotherm of an activated carbon (contaminant concentrations ranging

from 40 to 330 ppmv). It has been concluded that as the gas inlet concentration is increased, the amount of contaminant adsorbed on the organic material also increases, with the  $n$  constant of the Freundlich model being 1.55. However, it must be noted that the organic material has a poor adsorption potential compared to the activated carbon. A type I adsorption isotherm for the activated carbon and type III for the organic material have been obtained. The latter is related to a nonporous material with great cohesive forces between adsorbate molecules. Absorption contribution to the retention of  $H_2S$  on the moist organic bed is negligible. A high adsorption capacity of the bed material is desirable as a safety measure for an operating bio filter, but it can also be a double-edged sword when inlet contaminant concentration suddenly decreases or stops, as reversible desorption will undoubtedly take place

#### **2.4. Hydrogen sulfide removal by compost biofiltration: Effect of mixing the filter media on operational factors:**

Compost biofiltration is one of the most important biological processes for waste gases treatment and for odor control (Van Groenestijn and Hesselink, 1993). This system is based on the interaction of gas phase pollutants with an organic packed media, such as compost. The degradation activity derives from microorganisms that live and develop in the filter media, in such a way that undesirable compounds in the gas are absorbed and removed. Three important general factors determine compost bio filter performance: (a) the type of the filter media (including void fraction, particle size, moisture content, microbial diversity and nutrients), (b) the prevailing conditions of gas flow inside the biofiltration unit (including superficial velocity, gas distribution, temperature and inlet pressure) and (c) the substrate concentration, solubility and biodegradability. Research efforts are focused on the bio filter media in order to upgrade the performance of compost biofilters. Some use compost mixed with bulking agents in order to avoid high pressure drop, clogging and gas flow channels. Many materials have been used as bulking agents, such as activated carbon (Weber and Hartmans, 1995), polyurethane, polystyrene or glass particles (Zilli et al., 1996) as well as crushed oyster shells (Ergas et al., 1995). Other research efforts have been made on fluid distribution to overcome mass transfer problems associated with channeling and to increase substrate–microorganisms interaction using alternating flow direction (Ergas et al., 1994) or performing recycling streams (Ritchie and Hill, 1995). Special biofilter designs also have been developed such as the biorotor reactor (Buisman

et al., 1990) and a modified biofilter with horizontal gas flow and baffles (Lee et al., 2001) to increase back-mixing. Additionally, bed mixing has been mentioned in literature as an important method to increase efficiency (Van Lith et al., 1997) but there are very few studies (Wubker et al., 1997) that have systematically explored this possibility.

#### 2.4.1. Methods

##### 2.4.1.1. Filter media

The media used as bio filter packing was mature compost produced from food, and yard waste as well as horse manure. The compost was provided by the National University Compost Plant and was prepared in outdoor windows. The compost had a carbon/nitrogen ratio of 20:1, a moisture content of 65%, a pH of 7.48, an alkalinity of 357 mg CaCO<sub>3</sub>/L, a real and apparent density of 1.1 and 0.59 g/ml, respectively and a void fraction of 46%.

##### 2.4.1.2. Air humidifying columns

Two towers for air humidification were constructed. Both humidifiers were built using PVC cylinders of 0.15 m diameter and 1.2 m height. These towers were operated flooded, packed with Rashig rings (1/2<sub>00</sub> diameter) up to 0.90 m height.

##### 2.4.1.3. Biofiltration columns

The bio filtration columns were built using PVC cylinders 0.10 m diameter and 1.2 m height (volume = 9.6 l). These columns were packed with compost to a height of 1.0 m. The filter media was retained in each column using a fine screening mesh. Each column had five gas and compost sampling ports spaced 20 cm along the column.

##### 2.4.1.4. Packing procedure and bed mixing

The columns were packed manually following the same procedure on each experimental run. The compost was taken using a spatula (approximately 300 g wet basis) and it was dropped freely into the column until obtaining a height of 1 m. Additional compaction of the media was avoided in order to allow only the natural compaction expected by the weight of the compost. Compost mixing was accomplished each 2 days by removing the entire bed from the column; manually homogenizing the media and then returning it into the biofilter column.

#### 2.4.1.5. Water addition

Water addition rate was based on a recommended water–air ratio between 1.5 and 3 ml water/m<sup>3</sup> of gas . This resulted in a water addition rate of 57 ml tap water every 48 h considering a rate of 2 ml of water/m<sup>3</sup>.

#### 2.4.1.6. Pressure drop

A profile of pressure drop versus gas flow rate for the bio filters was fit to the Ergun equation in order to determine average particle diameter of the biofilter media as a function of height. Columns I, II and III were subjected to air flows from 10 to 70 l/min in 10 l/min increments to obtain plots of pressure drop versus gas flow rate. A water differential manometer was used for pressure drop measurements. The effect of the fine screen and other equipment at the bottom of each column was corrected by subtracting the pressure drop provided by those elements from each pressure drop measurement.

#### 2.4.1.7. Physicochemical measurements

The H<sub>2</sub>S concentration was measured along the length of the columns using electrochemical cells (SRII-U-100, BW Technologies). Sulfate concentration, moisture content and alkalinity were measured by removing small samples (approximately 1 g) of compost from each sample port. Sulfate (SO<sub>4</sub><sup>2-</sup>) concentration in the media was measured by the photometric method using Merk Spectroquant equipment. Moisture content of the compost was determined gravimetrically (Parent and Caron, 1993). Alkalinity and pH of the bio filter media was measured using the method reported by Klute (1986). The granulometry of compost was determined using the sieve tray analysis method (Parent and Caron, 1993).

#### 2.4.1.8. Tracer study

Butane gas was used as tracer for determining the retention time distribution (RTD) curves because it has very low solubility, 1.26 mM at 298 K (Perry and Green, 1988) and can be easily measured by the monitoring system. The tracer was injected into the columns using a pulse injection technique (Levenspiel, 1972). A continuous sample was collected, using a gas pump, from the gas sampling ports of the bio filter to an infrared CO<sub>2</sub> detector (Beckman Industrial TOC analyzer Model 915B). A CO<sub>2</sub> trap (KOH, 1 M) located between the gas sampler

and the TOC analyzer was used to avoid interferences due to CO<sub>2</sub> contained in the air. An automatic data recording system (Peaksimple II for SRI chromatographs) was connected to the TOC analyzer to reproduce the RTD curve on a screen and printer. Three tracer injections (1 ml each) per tracer study were performed and an average RTD curve was determined.

Mathematical analysis was performed using an Excel spread-sheet program to determine average gas retention time. Each tracer study was carried out using airflow rate of 10 l/min. To assure minimum interaction between the tracer input and compost, the compost was saturated with butane prior to each tracer study. This was carried out using a constant butane input into the inlet air stream until a constant butane concentration of 1.5 mg/l was reached in the biofilter outlet. Mass balance calculations showed that this technique resulted in practically 100% recovery of the tracer.

#### 2.4.1.9. Pilot plant

Compressed air (HAGEN-100 diaphragm compressor) was passed through two PVC humidification columns. The humidification columns provided close to 100% relative humidity. A controlled flow of H<sub>2</sub>S from a gas cylinder was mixed with the main humidified air stream, which then was fed to the bottom of Column I resulting in a H<sub>2</sub>S concentration of 100 ppm<sub>v</sub> or 7 g H<sub>2</sub>S/m<sup>3</sup>/h. Air flow rate was maintained at 10 l/min, which provided a superficial loading rate of 74 m<sup>3</sup>/m<sup>2</sup>/d with an empty bed residence time (EBRT) of 50 s. The second and third columns (II and III) were used as controls; only a humidified air stream was fed to Column II and either water or gas was fed to Column III. The bio filter columns were located on the roof of the Environmental Engineering Laboratory building at the barometric pressure of Mexico City (585 mm Hg) and at ambient temperature (20 ± 5 °C). Columns I, II and III were analyzed at the end of the experiment. Columns I and II were operated for 206 days; the first 142 days using conventional operating criteria. Columns I and II continued their operation for an additional 65 days (from day 143 until day 206) with bed mixing every 2 days. Media moisture content was controlled using water addition at the top of the columns. Air supply for the columns was controlled using a Cole Parmer mass flow controller and calibrated rotameters. The columns were operated in up flow mode.



# CHAPTER 3

## Removal of Hydrogen Sulfide

### 3.0. Removal of Hydrogen Sulphide

Hydrogen sulphide is a colourless and poisonous flammable gas with a strong smell of rotten eggs. It is also known as sewer gas and stink damp. It can be detected by smell at concentrations ranging from 0.01-0.3 parts per million (ppm). **However, relying solely on its odor is not a good idea because at concentrations above 100 ppm it deadens a person's sense of smell within a few minutes.** The pure gas is heavier than air and can collect in low areas such as sewers, pits, tunnels and gullies. Hydrogen sulphide can react with rust or corrosion deposits on equipment to form iron sulphide. This reaction occurs in an oxygen free atmosphere where hydrogen sulphide gas is present or where the concentration of hydrogen sulphide is greater than that of oxygen. This happens most often in closed vessels, tanks or pipelines. Iron sulphide is a pyrophoric material, which means that it can ignite spontaneously when it is exposed to air. High concentrations (between 4.3% and 46% of gas by volume in air) can catch fire and explode if there is a source of ignition. When the gas is burned, other toxic gases, such as sulphur dioxide are formed. Hydrogen sulphide is incompatible with strong oxidizers, such as nitric acid or chlorine trifluoride, and may react violently or ignite spontaneously. When hydrogen sulphide is released into the air, it will form sulphur dioxide and sulphuric acid in the atmosphere. Hydrogen sulphide ( $\text{H}_2\text{S}$ ) occurs naturally in the earth in crude petroleum, natural gas reservoirs, volcanic gases and hot springs.

#### **Hydrogen sulfide is also produced from,**

The breakdown of human and animal wastes by bacteria,

Industrial activities such as food processing,

Coke ovens,

Kraft paper mills,

Rayon textile manufacturing,

Wastewater treatment facilities,

Sulphur production,

Tar and asphalt manufacturing plants,

Tanneries and Refineries.

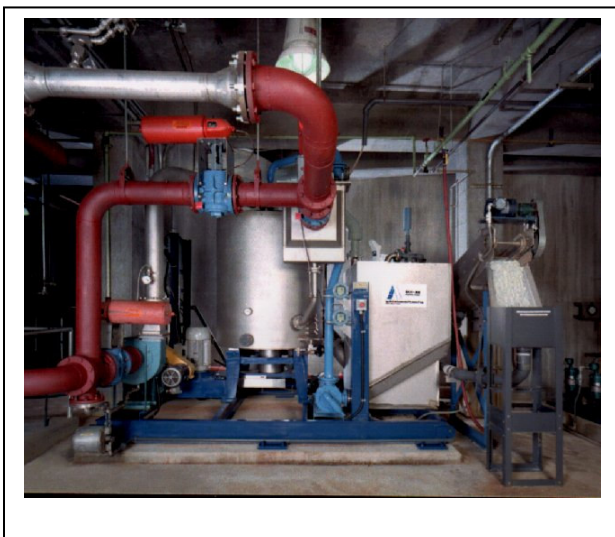
### 3.1. Conventional methods for the removal of Hydrogen Sulfide:

1. Removal of Hydrogen Sulphide from waste water and waste gases by biological conversion to elemental sulphur
2. by nitrox Process
3. by using Activated Sludge diffusion
4. Oil Remediation method
5. Recycling and filtration
6. Using Sulpha-test
7. by sulphidation of hydro ions (iii) oxides
8. By using a Biogas scrubber

#### 3.1.1. By using a biogas Scrubber:

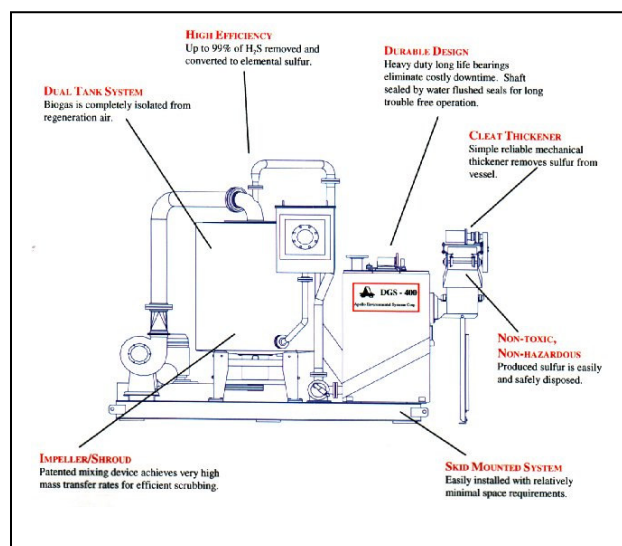
Apollo developed the DGS Series biogas scrubber for removal of hydrogen sulphide gas and particulate matter from biogas as it is produced. Hydrogen sulphide ( $H_2S$ ) itself has an offensive odour of "rotten eggs" at concentrations as low as 50 parts per billion by volume (ppbv) and is toxic at concentrations above 1000 parts per million by volume (ppmv).  $H_2S$  is a health and safety hazard, and when combined with carbon dioxide ( $CO_2$ ) and water vapour ( $H_2O$ ), corrodes plant equipment such as boilers and piping, and can ruin power-generating equipment. Energy recovery from biogas and other waste streams, a common practice today, is hampered if  $H_2S$  gas is present. High levels of  $H_2S$  can also interfere with other processes such as killing useful bacteria in anaerobic digesters. Reducing  $H_2S$  offers cost savings associated with less maintenance, increased process and energy efficiency, and reduced toxic emissions. First installed and tested at the Metropolitan Toronto Works Department's Main Treatment Plant at Ashbridges Bay in 1993/4, the Apollo scrubber was found to be up to 99 percent efficient in

the removal of hydrogen sulphide.



**Fig 7: A Biogas Scrubber**





- Fig 8: Schematic of a Biogas scrubber process

### 3.1.2 Activated Sludge Diffusion:

Odors from wastewater treatment plants comprise a mixture of various gases, of which hydrogen sulphide ( $H_2S$ ) is the main constituent. Microorganisms commonly found in wastewater can degrade sulphurous compounds. Therefore, the use of activated sludge (AS) for odor control offers an alternative to traditional waste gas treatment processes, such as biofilters, bioscrubbers and biotrickling filters, both in practical terms (use of existing facilities) and economically (minimal capital cost). The performance of AS diffusion as a bioscrubber for removing  $H_2S$  at concentrations at 25, 75 and 150 ppmv was evaluated. Pilot-scale trials were undertaken using parallel 60-L aeration tanks and 20-L clarifier reactors at the Bedford Sewage Treatment Works, Carington, UK. Olfactometry measurements were also carried out to determine whether there was any increase in odour concentration owing to  $H_2S$  diffusion. Hydrogen sulphide removal rates of 100% were obtained, with no noticeable increase in odour concentration throughout the trials as measured by olfactometry. Odour concentration was highest at the beginning of the trials and lowest during the high  $H_2S$  dosing period, with similar values being obtained for test and control. It was concluded that AS diffusion is an effective bioscrubber for the removal of  $H_2S$  odour.

### **3.1.3. USING SULPHA-TREAT PROCESS:**

The SulfaTreat process is a chemical reaction that removes the hydrogen sulfide from a gas stream via specifically designed reactant products. The apparatus consists of a fixed-bed or batch-type granular hydrogen sulfide reactant contained in a pressure vessel. The reactant in this case is one of the SulfaTreat products, and the vessel – provided it is engineered to treatment specifications – can be obtained from a variety of sources, including the customer's inventory. Both the unused and spent products are safe and stable.

The flexibility of the SulfaTreat process allows the system to adapt to variations in H<sub>2</sub>S outlet specifications that may result from changes in operating preferences or tighter regulations, often without additional capital equipment or system retrofitting. Predictable pressure drops, long bed life, easy and safe handling, and a simple, reliable operation are a few of the features of the SulfaTreat process.

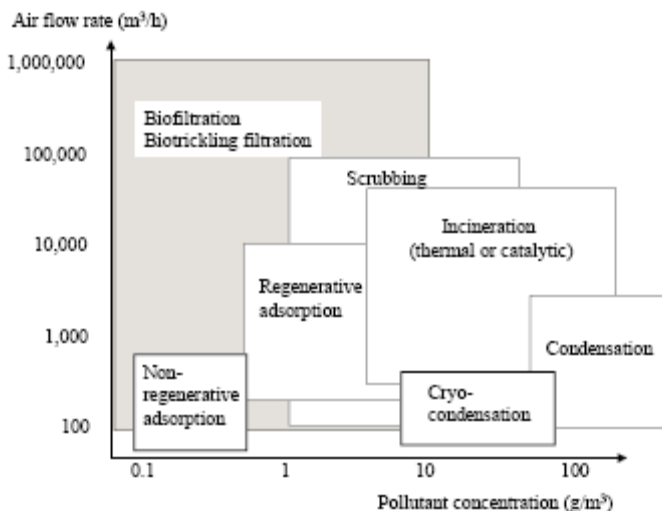
### **3.1.4. By sulphidation of hydrous ions (iii) oxides:**

A novel automated warning and removal system for hydrogen sulphide in aqueous flow-through systems has been developed based on the sulphidation of ferrihydrite sorbed to zeolite substrate. The system consists of a small flow-through reaction cartridge with photo-sensors positioned at the base. During the reaction, sulphide is initially oxidized to elemental sulphur by the ferrihydrite, and Fe<sup>2+</sup> is subsequently released to solution. This Fe<sup>2+</sup> then reacts with additional dissolved sulphide to form solid phase iron monosulphide. The colour change from orange ferrihydrite to black iron monosulphide is continuously monitored by the photo-sensors, which provide a rapid and reproducible response (via a voltage change) to pulses of sulphidic water. The response of the photo-sensors is linear with respect to inflowing sulphide concentration, while the most rapid response to dissolved sulphide occurs at a flow rate of approximately 200 ml min<sup>-1</sup> (equivalent to a hydraulic loading rate of 21 cm min<sup>-1</sup>). The presence of phosphate in solution substantially decreases reaction rates due to adsorption to reactive surface sites. However, the response time of the photo-sensors remains sufficient to provide a rapid indication of sulphidic conditions even in systems with high concentrations of dissolved phosphate. The cartridge has the advantage of partially or completely removing sulphide (depending on flow rate and substrate mass) from an initial pulse of water. At the optimal flow rate for the successful use of the cartridge as a sulphide warning system (200 ml min<sup>-1</sup>), required substrate masses for the complete removal of dissolved sulphide (over the experimental range of 0-1000 microM) are relatively small (0.5-2 kg).

### 3.2. Removal of H<sub>2</sub>S using a Bio trickling filter

Bio filters work by passing a humid stream of contaminated air through a damp packing material, usually compost mixed with wood chips or any other bulking agent, on which pollutant degrading bacteria are naturally immobilized. Bio filters are simple and cost effective. They require low maintenance and are particularly effective for the treatment of odor and volatile compounds that are easy to biodegrade and for compounds that do not generate acidic by-products. Bio filters are increasingly used in industrial applications.

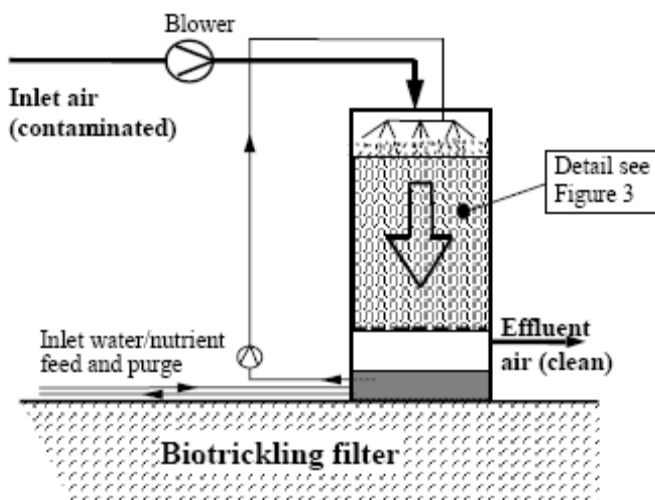
Bio trickling filters work in a similar manner to bio filters, except that an aqueous phase is trickled over the packed bed, and that the packing is usually made of some synthetic or inert material, like plastic rings, open pore foam, lava rock, etc. The trickling solution contains essential inorganic nutrients such as nitrogen, phosphorous, potassium, etc. and is usually recycled. Bio trickling filters are more complex than bio filters but are usually more effective, especially for the treatment of compounds that generate acidic by-products, such as H<sub>2</sub>S. They can be built taller than bio filters. Bio trickling filters are more recent than bio filters, and have not yet been fully deployed in industrial applications.



**Fig 9: Applicability of various air pollution control technologies based on air flow rates and concentrations to be treated**

### 3.2.1. BIOTRICKLING FILTRATION PRINCIPLE

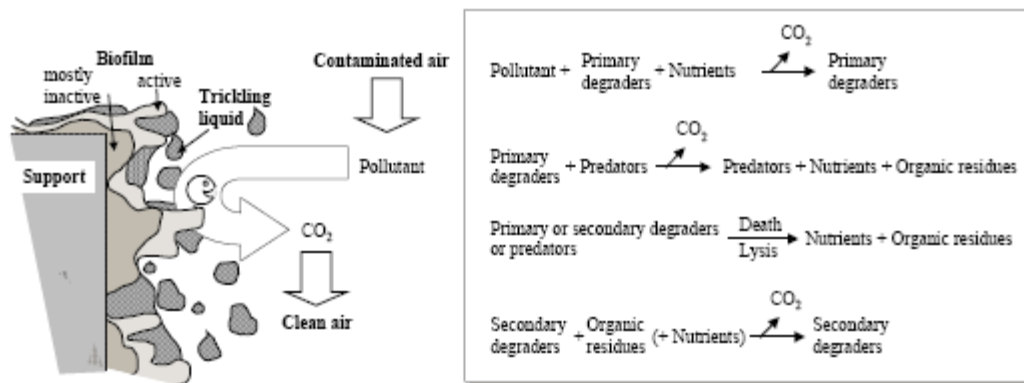
The principle of bio trickling filtration is schematically explained in Figures 10 and 11 while typical characteristics of bio trickling filters are listed in Table 3. Bio trickling filters are biological scrubbers. At a first glance, the mechanisms appear to be relatively simple: contaminated air is contacted with an immobilized culture of pollutant degrading organisms in a packed bed. A more detailed examination of the processes involved reveals that elimination of the pollutant is the result of a combination of physico-chemical and biological phenomena. Understanding these phenomena is a key to the successful deployment of the technology



**Fig 10: Schematic principle of bio trickling filtration; here co current operation is shown.**

In bio trickling filters, contaminated air is forced through a packed bed, either down flow or up flow. The packed bed is generally made of an inert material such as a random dump or a structured plastic packing, or less often, open pore synthetic foam or lava rocks. The packing provides the necessary surface for biofilm attachment and for gas-liquid contact. During treatment, an aqueous phase is recycled over the packing. It provides moisture, mineral nutrients to the process culture and a means to control the pH or other operating parameters. The system is continuously supplied with essential mineral nutrients such as nitrogen, phosphorus, potassium, and trace elements via a liquid feed. In general, most of the pollutant is biodegraded in the bio film, but part may also be removed by suspended microorganisms in the recycle liquid. Possible biodegradation metabolites will leave the system via the liquid purge along with small amounts

of biomass. Usually, less than 10% of the carbon-pollutant entering the system leaves via the purge.



**Fig 11: Mechanism of pollutant removal and main biological processes involved in bio trickling filters.**

Bio trickling filters work because of the action of the pollutant degrading microorganisms. In the case of the removal of hydrocarbon vapors, the primary degraders are aerobic heterotrophic organisms that use the pollutant as a source of carbon and energy. For  $\text{H}_2\text{S}$  or ammonia removal, the primary degraders are autotrophes, and will use the pollutant as a source of energy, and carbon dioxide as source of carbon for growth. The removal of compounds such as dimethyl sulfide or dimethyl disulfide will require both autotrophes and heterotrophes to be present. In any case, the bio trickling filter will host a wide variety of microorganisms, similar to those encountered in waste water treatment operations. The microorganisms responsible for pollutant removal in bio trickling filters are usually aerobic because bio trickling filters are well aerated systems. However, it has been proposed that the deeper parts of the bio film (see Figure 11), where anaerobic conditions probably prevail, can be utilized to perform anaerobic biodegradation (e.g., reductive de chlorination, or  $\text{NO}_x$  reduction) for the treatment of pollutants that are otherwise recalcitrant under aerobic conditions. Anaerobic treatment in aerobic bio trickling filters is still an experimental area.

Biotrickling filter bed height	1-5 m
Biotrickling filter cross section area	1-3,000 m <sup>2</sup>
Air flow treated	100-1,000,000 m <sup>3</sup> h <sup>-1</sup>
Packing void volume <sup>a</sup> -Plastic rings, foam, random or structured packing -Lava rock	90-95% ~50%
Empty bed gas retention time <sup>b</sup>	2-60 s
Pressure drop	< 1 cm of water column per m bed depth
Operating temperatures	15-50 °C
Trickling rates <sup>c</sup>	0.01-10 m h <sup>-1</sup>
Liquid dilution rate <sup>d</sup>	0.1-2 day <sup>-1</sup>
Usual pH of the recycle liquid -removal of VOCs or compounds difficult to degrade -removal of H <sub>2</sub> S	~7 1-2
Inorganic nutrient supply (N, P, K, traces)	Usually 0.05 to 1 times the amount calculated using biodegradation stoichiometry
Inlet pollutant concentration -VOCs -Odors	0.01-10 g m <sup>-3</sup> 500-50,000 odor units
Typical pollutant removal efficiencies	60-99.9+%

<sup>a</sup> Value at reactor startup; over time, biomass growth will decrease bed porosity, typically by 10-30%

<sup>b</sup> The empty bed gas retention time (EBRT) is defined as the bed volume / air flow

<sup>c</sup> Trickling flow rate / bed cross section area

<sup>d</sup> Liquid feed rate / recycle liquid volume

**Table 4: Typical characteristics of a bio trickling filter**

As Illustrated in figure 11, a major fraction of the bio film becomes inactive (mostly because of mass transfer limitations) as the bio film grows, and active primary degraders only constitute a minor fraction of the total population in the bio film. Secondary degraders feeding on metabolites, biopolymers, or predators feeding on the primary degraders include bacteria, fungi, and higher organisms such as protozoa, rotifers, even mosquito or fly larvae, worms or small snails. The importance of higher organisms for the overall process should not be underestimated. They have been shown to play an important role in reducing the rate of biomass accumulation and in recycling essential inorganic nutrients. As a matter of fact, comparison of traditional mineral growth media with bio trickling filter recycle liquid composition reveals that most biotrickling filters are operated under various degrees of inorganic nutrient limitation. The relationship between nutrient supply and biomass growth is discussed further in this chapter.

### 3.2.2. BIOTRICKLING FILTER PERFORMANCE

#### Definitions and Factors affecting performance

Operation and performance of biological reactors for air pollution control is generally reported in terms of removal efficiency, or pollutant elimination capacity as a function of the pollutant loading, or the gas empty bed retention time (EBRT). These terms are defined in Equations below:

$$\text{Removal} = \text{RE} = \frac{C_{\text{in}} - C_{\text{out}}}{C_{\text{in}}} \times 100 (\%) \quad (1)$$

$$\text{Pollutant Elimination Capacity} = \text{EC} = (C_{\text{in}} - C_{\text{out}})/V \times Q \text{ (gm}^{-3} \text{ h}^{-1}) \quad (2)$$

$$\text{Empty Bed Retention Time} = \text{EBRT} = V/Q \text{ (s or min)} \quad (3)$$

$$\text{Pollutant loading} = L = C_{\text{in}}/V \times Q \text{ (gm}^{-3} \text{ h}^{-1}) \quad (4)$$

Where  $C_{\text{in}}$  and  $C_{\text{out}}$  are the inlet and outlet pollutant concentrations (usually in  $\text{g m}^{-3}$ ), respectively,  $V$  is the volume of the packed bed ( $\text{m}^3$ ) and  $Q$  is the air flow rate ( $\text{m}^3 \text{ h}^{-1}$ ). Pollutant concentrations are usually reported as mass per volume; conversion of volumetric to mass concentrations is done using the ideal gas law which reduces to Equation 5 at room temperature

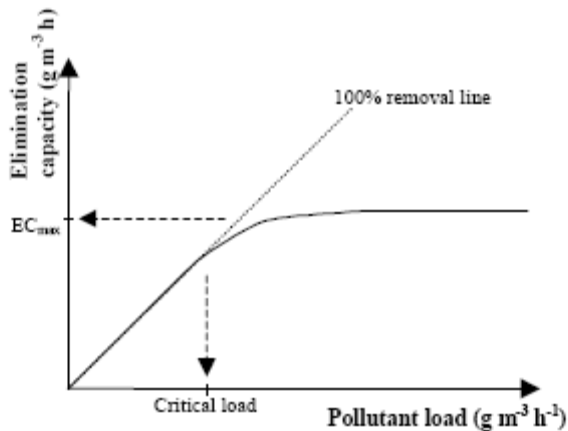
$$\text{Concentration (g m}^{-3}) = \text{Concentration (ppm}_v) \times \frac{\text{molecular weight of pollutant}}{24776}$$

It should be stressed that the elimination capacity and the loading are calculated using the volume of the packed bed and not to the total volume of the reactor. Depending on the reactor design, the volume of the packed bed volume will be about 40-90% of the total reactor volume. Also, the EBRT is calculated on the basis of the total volume of packed bed

(Equation 3). The actual gas residence time will be lower depending on the porosity of the packing, the dynamic liquid hold-up and the amount of biomass attached to the packing. The porosity of packing ranges from about 50% (lava rock) to 95% (all random or structured

packings), the liquid holdup is usually less than 5% of the bed volume, and biomass may occupy 5% to 30% of the bed volume. Hence, the actual gas residence can be less than half the EBRT.

It is usual to report the performance as a function of the load, i.e., inlet concentration  $\cdot$  air flow, rather than the concentration. This enables comparison of systems of different sizes operated under different conditions. One underlying assumption is that the performance depends only on the pollutant load, hence, that low concentrations high flow rates conditions lead to similar elimination capacities as high concentrations-low flow rates. This assumption is generally valid because the pollutant concentrations commonly encountered in bio trickling filters are high enough for the micro-kinetics to be of zero order. This is no longer true at very low pollutant concentrations (typically below  $0.05 - 0.1 \text{ g m}^{-3}$ ), in particular for pollutants with high Henry's law coefficients, because first order kinetics will prevail in the bio film resulting in a reduction of the maximum elimination capacity.



**Fig 12: Schematic of a typical elimination capacity vs. load characteristic for a bio trickling filter.**

Examination of Figure 12 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 bio trickling filter is operated well



below its maximum elimination capacity. The performance increases 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 pollutant concentration or of the air flow rate do not result in further increases in elimination capacity, the removal efficiency decreases.

For the evaluation of biotrickling filter performance, one should consider both the maximum elimination capacity and the removal efficiency. For practical reasons, academic research is mainly concerned with the maximum elimination capacity or with high performance, which occur at relatively high pollutant concentration and often less than ~90% removal efficiency. On the other hand, reactor design for industrial application often needs to meet a certain discharge requirement, or achieve a high removal percentage. Thus there might be some challenges in extrapolating research data for reactor design. In this context, the critical load defined as the maximum loading before the removal deviates significantly from the 100% removal line (Figure 12) is a valuable parameter. But there are limitations to the use of the critical loading. It is relatively sensitive to the pollutant inlet concentration, thus extrapolation of low flow-high concentrations to high flow low concentration should be avoided.

### **3.2.3. Examples of Bio trickling Filter Performance**

Research over the past ten years has greatly broadened the range of pollutants that can be treated in bio trickling filters, including volatile organic compounds (VOCs), chlorinated hydrocarbons, reduced sulfur compounds, and compounds containing nitrogen. Typical examples are presented in Table 4. Maximum elimination capacities generally are in the range of 5-200 g m<sup>-3</sup> h<sup>-1</sup>. Although many factors influence performance, a few general comments can be made. As bio trickling filters rely on microorganisms as the catalysts for pollutant conversion, biodegradability of the pollutant is of prime importance. Decreasing biodegradability causes lower elimination capacities and/or longer periods of adaptation. The use of specially acclimated or enriched microorganisms may be considered in these cases. Equally important is the

accessibility of the pollutant to the microorganisms. The overall rate of pollutant removal may be limited by mass transfer rate of the pollutant into the bio film, which depends mainly on the pollutant's air-water partition which is in turn best described by the Henry coefficient. Mass transfer limitation leads to a bio film not completely saturated with the pollutant, hence pollutant concentrations in the bio film are below those required for maximum biological activity. Means to improve the overall mass transfer rate in bio trickling filters include the selection of packing materials with a high specific surface area and intermittent trickling to reduce the thickness of the water film on the bio film. As illustrated in Table 4, many different types of packing materials have been used in bio trickling filters, and research in this area is still ongoing. The packing should combine a high porosity to minimize the pressure drop across the reactor and a high specific surface area to maximize bio film attachment and pollutant mass transfer. Other factors to consider for a packing include water holding capacity, structural strength, surface properties, weight, and stability over time, and cost.

Reaction conditions in the bio trickling filter can be optimized by controlling the pH, the concentrations of nutrients and metabolic end-products in the recycle liquid. Many biotrickling filters are equipped with a pH control, and with automatic water/nutrient addition to control ionic strength. The optimum pH depends on the process culture. Most VOC removing bio trickling filters are operated at a near neutral pH. On the other hand,  $H_2S$  oxidizing microorganisms such as *Thiobacillus sp.* are acidophilic and show maximum activity at low pH. pH values as low as 1-2 are not uncommon in bio trickling filters treating  $H_2S$  vapors. Treatment of sulfur and chlorinated compounds will result in the accumulation of sulfate and chloride in the recycle liquid, respectively. These salts will inhibit biodegradation if certain concentrations are exceeded, and frequent supply of fresh water and purge of the recycle liquid is required to prevent accumulation of inhibitory concentrations. The dilution rate can be controlled by continuous measurement of the conductivity of the recycle liquid

### **3.2.4. BIOMASS GROWTH IN BIOTRICKLING FILTERS**

#### **Growth Kinetics**

Clogging of bio trickling filters by growing biomass is one factor that has markedly slowed down the implementation of bio trickling filters at the industrial scale. A better understanding of biomass growth in bio trickling filters is warranted. In general, pollutants are used by the primary degraders to produce new biomass and to generate energy for maintenance

(see Figure 11). These processes have been extensively investigated in batch or continuous monocultures. The situation is much more complicated in bio trickling filters where a complex ecosystem exist. In a first approximation, neglecting heterogeneities and mass transfer effects, one can write that the rate of pollutant degradation depends on the intrinsic growth rate of the active fraction of the primary degraders ( $X_1$ ) and their maintenance requirement, as in Equation 6.

$$EC = \left( \frac{\mu}{Y_{X/S}} + m \right) \times X_{1(\text{active fraction})} \quad (6)$$

Where  $\mu$  is the specific growth rate of the primary degraders,  $Y_{X/S}$  is the biomass yield,  $m$  the maintenance energy requirement, and  $X_{1(\text{active fraction})}$  is the biomass content of active primary degraders per volume of reactor. The specific growth rate of the active fraction of the primary degraders can be expressed using a modified Monod type equation,

$$\mu = \frac{\mu_{\max} \times S}{K_s + S} \times \frac{N}{K_{sN} + N} \times \frac{O}{K_{sO} + O} \times \frac{I}{1 + \frac{I}{K_I}} \quad (7)$$

Where  $S$  is the pollutant and substrate,  $N$  is any nutrient,  $O$  is the oxygen, and  $I$  any inhibitor, and  $K_s$ ,  $K_{sN}$ ,  $K_{sO}$ , and  $K_I$  are the respective half-saturation and inhibition constants. A similar equation can be written for all the species (or group of species) present in the system. Each will have one or several specific substrates, specific kinetic constants, and thus a specific growth rate. The overall rate of biomass accumulation is the sum for all the different species (designated by the indices  $i$ ) of the growth rate minus death and lyses ( $d$  term), the predation by other species and the wash-out via the recycle liquid purge. This is expressed in Eq. 8.

$$\begin{aligned} \text{Rate of biomass accumulation} = \\ \sum_i ((\mu_i - d_i) \times X_i - \text{Predation}_i - \text{Wash out}_i) \end{aligned} \quad (8)$$

Equations 6-8 are highly simplified since they do not take local heterogeneities into account. Still they define a number of parameters that are impossible to determine. A possible solution is to split the process culture into large classes of organisms, such as primary degraders, secondary degraders, predators, etc. and use lumped kinetic parameters. This is an area of current research.

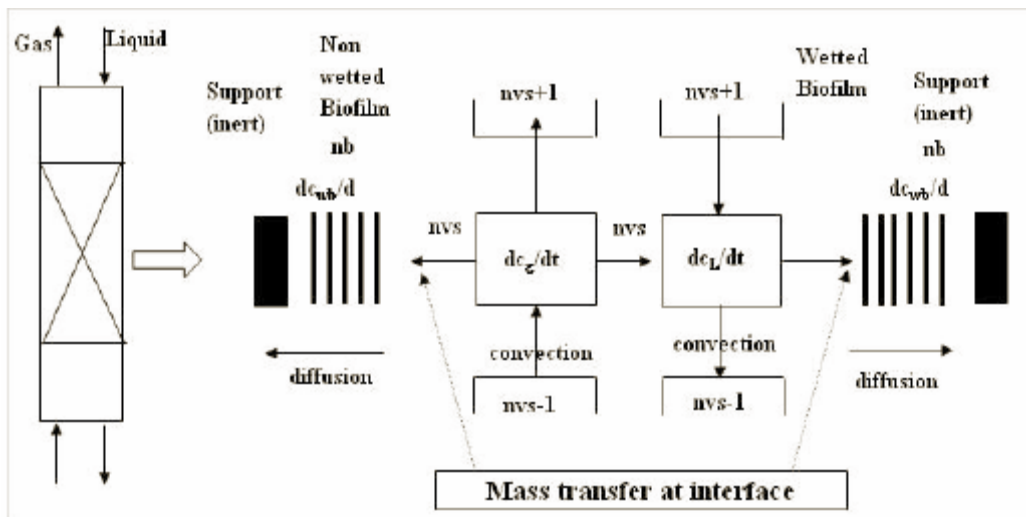
Even so, Esq.'s 6-8 reflects the act that the pollutant elimination and the observed biomass growth are interrelated in a complex manner. The equations further allow development of biomass control strategies for bio trickling filters.

### 3.3. Mathematical modeling of a Bio filter

#### 3.3.1. MODEL DEVELOPMENT

##### Model Concept

The model attempts to make an exact representation of the processes occurring in the bio trickling filter. This considers three phases in the reaction gas, liquid, and bio films, with gas and liquid flowing counter-currently (fig.1). The pollutant ( $H_2S$ ) is removed by the process culture immobilized on the packing of the bio trickling filter. For  $H_2S$  present in the gas phase to be degraded, it has to be transferred to the bio film. However, the bio film on the packing material is not completely wetted by the trickling liquid. Therefore, some of the pollutant will transfer directly from the gas phase to the biofilm without passing through the liquid. While some will be transferred to the liquid first and then to the bio film. In the bio film, diffusion and biodegradation occurs.



**Fig 13: Schematic of the model structure with wetted and non-wetted bio films.**

## Model Assumptions:

The model depicted schematically in Figure 13 embodies the following assumptions.

1. The packing material is completely covered by the bio film, which has a uniform thickness.
2. The bio film is not fully wetted by the liquid, so both wetted and non-wetted bio film are included. This is consistent with visual observation of non-wetted packing during bio trickling filter operation, and with the application of correlations such as the one developed by Onda. *et al.* that indicates significant fraction of the packing is not wetted.
3. Wetted bio film remains wetted and non-wetted bio film remains non-wetted i.e. dynamic changes in wetting are not considered.
4. Adsorption of pollutant onto the support is neglected.
5. For finite differentiation, each subdivision shown in Figure 13 is ideally mixed.
6. The flow in the axial direction is by plug flow. There is no radial velocity gradient or axial dispersion. This can be justified by the high gas velocity in the bio trickling filter systems considered, and that peclet numbers in bio trickling filters are usually large(>10), indicating a near plug-flow behavior.
7. The mass flux at the gas-liquid, gas-bio film, and liquid-bio film interfaces can be expressed by mass transfer coefficients ( $k_{g1}$ ,  $k_{g2}$ , and  $k_L$ )
8. The mass transfer coefficients from gas to liquid ( $k_{g1}$ ) and from gas to non-wetted bio film ( $k_{g2}$ ) have the same value.
9. Consistent with the film theory, gas-liquid, liquid-bio film, and gas-bio film interfaces are at equilibrium.
10. The diffusion in the bio film is described by Fick's Law.
11. The biodegradation kinetics in the bio film are described by a Michaelis-Menten relationship, with  $H_2S$  as only rate-limiting substrate. The  $H_2S$  is used as an energy source, and it is assumed that the carbon source ( $CO_2$ ) is not rate-limiting. Further the use of Michaelis-Menten Kinetics rather than Monod Kinetics, is justified by the essentially no growth situation of the process culture bio trickling filter. The bio kinetic constant are the same for wetted and non-wetted bio films.
12. There is no reaction in the liquid phase. This can be justified since only a negligible amount of biomass is present in the recycle liquid.

13. The effect of pH is neglected. This can be easily changed, but is a reasonable assumption since all experiments were conducted at the same pH. Consequently the acid/base reaction of H<sub>2</sub>S is neglected, and sulfur species are lumped as H<sub>2</sub>S in the Kinetic relationships.

### 3.3.2. Model Equations:

The model equations were derived from the assumptions and the model structure. The main mass balances in each phase are described by the following equations, where j refers to the vertical segment along the height of the bio trickling filter, numbered from bottom of the reactor, and i refers to the segment depth in the bio film numbered from the interface.

*Gas Phase:*

$$V_g \frac{dC_g[j]}{dt} = F_g(C_g[j-1] - C_g[j]) - k_{g1}A_w(C_g[j] - C_{gi1}[j]) - k_{g2}A_{nw}(C_g[j] - C_{gi2}[j]) \quad (1)$$

*Liquid phase:*

$$V_L \frac{dC_L[j]}{dt} = F_L(C_L[j+1] - C_L[j]) - k_{g1}A_w(C_g[j] - C_{gi1}[j]) - k_{g2}A_w(C_L[j] - C_{Li2}[j]) \quad (2)$$

The mass balance for the most wetted filter is expressed by equation 3, except for the last layers which bear boundary constraints. The equation for the first bio film layer near the interface takes the form of equation 4, while that of the last layer before the substrate is represented by equation 5. In a similar manner pollutant balances for the non-wetted bio film segments described by equation 6-8

*Wetted Biofilm Phase:*

$$\frac{dC_{wb}[j]}{dt} = D/(FT)^2 (C_{wb}[i-1,j] - 2C_{wb}[i,j] + C_{wb}[i+1,j] - R_{wb}[i,j]) \quad (3)$$

$$\frac{dC_{wb}[1,j]}{dt} = D/(FT)^2 (C_L[j] - 2C_{wb}[1,j] + C_{wb}[2,j] - R_{wb}[1,j]) \quad (4)$$

$$\frac{dC_{wb}[N,j]}{dt} = D/(FT)^2 (C_{wb}[N-1,j] - C_{wb}[N,j] - R_{wb}[N,j]) \quad (5)$$

*Non-wetted biofilm segments:*

$$\frac{dC_{nwb}[i,j]}{dt} = D/(FT)^2 (C_{nwb}[i-1,j] - 2C_{nwb}[i,j] + C_{nwb}[i+1,j] - R_{nwb}[i,j]) \quad (6)$$

$$\frac{dC_{nwb}[1,j]}{dt} = D/(FT)^2 (C_g[j]/H - 2C_{nwb}[1,j] + C_{nwb}[2,j] - R_{nwb}[1,j]) \quad (7)$$

$$\frac{dC_{nwb}[N,j]}{dt} = D/(FT)^2 (C_{nwb}[N-1,j] - C_{nwb}[N,j] - R_{nwb}[N,j]) \quad (8)$$

**Reaction rates:**

*For Wetted biofilm:*

$$R_{wb}[i,j] = \frac{R_{max} C_{wb}[i,j]}{K_s + C_{wb}[i,j]}$$

*For Non-Wetted Biofilm*

$$R_{nwb}[i,j] = \frac{R_{max} C_{nwb}[i,j]}{K_s + C_{nwb}[i,j]}$$

**Table 5: summary of main parameter values for main simulation**

Symbol	Parameter	Numerical Value	Methodfor determination/reference
$k_g$	Gas-liquid mass transfer co-efficient	1,215( $m\ h^{-1}$ )	Onda correlation[9].
$k_L$	Liquid-biofilm mass transfer coefficient	109( $m\ h^{-1}$ )	Onda correlation[9].
FT	Biofilm Thickness	23 $\mu m$	Calculation based on biomass and packing area
$R_m$	Maximum Reaction Rate	58,400 ( $g\ m^{-3}\ h^{-1}$ )	Experimental fitting of $H_2S$ decrease at high concentration
$K_s$	Michaleis-Menten constant	0.0279( $g\ m^{-3}$ )	Experimental fitting of $H_2S$ decrease at low concentration
H	Henry's Constant of $H_2S$	0.387	Perry's Handbook.[10]
D	$H_2S$ diffusion coefficient	5.796e-6( $m^2\ h^{-1}$ )	Perry's Handbook.[10]
A	Specific Interfacial area	600 $m^2\ m^{-3}$	Packing Manufacturer
$V_L$	Dynamic Hold up	0.00001 x liquid flow( $m^3\ h^{-1}$ ) + 0.0000008( $m^3$ per cube of foam.	Experimental Determination with clean foam.
Nb	Number of segments in biofilm	10	Determined by study of sensitivity to nb.
Nvs	Number of vertical segments in the biotrickling filter	10	Determined by study of sensitivity to nvs.



Equations (1-8) comprise a set of coupled ordinary differential equations that describe the simultaneous mass transfer and metabolic reactions. The numerical evaluation is performed using MATLAB 6.0

## RESULTS

Solution of this model requires parameter values. Parameters required to solve this model are obtained from previous works of Deshusses. M .A (2003). For validating the model, the experimental data of Deshusses .M.A (2003) are used. The concentration profile as obtained in the figure

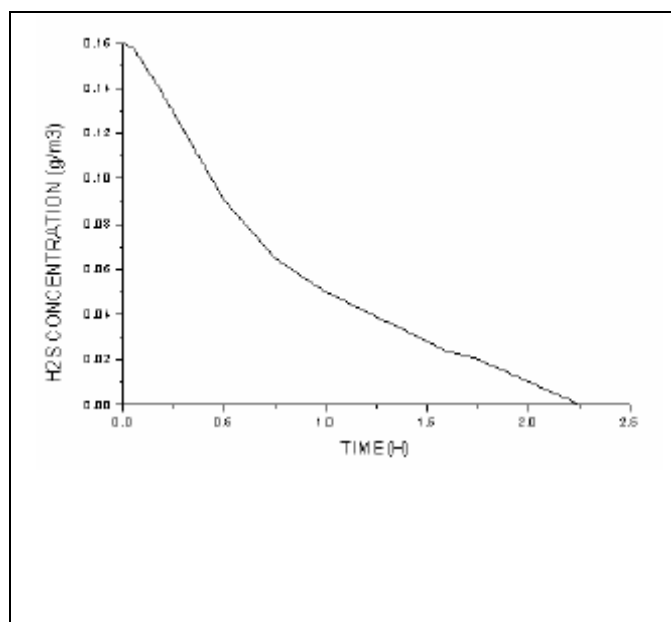


Fig 14

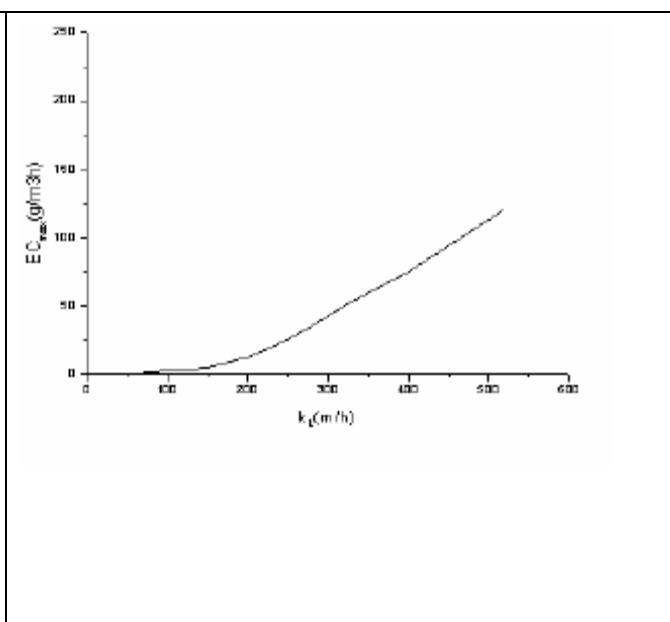


Fig 15

### 3.4. Mass balance of Off-gas coming from refineries (IOCL Haldia):

Basis: 60 metric tons of sulphur produced per day

Therefore amount of H<sub>2</sub>S consumed = 60,000 / 34 k-mole day<sup>-1</sup>

$$= 1875 \text{ k-mole day}^{-1}$$

Volume of H<sub>2</sub>S consumed =  $nRT / P$

$$= 1875000 \times .0821 \times 423 / 1$$

$$= 65115.56 \text{ m}^3 \text{ day}^{-1}$$

$$= 2713.14 \text{ m}^3 \text{ hr}^{-1}$$

Pressure = 1 atm

Temperature = 150°C

H<sub>2</sub>S concentration = 0.3%

Therefore, gas rate = 904382.8125 m<sup>3</sup> hr<sup>-1</sup>

Average Height of Bio filter = 1.5 m

Volume = 9450 m<sup>3</sup>

$$A = Q / V$$

$$= Q (\text{EBRT} / (h \times 60))$$

$$= 904382.8125 (3 / (1.5 \times 60))$$

$$= 315.0 \text{ m}^2$$

Where A= cross sectional area or footprint ( m<sup>2</sup>), Q= volumetric flow rate(m<sup>3</sup>/hr), v=surface loading rate or face velocity(m/hr), h=filter bed height(m) and EBRT=Empty bed resistance time in minutes.

$$\text{EC} = (C_{\text{in}} - C_{\text{out}}) (Q/v)$$

$$= C_{\text{in}} (\text{RE}) (Q/v)$$

$$= \Delta C (60/\text{EBRT})$$

$$= (979.03-9.79) (60 / 3)$$

$$= 19384.8$$

Where EC= elimination capacity (g/m<sup>3</sup>.h), C<sub>in</sub> = inlet concentration(gm/m<sup>3</sup>) ,C<sub>out</sub> = outlet concentration(gm/m<sup>3</sup>) ,v= media volume(m<sup>3</sup>) , RE=Removal efficiency(Δ%), C = Concentration difference=C<sub>in</sub>-C<sub>out</sub>

$$\begin{aligned} L &= C_{in} (Q/v) \\ &= (C_{in} \times 60) / EBRT \\ &= (979.03 \times 60) / 3 \\ &= 19580.6 \end{aligned}$$

Pollutant loading= L (gm/m<sup>3</sup>.h)

$$\begin{aligned} RE\% &= EC / L \\ &= 19384.8 / 19580.6 \\ &= 99.0 \% \end{aligned}$$



# CHAPTER 4

## Design of a Hydrogen sulfide Scrubber

#### 4.0.Design of Hydrogen Sulphide scrubber:

##### 4.1. Data and Assumptions:

1. Gas Rate	= 60 MT of sulphur produced everyday
Therefore amount of H <sub>2</sub> S produced	= 60000/ 34 k mol/ day
Volume of H <sub>2</sub> S consumed	= 1875 k mol /day
Pressure	= 1atm
Temperature	= 150°C
	= $n RT / P$
	= 2713.14 m <sup>3</sup> / hr
Therefore Gas rate	= 904382.8125 m <sup>3</sup> /min
	= 15073 m <sup>3</sup> / min
2. H <sub>2</sub> S concentration (entering stream)	= 0.3 %
3. Recovery of H <sub>2</sub> S	= 96%
4. Average mol.wt of entering gas	= 29.4
5. Packings used staggered wood grid packings	= 85.8%
Free cross sectional area	= 44.9 m <sup>2</sup> / m <sup>3</sup>
6. Solvent rate	= 3280 kg /hrm <sup>2</sup>
Density	= 1122 kg /m <sup>3</sup>
7. Mass transfer co efficient (Kg)	= $0.003G^{0.8}$
8. Pressure Drop in packings $\Delta h_w / z$	= $0.11 \times 10^{-7} G^{1.8}$

Where G = gas mass velocity,  $\Delta h_w$  = cm of water / meter height, Z = packed height  
 Q = Vol.flow rate of solvent m<sup>3</sup> / hr, p=liquid discharge pressure = 2.45 kg / cm<sup>2</sup>

##### 9. Power required for pumping

$$P_L = Q [0.0011 Z + p + 0.1 X]$$

$$0.1 X = \text{Losses in pumping system}$$

$$X = (0.0011 Z + p)$$

##### 10. Efficiency

$$\text{Pump} = 65\%$$

$$\text{Blower} = 55\%$$

11. Equation Relation  $\rightarrow y = 0.35 x$

$y$  = mole fraction  $H_2S$  in stackges

$x$  = mole fraction  $H_2S$  in solvent

12. for calculation of packed volume of tower

$$V = N / K_G \times a(\Delta p)_{ln}$$

$N$  = No. of moles of  $H_2S$  absorbed

$K_G$  = Mass transfer co-efficient  $Kg \text{ mol} / \text{hr m}^2 \text{ atm}$

$(\Delta p)_{ln}$  = Log mean partial pressure of solute at inlet and outlet

Assuming Ideal gas:

$n$ - no of moles of stack gas per minute

$$= PV / RT$$

$$= 434.026 \text{ k mol / min}$$

$$= 765622.621 \text{ kg / hr}$$

$H_2S$  concentration:

Entering Concentration = 0.3%  $n$

$$Y_1 = 0.3 / 99.7$$

$$= 0.003009$$

$$Y_2 = 0.04 Y_1$$

$$= 0.00012$$

$$y_1 = Y_1 / 1 + Y_1$$

$$= 0.003$$

Similarly  $y_2 = 0.00012$

$$P_1 = P T. y_1$$

$$= 0.003 \text{ atm}$$

Similarly  $P_2 = 0.00012 \text{ atm}$

$$(\Delta P)_{ln} = 8.947 \times 10^{-4} \text{ atm}$$

$H_2S$  absorbed:

$$\text{Moles of } H_2S \text{ entering} = 2604.59 \times 0.3 / 100 \text{ k mol / hr}$$

$$\text{Moles of } H_2S \text{ out} = 26041.59 \times 0.00012 \text{ kg mole / hr}$$

$$\text{Moles of } H_2S \text{ absorbed} = 74.995 \text{ kg mol / hr}$$

Solvent Used:

$$\text{Let Average Wt (molecular) of the used solvent} = 19.65$$

Calculation of minimum solvent  $(L_M)_{\min}$ :

$$\text{Equilibrium Relation is } y=0.35x$$

$$\text{I.E. } Y / 1+Y = 0.35 \times X / 1+X$$

$$\text{With } y = Y_1 = 0.003009$$

$$X = 0.00864$$

This refers to equilibrium liquor composition with solvent rate being the minimum

$$\begin{aligned} G_M &= 26041.56 \times 0.997 \\ &= 25963.43532 \text{ kg mol / hr} \end{aligned}$$

Assuming solvent to be  $H_2S$  free while entering,

$$X_2 = 0$$

$$\text{Therefore } G_M (Y_1 - Y_2) = (L_M)_{\min} X_1$$

$$\text{Therefore } (L_M)_{\min} = 170591.94 \text{ kg / hr}$$

In order to avoid excess height for packed absorber, solvent rate has to be more than minimum with 20% over the minimum,

$$\begin{aligned} L_M &= 1.20(L_M)_{\min} \\ &= 204710.33 \text{ kg / hr} \end{aligned}$$

$$\text{Therefore for the first trial} = 200000 \text{ kg / hr}$$

**1<sup>st</sup> trial:**

$$\text{Solvent rate} = 200000 \text{ kg / hr}$$

$$\text{Volumetric flow rate} = 178.253 \text{ m}^3 / \text{hr}$$

$$\text{Liquid mass velocity} = 3280 \text{ kg / hr. m}^2$$

$$\text{Cross. Sec area of absorber} = 60.976 \text{ m}^2$$

$$\text{Gas mass velocity} = 12556.211 \text{ kg / hr m}^2$$

$$\text{Mass transfer co-efficient} = K_G$$

$$= 5.704 \text{ kg mol / m}^2 \text{ atm}$$

$$\text{Packed volume} = N / K_G \cdot a \cdot (\Delta p) h_w$$

$$= 327.266 \text{ m}^3$$

$$\begin{aligned}
 \text{Packet height} &= V/a.t \\
 &= 327.266 / 60.976 \\
 &= 5.367 \text{ m} \\
 \text{Pressure drop} &= \Delta h_w / Z \\
 &= 0.11 \times 10^{-7} G^{1.8} \\
 &= 0.2626 \text{ cm water / metre} \\
 \text{Total drop} &= \Delta P_G \\
 &= (\Delta h_w \times Z) \text{ cm water} \\
 &= 1.4095 \times 10^{-3} \text{ Kg / cm}^2 \\
 \text{Power required for blowing} &= 1.2747 \times 10^9 \text{ kg cm /hr} \\
 \text{55\% efficient blower:} \\
 \text{Actual power required} &= P_G \\
 &= 1.2747 \times 10^9 / 0.55 \\
 &= 2.3177 \times 10^9 \text{ kg cm / hr} \\
 \text{Power required for pumping solvent} &= P_L \\
 &= Q [0.0011 Z + p + 0.1X] \\
 X &= 0.0011 \times 5.367 + 2.45 \\
 &= 3.04037 \\
 P_L &= 5.9615 \times 10^8 \\
 \text{65\% efficient pump:} \\
 \text{Power required} &= P_L / 0.65 \\
 &= 1.834 \times 10^8 \\
 \text{Total Power required} &= P_G + P_L \\
 &= 2.43 \times 10^9 \text{ kg cm /hr}
 \end{aligned}$$

## 2<sup>Nd</sup> trial:

$$\begin{aligned}
 \text{Solvent rate} &= 300000 \text{ kg /hr} \\
 \text{Volumetric flow rate} &= 267.38 \text{ m}^3 \text{ /hr} \\
 \text{Liquid mass velocity} &= 3280 \text{ kg / hr. m}^2 \\
 \text{Cross. Sec area of absorber} &= 91.46 \text{ m}^2 \\
 \text{Gas mass velocity} &= 8370.81 \text{ kg / hr m}^2
 \end{aligned}$$



Mass transfer co-efficient	$= K_G$ $= 4.124 \text{ kg mol} / \text{m}^2 \text{ atm}$
Packed volume	$= N / K_G \cdot a \cdot (\Delta p) h_w$ $= 452.66 \text{ m}^3$
Packet height	$= V/a \cdot t$ $= 4.9493 \text{ m}$
Pressure drop	$= \Delta h_w / Z$ $= 0.11 \times 10^{-7} G^{1.8}$ $= 0.1266 \text{ cm water} / \text{metre}$
Total drop	$= \Delta P_G$ $= (\Delta h_w \times Z) \text{ cm water}$ $= 6.265 \times 10^{-4} \text{ Kg} / \text{cm}^2$
Power required for blowing	$= 5.666 \times 10^8 \text{ kg cm} / \text{hr}$
55% efficient blower:	
Actual power required	$= P_G$ $= 5.666 \times 10^8 / 0.55$ $= 1.0302 \times 10^9 \text{ kg cm} / \text{hr}$
Power required for pumping solvent	$= P_L$ $= Q [0.0011 Z + p + 0.1X]$
X	$= 0.0011 \times 494.93 + 2.45$ $= 2.994$
$P_L$	$= 8.80714 \times 10^8$
65% efficient pump:	
Power required	$= P_L / 0.65$ $= 1.355 \times 10^9$
Total Power required	$= P_G + P_L$ $= 2.385 \times 10^9 \text{ kg cm} / \text{hr}$

**3<sup>Rd</sup> trail:**

Solvent rate	= 400000 kg /hr
Volumetric flow rate	= 365.51 m <sup>3</sup> /hr
Liquid mass velocity	= 3280 kg / hr. m <sup>2</sup>
Cross. Sec area of absorber	= 121.95 m <sup>2</sup>
Gas mass velocity	= 6278.11 kg / hr m <sup>2</sup>
Mass transfer co-efficient	= K <sub>G</sub>
	= 3.2763 kg mol / m <sup>2</sup> atm
Packed volume	= N / K <sub>G</sub> .a.(Δp)h <sub>w</sub>
	= 569.80 m <sup>3</sup>
Packet height	= V/a.t
	= 4.672 m
Pressure drop	= Δ h <sub>w</sub> / Z
	= 0.11 × 10 <sup>-7</sup> G <sup>1.8</sup>
	= 0.7542 cm water / metre
Total drop	= ΔP <sub>G</sub>
	= (Δh <sub>w</sub> × Z) cm water
	= 3.523 × 10 <sup>-4</sup> Kg / cm <sup>2</sup>
Power required for blowing	= 3.198 × 10 <sup>8</sup> kg cm /hr
55% efficient blower:	
Actual power required	= P <sub>G</sub>
	= 3.198 × 10 <sup>8</sup> / 0.55
	= 5.792 × 10 <sup>8</sup> kg cm / hr
Power required for pumping solvent	= P <sub>L</sub>
	= Q [0.0011 Z +p+0.1X]
X	= 0.0011 × 467.20 + 2.45
	= 2.964
P <sub>L</sub>	= 1.19 × 10 <sup>9</sup>
65% efficient pump:	
Power required	= P <sub>L</sub> / 0.65

$$\begin{aligned}
 &= 1.834 \times 10^9 \\
 \text{Total Power required} &= P_G + P_L \\
 &= 2.41 \times 10^9 \text{ kg cm /hr}
 \end{aligned}$$

#### 4<sup>th</sup> trial:

$$\begin{aligned}
 \text{Solvent rate} &= 500000 \text{ kg /hr} \\
 \text{Volumetric flow rate} &= 445.633 \text{ m}^3 \text{ /hr} \\
 \text{Liquid mass velocity} &= 3280 \text{ kg / hr. m}^2 \\
 \text{Cross. Sec area of absorber} &= 152.44 \text{ m}^2 \\
 \text{Gas mass velocity} &= 5022.484 \text{ kg / hr m}^2 \\
 \text{Mass transfer co-efficient} &= K_G \\
 &= 2.7401 \text{ kg mol / m}^2 \text{ atm} \\
 \text{Packed volume} &= N / K_G \cdot a \cdot (\Delta p) h_w \\
 &= 681.306 \text{ m}^3 \\
 \text{Packet height} &= V/a \cdot t \\
 &= 4.4693 \text{ m} \\
 \text{Pressure drop} &= \Delta h_w / Z \\
 &= 0.11 \times 10^{-7} G^{1.8} \\
 &= 0.0505 \text{ cm water / metre} \\
 \text{Total drop} &= \Delta P_G \\
 &= (\Delta h_w \times Z) \text{ cm water} \\
 &= 2.257 \times 10^{-4} \text{ Kg / cm}^2 \\
 \text{Power required for blowing} &= 2.041 \times 10^8 \text{ kg cm /hr}
 \end{aligned}$$

55% efficient blower:

$$\begin{aligned}
 \text{Actual power required} &= P_G \\
 &= 2.041 \times 10^8 / 0.55 \\
 &= 3.7112 \times 10^8 \text{ kg cm / hr}
 \end{aligned}$$

$$\begin{aligned}
 \text{Power required for pumping solvent} &= P_L \\
 &= Q [0.0011 Z + p + 0.1X]
 \end{aligned}$$

$$X = 0.0011 \times 446.93 + 2.45$$

$$= 2.9416$$

$$P_L = 1.442 \times 10^9$$

65% efficient pump:

$$\text{Power required} = P_L / 0.65$$

$$= 2.2184 \times 10^9$$

$$\text{Total Power required} = P_G + P_L$$

$$= 2.59 \times 10^9 \text{ kg cm /hr}$$

**5<sup>th</sup> trail:**

$$\text{Solvent rate} = 600000 \text{ kg /hr}$$

$$\text{Volumetric flow rate} = 534.76 \text{ m}^3 / \text{hr}$$

$$\text{Liquid mass velocity} = 3280 \text{ kg / hr. m}^2$$

$$\text{Cross. Sec area of absorber} = 182.93 \text{ m}^2$$

$$\text{Gas mass velocity} = 4185.040 \text{ kg / hr m}^2$$

$$\text{Mass transfer co-efficient} = K_G$$

$$= 2.3687 \text{ kg mol / m}^2 \text{ atm}$$

$$\text{Packed volume} = N / K_G \cdot a \cdot (\Delta p) h_w$$

$$= 788.13 \text{ m}^3$$

$$\text{Packet height} = V/a \cdot t$$

$$= 4.3084 \text{ m}$$

$$\text{Pressure drop} = \Delta h_w / Z$$

$$= 0.11 \times 10^{-7} G^{1.8}$$

$$= 0.03635 \text{ cm water / metre}$$

$$\text{Total drop} = \Delta P_G$$

$$= (\Delta h_w \times Z) \text{ cm water}$$

$$= 1.566 \times 10^{-4} \text{ Kg / cm}^2$$

$$\text{Power required for blowing} = 1.416 \times 10^8 \text{ kg cm /hr}$$

55% efficient blower:

$$\text{Actual power required} = P_G$$

$$= 1.416 \times 10^8 / 0.55$$

$$= 2.575 \times 10^8 \text{ kg cm / hr}$$

Power required for pumping solvent =  $P_L$

$$= Q [0.0011 Z + p + 0.1X]$$

$$X = 0.0011 \times 430.84 + 2.45$$

$$= 2.924$$

$$P_L = 1.72 \times 10^9$$

65% efficient pump:

$$\text{Power required} = P_L / 0.65$$

$$= 2.646 \times 10^9$$

Total Power required

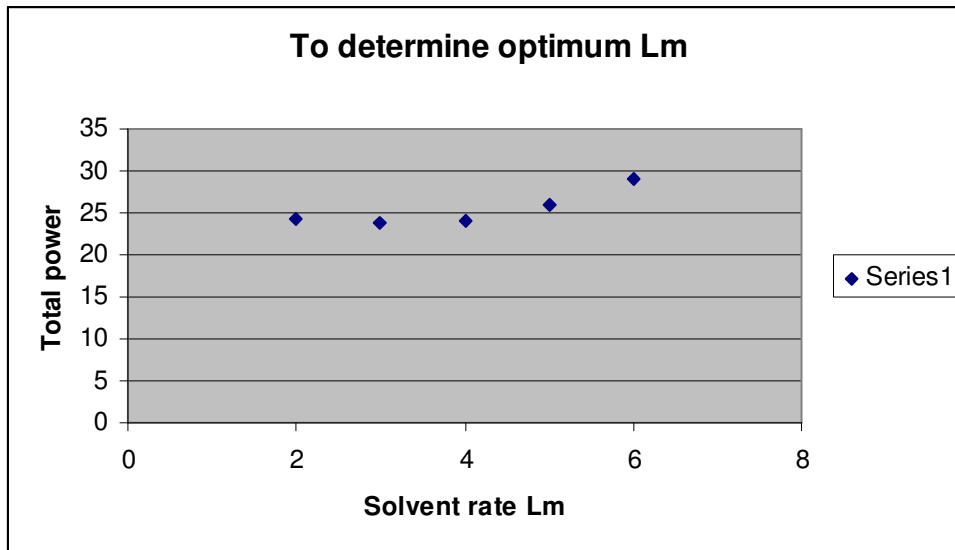
$$= P_G + P_L$$

$$= 2.904 \times 10^9 \text{ kg cm /hr}$$

**Table 6: Results, Summary**

$L_{M1} \text{ kg / hr}$	$P_G \times 10^{-8} \text{ kg cm / hr}$	$P_L \times 10^{-8} \text{ kg cm / hr}$	Total power $\times 10^{-8}$
200000	23.177	18.34	24.31
300000	10.302	13.55	23.85
400000	5.792	18.334	24.1
500000	3.7112	22.184	25.9
600000	2.575	26.46	29.06

**Fig 16: A plot of total Power Vs Solvent rate ( $L_M$ ) is made to determine ( $L_M$ )<sub>min</sub>**



From the Graph,

$$\text{Optimum solvent rate} = 350000 \text{ kg / hr}$$

$$a_t = 350000 / 3280$$

$$= 106.7073 \text{ m}^2$$

$$D = 11.66 \text{ m}$$

$$G = 765622.62 / 106.7073$$

$$= 7174.98 \text{ kg/hr m}^2$$

$$K_G = 0.003(7174.98)^{0.8}$$

$$= 3.646 \text{ kg mol/ hr m}^2\text{atm}$$

$$V = 74.995 / 3.646 \times 44.9 \times 8.947 \times 10^{-4}$$

$$= 512.07 \text{ m}^3$$

$$Z = 512.07 / 106.7073$$

$$= 4.7988$$

$$= 4.8 \text{ m}$$

Therefore Optimum Dimensions of the scrubber would be:

$$\text{Diameter} = 11.66\text{m}$$

$$\text{Height} = 4.8 \text{ m}$$



**Fig 17:Hydro-lance Particulate Scrubber**

**Fig 18: Venturi gas scrubber**

Model LEV ►  
Venturi gas and  
particulate  
scrubber





# CHAPTER 5

Assessment of Operation and Cost



## 5.0. Analysis of Bio filters and assessment of its operation and cost

Biofiltration is an alternative to conventional air pollution control technologies (e.g. thermal oxidizers, scrubbers) for several reasons:

1. Removal efficiencies of greater than 90% have been demonstrated for many of the more common air pollutants; including some of those listed by the Environment Protection Agency as Hazardous air pollutants.
2. Due to lower capital and operating costs, biofiltration may offer economic advantages in applications where the air stream contaminants at relatively low concentrations (up to 1000 ppmv, although this is very contaminant specific and varies widely) and moderate to high flow rates (generally 20000 to 100000 scfm depending on the contaminant).
3. Bio filtration does not require large quantities of energy during operation and produces a relatively low-volume, low toxicity waste stream.

However, it does not typically achieve the very high (e.g., >99%) destruction and removal efficiencies (DREs) or maintain the relative consistency of treatment demonstrated by technologies that do not depend on microorganism. Also, because there is a lack of U.S. experience, bio filtration is not well understood by the regulators

### 5.1. BIOTRICKLING FILTRATION COSTS

#### Capital Costs

Capital costs for bio trickling filters vary a great deal with the size of the bio trickling filter and the material of construction. The size of the bio trickling filter is a function of the air flow, the nature and concentration of the pollutant treated and the required removal efficiency. The presence of corrosive gases (e.g.,  $H_2S$ ) or solvent vapors will influence the choice of the construction material (polyethylene, fiberglass, steel or concrete). The cost of the bio trickling filter will be further influenced by the presence of dust or fine particles, by excessively high or low temperatures, by highly fluctuating pollutant concentrations, etc. Controls and ducting can also be a significant expense. Hence before reactor design and construction, extended problem definition which includes a detailed characterization of the exhaust air is required. Deshusses and Cox have recently proposed a simple relationship to estimate the capital cost of a bio trickling filter based on the volume of the bed. The costs include basic instrumentation (pumps, level switch) but no ducting and are for a simple bio trickling filter

constructed out of inexpensive materials. For expensive materials such as stainless steel, a multiplication factor should be used. The cost obtained by Equation below is a rough estimation, with  $\pm 20\%$  accuracy

$$\text{Bio trickling Filter Capital Cost (\$)} = 13,000 \times \text{Bed Volume}^{0.757}$$

for bed volumes ranging from 5 to 1000 m<sup>3</sup> where the reactor volume is in m<sup>3</sup>. Based on the concentration of the pollutant, the target removal efficiency, and the air flow to be treated, the bed volume can be determined. Equation 9 is then used to estimate the capital cost (Table 5). Of course vendor quotes are more appropriate for a detailed economic evaluation of the final installed costs.

## 5.2. Operating Costs

The determination of the cost of operating a biotrickling filter should include: 1) nutrients and water expenses, 2) electricity for the blower and the recycle pump and miscellaneous electrical equipment, 3) maintenance, 4) costs associated with controlling the growth of biomass, 5) capital costs (amortization). A detailed discussion of each of these costs is beyond the scope of this chapter. The reader is referred to specialized literature and vendor information for more details (15). Even so, in general the following applies:

Nutrients, chemicals (e.g., for pH control) and water are usually a relatively small fraction (10- 30%) of the total operating costs.

Electricity for the blower is often a major fraction of the total operating expenses.

Maintenance of bio trickling filters is minimal. A reasonable estimate is 2-4 hours per week. Most important is to inspect spray nozzles for possible clogging which would result in inadequate bed wetting.

If the bio trickling filter is likely to experience clogging problems, the costs associated with controlling the growth of biomass must be included. These can be significant up to half of the total operating costs. As discussed in the previous section, various approaches exist to control biomass growth. Unfortunately, there is only limited experience at the industrial scale. Careful evaluation of the various options is recommended.

Since biotrickling filter operation is relatively inexpensive; capital cost amortization will be significant compared to other costs. An average fraction, assuming a plant life of 10-20 years is

between 20 and 40% of the total treatment costs. This stresses the importance of proper sizing and careful selection of the materials to minimize the actual capital costs.

A convenient way to compare the operating costs of bio trickling filters is to report the costs per thousands of cubic meter of air treated, i.e., to divide the yearly costs incurred by the volume of air treated in a year (in thousands of  $m^3$ ). Usual values for the operating costs range from \$0.05 to \$1.5 per 1000  $m^3$  of air treated not including capital costs, and from \$0.1 to \$3 per 1000  $m^3$  when capital amortization is included. The wide range reflects the variety of possible applications and sizes of bio trickling filters. Typically, large bio trickling filters tend to be more economical per unit volume of air treated than small bio trickling filters.

### **5.3. Technology assessment, design, and operation**

The first step is to conduct an initial assessment to determine if bio filtration is a desirable alternative. Bio filtration requires special consideration because of the relative lack of experience with this technology for many Off-gases streams. It has only recently become an “off the shelf” technology and generally requires the development of the design criteria on a case basis.

Design, operation and control of a Biofilter are complicated by several characteristics of the technology. First, the microorganisms responsible for degrading the air pollutants often are not well characterized and are difficult to monitor directly. Second, a heterogeneous filter media adds complexity to modeling and controlling Biofilter behavior, third, there are a number of sensitive and interrelated variables, such as moisture content, pH, temperature and influent air stream characteristics and a small change in one variable can affect the behavior of others. For anything but the most routine application, a careful pre-design analysis, including some form of pilot testing, is essential.

The following aspects of bio filtration affect Biofilter design and operation.

**5.3.1. Flow rate and composition variability:** Most off-gases or vent streams that originate in industrial processes or tank filling /venting operations have variable flow rates and compositions. The regulatory community generally expects emission controls to be capable of maintaining adequate treatment performance even though these fluctuations may be significant and/or frequent

In bio filtration however over design is not typically a cost effective solution for addressing peak load concerns and inlet fluctuation may result in variation in performance. As a result selecting bio filtration for applications with fluctuating inlet stream characteristics risk violating emission discharge restrictions. The inability to maintain consistent removal efficiency can be a major limitation unless full support of the regulatory authority and community can be achieved

**5.3.2. Cost:** The cost of Biofilter installation and operation is highly application specific. It depends of flow rate, concentration and sorptive and bio degradability properties of target pollutants; desired removal efficiency; reactor design; type of medium; level of monitoring and control and materials of construction. Capital costs for large bio filter are driven by reactor volume and sophistication of design.

**5.3.3. Enclosed Biofilter:** Fully enclosed Biofilter are generally more expensive per volume of media than partially open beds. They are preferable where reliable VOC and HAT control needs to be maintained even under very hot, cold, wet or dry conditions

Micro biological hazard concern: The presence of micro organism in the Biofilter media has raised concerns over their potential realize into the treated off-gas and resultant exposure to the pathogens of workers on site and individuals off-site. Thus the use of respiratory protection by workers involved in such activities is advisable

#### **5.4. Bio filtration equipment manufactures.**

Several equipment makers and technology companies supply bio-filtration services. Some manufacturing companies and a few engineering and design firms have developed in-house capabilities for Biofilter system testing and design. Many vendors also offer Biofilter engineering and design services, but typically are restricted to offering basic system design. The complexity of the application will probably determine the engineering and design expertise is necessary .For relatively common and simple applications, several vendors offer readily available off-the-shelf systems. The industry is currently undergoing consolidation and some of the smaller companies with relatively weaker capabilities to provide support and disappearing. The capabilities and services are expected to change significantly over the next few years

**5.4.1. Future Developments:** The development of bio filtration has relied on the extensive gained in G8 nations which have provided a significant theoretical and practical knowledge base.

Research groups all over the world especially the countries like Netherlands, Japan, and the U.S. are now developing and improving more innovative applications for bio filtration.

This expansion of applications is de primarily to:

1. Advances in filter bed media and packing design and bed loading technologies and techniques
2. Fundamental microbiological and biochemical research into the mechanisms of microbial degradation and the characterization of microbial cultures suitable for achieving bio filtration;
3. Development of models to predict Biofilter behavior during exposure to mixtures of VOCs , which may reduce the need for extensive pilot and field testing ;
4. Development of alternative vapor-phase biological treatment systems, such as bio scrubbers and bio trickling filters;
5. A growing understanding of the potential economic and environmental advantages of bio filtration within industry and the regulatory community.

## REFERENCES

1. Kyung-Suk Cho Hee Wook Ryu & Nae Yoon Lee :Biological deodorization of hydrogen sulfide using porous lava as a carrier, 2000
2. Sardesai Pushkraj, Seames Waynes : Exploring the gas phase anaerobic bioremoval of Hydrogen Sulfide for coal gasification fuel cell feed streams, 2005
3. J.M. Morgan-Sagastume,A. Noyola: Hydrogen sulfide removal by compost biofiltration: Effect of mixing the filter media on operational factors, 2005
4. Deshusses Marc A H.J. Cox Huub: Bio trickling filters for air pollution control
5. Warren J.Swanson, Raymond C.Loehr, Biofiltration: Fundamentals, Design and Operations Principles,and applications,2004
6. Seongyup Kim,Marc.A.Deshusses, Development and Experimental Validation of a Conceptual Model for Biotrickling Filtration of H<sub>2</sub>S,july 2003
7. Chemical Engineering Progress, An AIChE Publication ,April 2001 Issue
8. Roy G.K : Fundamentals of Heat and Mass transfer
9. [http://www.sciencedirect.com/science/ob=MImg&\\_imagekey=B6TFJ-4G7GG1G-1-W&\\_cdi=5228&\\_user=4966651&\\_orig=search&\\_coverDate=10%2F20%2F2005&\\_sk=998869997&\\_view=c&\\_wchp=dGLbVtb-zSkWz&\\_md5=4af0d52d323218ffd3f1be97d2f54934&\\_ie= sdarticle](http://www.sciencedirect.com/science/ob=MImg&_imagekey=B6TFJ-4G7GG1G-1-W&_cdi=5228&_user=4966651&_orig=search&_coverDate=10%2F20%2F2005&_sk=998869997&_view=c&_wchp=dGLbVtb-zSkWz&_md5=4af0d52d323218ffd3f1be97d2f54934&_ie= sdarticle)

