BIOLOGICAL REACTOR FOR ODOROUS FATTY ACIDS TREATMENT

By

Tam Chung Yuen

A Thesis for the Degree of Master of Philosophy

Department of Civil and Structural Engineering

The Hong Kong Polytechnic University

1999

DECLARATION

I hereby declare that the thesis entitled "Biological Reactor for Odor Treatment" is original and has not been submitted for other degrees or the like in this University or any other institutes. It does not contain any material, partly or wholly, published or written by others, except those references quoted in the text.

Tam Chung Yuen

ACKNOWLEDGMENTS

This thesis is based on the research work carried out in the Department of Civil and Structural Engineering, The Hong Kong Polytechnic University, during the period from March 1997 to February 1999 under the supervision of Dr. H. Chua (Chief Supervisor), Associate Professor of the Department of Civil and Structural Engineering, Dr. X.Z. Li (Co-Supervisor), Associate Professor of the Department of Civil and Structural Engineering and Dr. P.H.F. Yu (Co-Supervisor), Assistant Professor of the Department of Applied Biology and Chemical Technology.

I would like to thank Dr. H. Chua for his guidance, encouragement and valuable suggestions during the course of study.

I am also indebted to Dr. X.Z. Li and Dr. P.H.F. Yu for their supervision.

I also wish to thank Prof. S.T. Yang, Professor of the Department of Chemical Engineering and Dr. Y.L. Huang, Research Fellow of the Department of Chemical Engineering, for their guidance during the period of my attachment study in The Ohio State University.

My appreciation is also extended to all the technical staffs of the Water and Waste Laboratories for their assistance.

Finally, I would like to thank the Hong Kong Polytechnic University Research Committee for the support in this research project and the awarding of a studentship.

Abstract of thesis entitled:

Biological Reactor for Odorous Fatty Acids Treatment

Submitted by Tam Chung Yuen

For the Degree of Master of Philosophy

At The Hong Kong Polytechnic University

March 1999

ABSTRACT

A fibrous bed bioreactor was applied for treatment of odorous gas. The column reactor was packed with spirally wound fibrous sheet material on which a consortium of microorganisms selected from activated sludge was immobilized. The first stage of this work comprised a preliminary study which aimed at investigating the feasibility of the fibrous bed bioreactor for treatment of odorous volatile fatty acids (VFAs). In this part, the microbial kinetics in the selection culture and the performance of fibrous bed bioreactor at increasing mass loadings ranged from 9.7 to 104 $g/m^3/hr$ were studied. VFA removal efficiencies above 90 % were achieved at mass loadings up to 50.3 $g/m^3/hr$. At a mass loading of 104 $g/m^3/hr$, removal efficiency was found to be 87.7 %.

In the second stage of the work, the process was scaled up with design and operational considerations, namely packing medium, process condition and configuration selections. A biochemically inert, synthetic fibrous material was employed as the packing medium. The submerged biofilter configuration failed to operate due to the shear force generated by the gas bubbles, which hindered microbial attachment on the packing medium. The selected trickling biofilter configuration was operated under counter-current flow of gas and liquid streams. Odorous VFAs were introduced into the bioreactor at various inlet concentrations and flow rates. The effect of inlet concentration was studied by increasing the gaseous VFA concentrations at fixed empty bed retention times (EBRTs) of 90, 60, 45 and 30 seconds. While the effect of EBRT was

investigated by increasing the gas superficial velocity or shortening the EBRT, at different inlet VFA concentrations of 0.08, 0.2, 0.4 and 0.7 g/m^3. The bioreactor was effective in treating odorous VFAs at mass loadings up to 32 $g/m^3/hr$, at which VFAs started to accumulate in the recirculation liquid indicating the biofilm was unable to degrade all the VFAs introduced. Although VFAs accumulated in the liquid phase, the removal efficiency remained above 99 %, implying that the biochemical reaction rate, rather than gas-to-liquid mass transfer rate, was the limiting factor of this process. The bioreactor was stable for long term operation; relatively low and steady pressure drop, no clogging and degeneration of the packing medium were observed during the 4-month operation.

TABLE OF CONTENTS

LIST OF FIGURES (PAGE NUMBER)

LIST OF TABLES (PAGE NUMBER)

CHAPTER 1. INTRODUCTION

1.1 Odor Pollution Problem

Odorous gases are emitted in the waste gas stream from such industries as chemical production (Fouhy, 1992; Ottengraf, 1986), municipal sewage treatment (Bohn, 1975), bioprocesses (Ottengraf and Van den Oever, 1983) and food processing (Ottengraf, 1986).

For human, the threshold of smelling and tolerance limit for the odorous components in air are often at very low concentrations (at ppm or even ppb levels). As a consequence, small emissions of malodorous compound often result in odor nuisance. In the populous city of Hong Kong, odor problems are even more significant because the industrial emission sources are often close to residential areas. These problems are attributed to the lack of buffer zones, shorter dispersion distances and less effective dilution of the odorous gases.

Odor nuisance has often led to a significant number of complaints to those responsible for generating the odors and to the relevant authorities. The numbers of complaints has been increasing in the past decades, mainly because of growing environmental consciousness of the public and realizing of their rights to have a cleaner environment (Ottengraf, 1986).

In countries like the Netherlands, Singapore, Japan, Australia, England, Canada and the United States, in order to reduce odor pollution problems, statutory control has been established to restrict the emission of the odorous or toxic

compounds into the environment. Hong Kong is currently in the process of enactment of odor emission legislations. These have opened up a demand for appropriate on-site odor treatment technology for various industries and emission sources.

1.2 Limitations of Existing Odor Treatment Technologies

To meet the emission standards required by the regulations, various odor treatment technologies have been developed and applied. Amongst these are physico-chemical methods, namely masking, activated carbon adsorption, catalytic thermal oxidation, ozonation, wet chemical scrubbing, and biological methods. Recently, biological abatement technologies have attracted an increasing popularity because of low operational and maintenance cost, good stability and reliability, operational simplicity, along with minimal requirement for energy and raw materials as well as minimal secondary waste production (Bohn, 1992; Ottengraf, 1986; van Groenestijn and Hesselink, 1993). In biological treatment systems, odorous compounds are converted by microorganisms to end products such as water, carbon dioxide, inorganic salts and biomass (Leson and Winer, 1991; Swanson and Loehr, 1997).

There are three classes of biological odor treatment systems that have been developed over the years, namely biofilters, bioscrubbers and trickling biofilters. They are distinguished and classified by the behavior of the liquid

phase (continuously moving or stationary in the contact apparatus) and of the microorganisms (freely suspended in the aqueous phase or immobilized on a carrier or packing material) (Ottengraf, 1987). The details of configurations, operation principles and applications of each reactor type will be discussed in the next chapter.

Although high odor removal efficiency can be achieved with the biological systems (Bohn, 1975, 1992; Ottengraf, 1987; Pomeroy, 1982; Tang *et al.*, 1996; Webster *et al.*, 1996; Weckhuysen *et al.*, 1994), several drawbacks are inherent to biological processes and are often encountered. Biofilters suffer from various disadvantages such as difficulty in control and disposal of excess biomass (Lau *et al.*, 1996; Edwards and Nirmalakhandan, 1996; Wittorf *et al.*, 1993). Moreover, the typically large footprint of biofilters limit their use in small and congested areas. While applications of bioscrubber is limited to treat odorous compounds with low dimensionless Henry's constant, plugging problems and high capital and running costs are additional disadvantages (Edwards and Nirmalakhandan, 1996). For trickling biofilters, on the other hand, accumulation of biomass which often leads to clogging problem. Backwashing is a means to remove the excess biomass, nevertheless, the stable performance of the reactor would be disturbed. Furthermore, cyclical thickening and sloughing of the biofilms render an added complication in trickling biofilter operation and control.

1.3 Fibrous Bed Bioreactor

In recent years, a new type of biofilter that can overcome the aforementioned disadvantages has been developed for various bioprocessing purposes (Silva and Yang, 1995: Yang *et al.*, 1992; 1994; 1995; 1996). The bioreactor contains a packed bed of spiral-wound porous fibrous sheet materials with built-in vertical spaces or interstices between adjacent fibrous sheets to allow gas to flow upward relatively freely through the packed bed. The fibrous bed with high porosity (>90%) and high surface area provides good multiphase contacts and an environment ideal for microbial growth and biochemical reactions to take place. In environmental application, the fibrous bed bioreactor has been studied for applications in the treatment of BTEX-contaminated ground water and waste streams (Shim and Yang, 1999).

1.4 Objectives and Design of this Research

The general objective of this study is to develop a novel fibrous bed bioreactor to treat odorous pollutants present in contaminated air streams from the various industries. In addition, two specific objectives are focused. Firstly, to study the feasibility of the fibrous bed bioreactor for odor treatment, and the biofilm growth and odorant degradation kinetics. Secondly, to design the odor

treatment operation, and to study the process performance under different operational conditions. Hence, the work was carried out in two stages.

The first stage comprised a preliminary study aimed at investigating the feasibility of the fibrous bed bioreactor for the treatment of odorous compounds using microorganisms selected from activated sludge. The microbial growth and odorant degradation kinetics in the selection culture and the performance of fibrous bed bioreactor at increasing mass loadings were studied. The works in this stage were evaluated in bench top apparatus.

In the second stage, the process was scaled up with design and operation considerations, such as packing medium, process condition and configuration selections. The bioreactor was operated at two possible configurations, namely submerged biofilter and trickling biofilter. In addition, to obtain reliable operational information on the bioreactor performance under realistic operational conditions, the reactor performance under changing loading conditions was studied. Hence, the effect of inlet odorant concentration and gas empty bed retention time (EBRT) on bioreactor performance were investigated. The pressure drop and the long term process stability of the fibrous bed bioreactor were also studied. The works in this stage were studied by laboratory simulator of odor treatment system.

Volatile fatty acids (VFAs) were chosen as the model compounds. They are malodorous compounds which generate rancid and pungent smell and have low odor thresholds (Williams and Miller, 1992). They are produced from the livestock industry, especially in animal wastes stored under anaerobic

conditions (Tanaka *et al.*, 1992), and are generated from composting facilities as intermediate products in the compost pile (Lau *et al.*, 1996). Additionally, VFAs can enhance offensive odors in the presence of other components, such as sulfur compounds, phenols and indoles (Tanaka *et al.*, 1991)

CHAPTER 2. LITERATURE REVIEW

2.1 Sources of Odor Nuisances

Many industrial and agricultural activities are origins of odor nuisances. Arbitrarily, the sources of odorous emissions can be grouped into two categories: industrial emissions and nuisances due to wastes (LeCloirec *et al.*, 1994).

2.1.1 Industrial Gaseous Emissions

2.1.1.1 Chemical and Petrochemical Industries

Cheremisinoff and Young (1975) listed the principle odorous components found in the gaseous emissions from different chemical and petrochemical industries (Table 2.1), The main odorants are sulfur dioxide, ammonia, hydrogen sulfide and organics such as hydrocarbons and aldehydes.

Table 2.1 Examples of odorous products in chemical and petrochemical industries (Cheremisinoff and Young, 1975).

Industry	Source of Odors	Types of Odor
Refineries	Gas and gas recycling systems	SO_2, H_2S, NH_3, organic hydrocarbon acids, aldehydes, mercaptans
	Catalytic cracking	SO_2, NH_3, aldehydes
	Fluid catalysis	SO_2, NH_3, aldehydes, hydrocarbons
	Boilers	SO_2, NH_3, H_2S, aldehydes, hydrocarbons
	Warehouses	hydrocarbons
Inorganic chemical industry	Fertilizer/phosphate production	NH_3, aldehydes, SO_2
	Phosphoric acid	SO_2, H_2S, aldehydes, and other odorants
	Soda	NH_3
	Nitric and sulfuric acids and lime	NH_3, aldehydes, SO_2
Organic chemical industry	Organic chemistry	Mercaptans, NH_3, hydrocarbons, SO_2, organic acids, and other odorants
	Paints	NH_3, hydrocarbons, SO_2, aldehydes, organic acids, and other odorants
	Plastics	NH_3, hydrocarbons, SO_2, aldehydes, organic acids
	Rubber products	NH_3, hydrocarbons, SO_2, aldehydes, organic acids
	Soaps, detergents	NH_3, hydrocarbons, SO_2, aldehydes, organic acids, and other odorants
	Textiles	NH_3, hydrocarbons, SO_2, aldehydes, organic acids, and other odorants

2.1.1.2 Wood and Paper Industries

In the paper industry, the strongest odors are generated by wood shaving degasification, recycling, drying and pyrolysis of black liquors and eventually lime kiln vents. The emitted odorous compounds include dimethyl diethylsulfur and methyl mercaptan. While formic aldehyde is an important odorous components produced from wood working industries like panels and small logs (LeCloirec *et al.*, 1994). In paper pulps, high concentration of hydrogen sulfide and mercaptans are emitted (Roberts *et al.*, 1971)

2.1.1.3 Food Industries

2.1.1.3.1 Yeast Manufactory

The fermentation process in yeast production implies emission of odorous gas. Numerous types of odorants are present especially alcohols (methanol, ethanol, n-butanol and isobutanol) and ketones (acetone, methyl ethyl ketone, dimethyl ketone) because of the anaerobic operation. In addition, hydrogen sulfide, mercaptans, ammonia, amines as well as organic acids are commonly encountered. (LeCloirec *et al.*, 1994)

2.1.1.3.2 Sugar Production

Several steps in sugar manufacturing are found to be odor causing, namely extraction, pulp drying, carbonation, evaporation of gas, building ventilation and condensation (LeCloirec *et al.*, 1994). Huisman *et al.* (1987) identified 38 products that are responsible for the typically stinks, including furane-type compounds, pyrazines, nitrosamines, polycyclic hydrocarbons, aldehydes, ketones, sulfurized hydrogen, phenols and alcohols.

2.1.2 Odor Nuisances Due To Wastes

2.1.2.1 Wastewater Treatment Plants

Another principal source of odor nuisances are municipal sewage treatment plants and industrial wastewater treatment plants (Shanahan, 1993). Municipal sewage, which are loaded with organic particles and dissolved matter, nitrogen compounds and phosphorus, can lead directly or indirectly to the formation of unpleasant odors by the intermediary reaction or degradation by-products (greases, sludges), following a well-known biological degradation process that is activated in reduction conditions (LeCloirec *et al.*, 1994). Moreover, some industrial discharges contain, from the start extremely volatile compounds used in manufacturing processes. These includes sulfides (Harkness, 1980),

aldehydes, alcohols (Brandl and Stover, 1988), or even ammonia compounds, which can be the sources of odor pollution. In addition to these malodorous compounds, the other main odorous compounds given off by wastewaters basically belong to families of reduced sulfur and nitrogen compounds.

On the other hand, the major malodorous compounds found in wastewater treatment plants are sulfur compounds, including hydrogen sulfide, mercaptans, organic sulfurs and disulfurs, which are formed by reduction of organic sulfurs (amino acids, detergents) (Harkness, 1980).

Nitrogen compounds are another source of olfactive nuisances, including ammonia, amines, indole and scatole. The nitrogen contents in wastewater are mainly from urine, biological protein and amino acid degradation. End products such as methylamine and dimethylamine are present in low concentrations of urine, while ammonia compounds are formed by hydrolysis of organic nitrogen compounds (Harkness, 1980).

Other odorous compounds, such as volatile fatty acids (VFAs), aldehydes, alcohol and ketones are from direct industrial discharges, anaerobic sludge or effluent digestion intermediates, as well as thermic treatment of purification sludges after anaerobic digestion. These compounds are produced by biodegradation of carbohydrates which are first transformed into acids, then into alcohols, aldehydes, and ketones (LeCloirec *et al.*, 1994). The principal compounds responsible for the unpleasant odor in wastewater treatment processes are given in Table 2.2.

Table 2.2 Characteristics of principal compounds responsible for odors in wastewater treatment plants (LeCloirec *et al.*, 1994)

Compound Type	Compound	Molar Mass	Chemical Formula	Odor Characteristics	Odor Threshold (mg/N m^3 air)	Vapor Pressure (atmosphere)	Boiling Temperature (^{0}C, 760 mm Hg)
Sulfurized	Hydrogen sulfide	34.1	H_2S	Rotten egg	0.0001-0.03	20 (25 °C)	.62
	Methylmercaptan	48.1	CH_3SH	Cabbage, garlic	0.0005-0.08	2 (26 °C)	8
	Ethylmercaptan	62.1	C_2H_5SH	Rotting cabbage	0.0001-0.03	0.53 (18 °C)	23
	Dimethylsulfide	62.13	$(CH_3)_2S$	Rotting vegetables	0.0025-0.65	0.53 (18 °C)	37
	Diethylsulfide	90.2	$(C_2H_5)_2S$	Ether	0.0045-0.31	0.05 (18 °C)	92
	Dimethyldisulfide	94.2	$(CH_3)_2S_2$	Putrid	0.003-0.014	0.078 (24 °C)	109
Nitrogenous	Ammoniac	17	NH_3	Very pungent, iritating	0.5-3.7	0.016 (20 °C)	.33
	Methylamine	31.05	CH_3NH_2	Rotting fish	0.021	2 (10 °C)	.7
	Ethylamine	45.08	$C_2H_5NH_2$	Pungent, ammoniacal	0.05-0.83	1 (16.6 °C)	17
	Dimethylamine	45.08	$(CH_3)_2NH$	Rotting fish	0.047-0.16	2 (25 °C)	7
	Indole	117.5	C_8H_6NH	Fecal, nauseating	0.0006	<0.001 (25 °C)	254
	Scatole	131.5	C_9H_8NH	Fecal, nauseating	0.0008-0.10	<0.001 (25 °C)	266
	Cadaverine	102.18	$NH_2(CH_2)_5NH_2$	Rotting meat		<0.001 (25 °C)	178
Acids	Acetic	60.05	CH_3COOH	Vinegar	0.025-6.5	0.001 (25 °C)	118
	Butyric	88.1	C_3H_7COOH	Rancid butter	0.0004-3	0.001 (25 °C)	163.5
	Valeric	102.13	C_4H_9COOH	Sweat, perspiration	0.0008-1.3	0.001 (35 °C)	186.5
Aldehydes & Ketones	Formaldehyde	30.03	HCHO	Acrid, suffocating	0.033-12	1 (-20 °C)	-19.5
	Accaldehyde	40.05	CH_3CHO	Fruit, apple	0.04-1.8	1 (20 °C)	21
	Butyraldehyde	72.1	C_3H_7CHO	Rancid	0.013-15		74.8
	Isovaleraldehyde	86.13	$(CH_3)_2CHCH_2CHO$	Fruit, apple	0.072		92.5
	Acetone	58.08	CH_3COCH_3	Sweet/fruit	1.1-240	0.26 (23 °C)	56.5

2.1.2.2 Composting Plants

Composting is a waste recycling technology for diverting agricultural and food wastes from landfills. It is a controlled biodegradation process that converts solid organic matter into a stable humus-like material to be used as fertilizer or soil conditioner (Lau *et al.*, 1996). Commonly, odors generated from composting plants are gaseous volatile organic compounds. Williams and Miller (1992) reported that the major groups of odorous contaminants are sulfur compounds, ammonia and amine compounds, VFAs, ketones, aldehydes and phenol. Ammonia is emitted in large amounts, and it usually masks the other offensive odorous compounds (Terasawa *et al.*, 1986). Mercaptans, alkyl amines, scatoles, alcohols and aldehydes are usually generated by anaerobic decomposition as a result of a poorly controlled environment of composting. In any case, VFAs are ubiquitously produced as the intermediate products in the compost pile (Lau *et al.*, 1996).

2.2 Odor Treatment Technologies

In order to reduce odor pollution problems, statutory controls have first been established on the emission of the odorous or toxic compounds into the environment in countries like England and Wales (Air Noise Administration Division, Dept. of the Environment, 1980), The United States (Hellwig, 1998) and Canada (Rix, 1998). Other countries, namely Netherlands, Singapore, Japan and Australia also have regulations restricting odorous emissions. To meet the emission standards required by these regulations, various odor treatment technologies including physical, chemical and biological methods have been developed and applied.

2.2.1 Physical and Chemical Methods

2.2.1.1 Masking

Masking agents such as terpenes can be added to discontinuous or small volumes of odorous emissions in order to overcome their environmental nuisance. However, the application of these chemicals cannot eliminate the undesired compounds, which is the main disadvantages of this method. In addition, it becomes dangerous if the masking agent masks the odor of high and toxic concentrations of odorous compounds (Smet *et al.*, 1998). Moreover, when dilution of the masking agent to below its threshold value occurs before

the malodorous compounds have reached their odor threshold value, odor problems can arise at a certain distance from the source (Anderson, 1994).

2.2.1.2 Adsorption

Among the available adsorbents such as silica gel, activated carbon, zeolites, activated alumina and synthetic resins, activated carbon is most often used for odor removal (Figure 2.1). Activated carbon is produced from carbonaceous materials such as coal and nut shells by dehydration and carbonization process, followed by thermal or chemical activation. Physical adsorption, which is principally based on a set of attractive and repulsive electrostatic forces, is maximized by using activated carbon with a high specific surface (750 to 1500 m^2g^{-1}) and a significant portion of its total pore volume in the micropore range (less than 2.5 nm diameter) (Turk *et al.* 1989). However, it is difficult to produce activated carbons with a large proportion of very small pores suited to the removal of the small molecules associated with odor (Shanahan, 1993). Activated carbon is limited to adsorb odorous emission with low humidity since a water film, which formed on the carbon surface in humid environments (over 85 %), would greatly reduce its performance. Other disadvantages of this method include high capital cost and cost of the base material. Furthermore, since a new waste is generated by the treatment, there are additional high costs associated with disposal of this secondary waste.

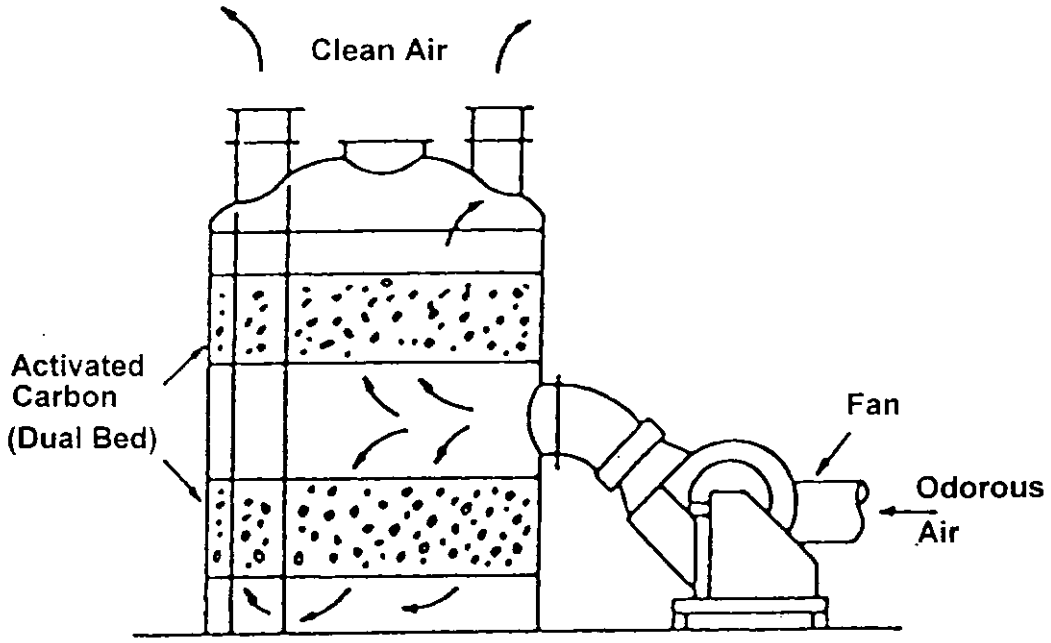

Figure 2.1 Schematic diagram of a dual activated carbon bed (Turk, *et al.*, 1993).

2.2.1.3 Thermal Oxidation

Thermal oxidation is the destruction of odorants by heating the contaminated gas to a high temperature (700 to 1000 °C) with gas residence time of 0.5 to 1 second (Smet *et al.*, 1998). If oxidation is complete, the end products should be carbon dioxide, water, sulfur dioxide and oxides of nitrogen. In the presence of a catalyst, the incineration process can take place at a lower temperature (300 to 450 °C) (Moss, 1980; Smet *et al.*, 1998). Thermal oxidation is a universal method applicable to all odorous compounds since all organic odorants can be oxidized into inorganic products at high temperatures. Besides, high efficiency and stable performance can be achieved. Moreover, there is no secondary disposal problem like the liquid effluents from scrubbers or the spent carbon of adsorption system. Since all the outlet gases from incinerators are hot (or at least warm), formation of the buoyant plume allows good dispersion in the atmosphere (Carleton, 1980).

However, the main disadvantage of this method is the high investment cost. Besides, the catalyst used can be poisoned by the presence of sulfur compounds such as hydrogen sulfide and sulfur dioxide. Additionally, thermal oxidation of reduced sulfur compounds may lead to sulfur dioxide emission, which requires an additional post-treatment to prevent acid rain that damages the environment (Tichy *et al.*, 1998).

2.2.1.4 Chemical Scrubbing

Scrubbing aims to transfer the odorous contaminant from the gas to the liquid phase by intensely contacting the polluted air with a scrubbing liquid. The mass transfer depends on the concentration and air/water partition properties (Henry's constant) of the odorant and the mass transfer resistance of the scrubber system. The most common scrubbing system is the packed scrubber (Figure 2.2) which can be dimensioned according to the data given by Laplanche *et al.* (1994). For waste gases in which particulates and aerosols are present, a venturi scrubber should be installed before the odorant scrubber to prevent clogging (Prokop and Bohn, 1985). The efficiency of scrubbing action can be increased by a large water surface area in the scrubber as well as counter-current operation (Carleton and Valentin, 1980), and also by increasing the water solubility of the odorants, which can be achieved by making the scrubbing water alkaline or oxidizing the odorous compounds into more water soluble forms. However, precipitation occurs in the presence of high carbon dioxide concentration under alkaline conditions, in which carbon dioxide reacts with calcium and magnesium in the scrubbing water to form calcium carbonate and magnesium carbonate, resulting in clogging of the scrubber (Smet *et al.*, 1998). Chlorine dioxide (ClO_2) and potassium permanganate ($KMnO_4$) are commonly used as oxidizing agent in chemical scrubber. Yet, ClO_2 produces toxic chlorine and chlorine dioxide in the outlet gas, while use of $KMnO_4$ results in the formation of MnO_2 precipitates that can also result in clogging of

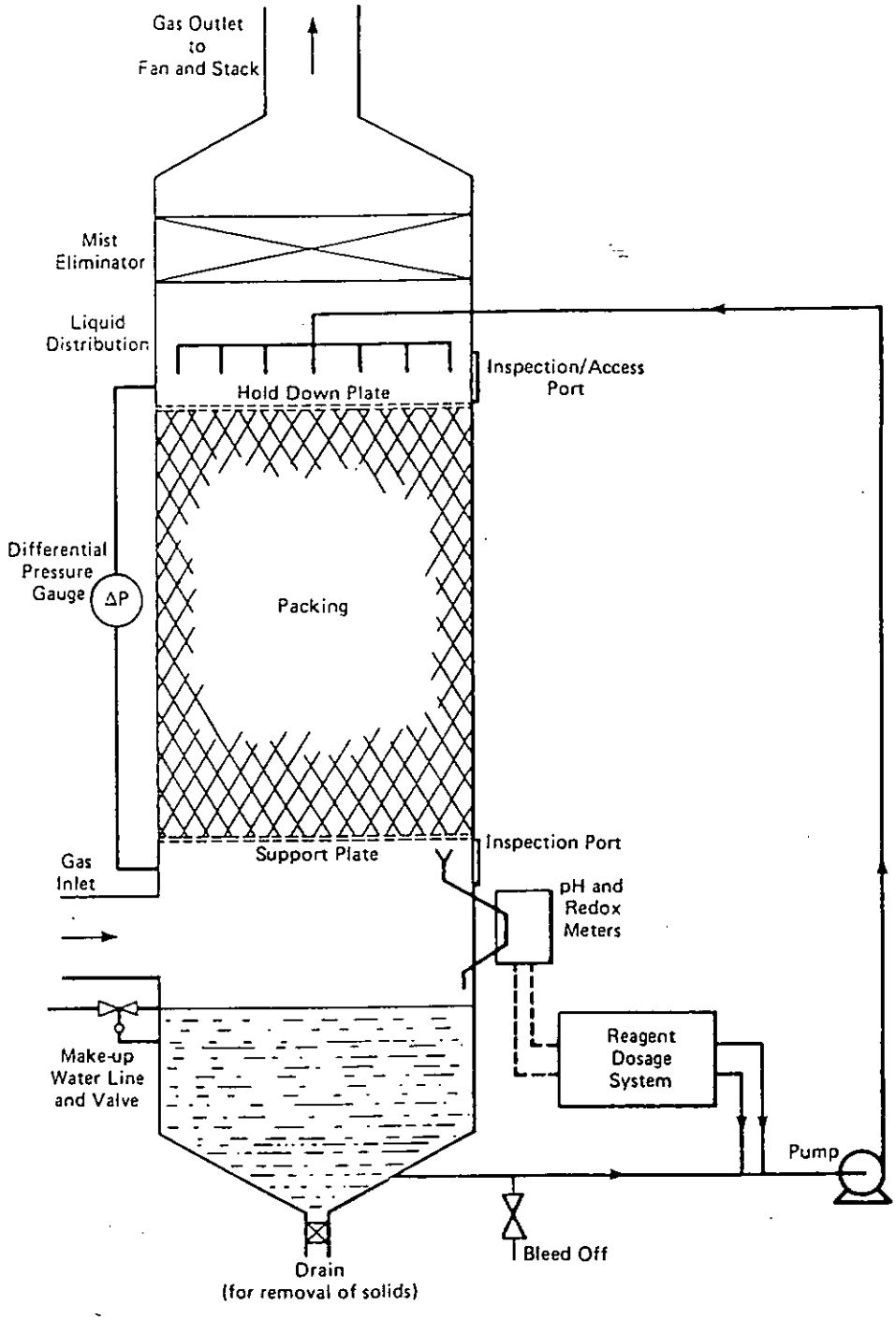

Figure 2.2 Schematic diagram of a packed scrubber (Carleton and Valentin, 1980)

the scrubber (Smet *et al.*, 1998). Deodorization of gases by chemical scrubbing fails if the odorous compounds are water insoluble and difficult to oxidize (Carleton and Valetin, 1980; Ottengraf, 1986). The capital and operation costs as well as labor requirements are higher than for virtually any other method, and the liquid waste generated from the scrubbing process is an additional disadvantage (Shanahan, 1993).

2.2.1.5 Ozonation

Ozone can oxidize waste gases by destructing or modifying the odorous compounds, it gives good performance as it is a powerful oxidizing agent (Figure 2.3). Hwang *et al.* (1994) reported that ozone effectively converted odorous compounds, namely methyl mercaptan to sulfonic acid, while ammonia and trimethylamine were converted to the oxidized product, nitrate and nitromethane respectively. Ozone can also be added into scrubbers as well as carbon adsorption system to enhance their performance (Dorling, 1980; Shanahan, 1993). However, the capital and operating costs of ozonation are high. Ozone itself is a pollutant in the troposphere, it also has harmful effects on the bronchial tubes (Ottengraf, 1986; Shanahan, 1993), and its use is thus undesirable.

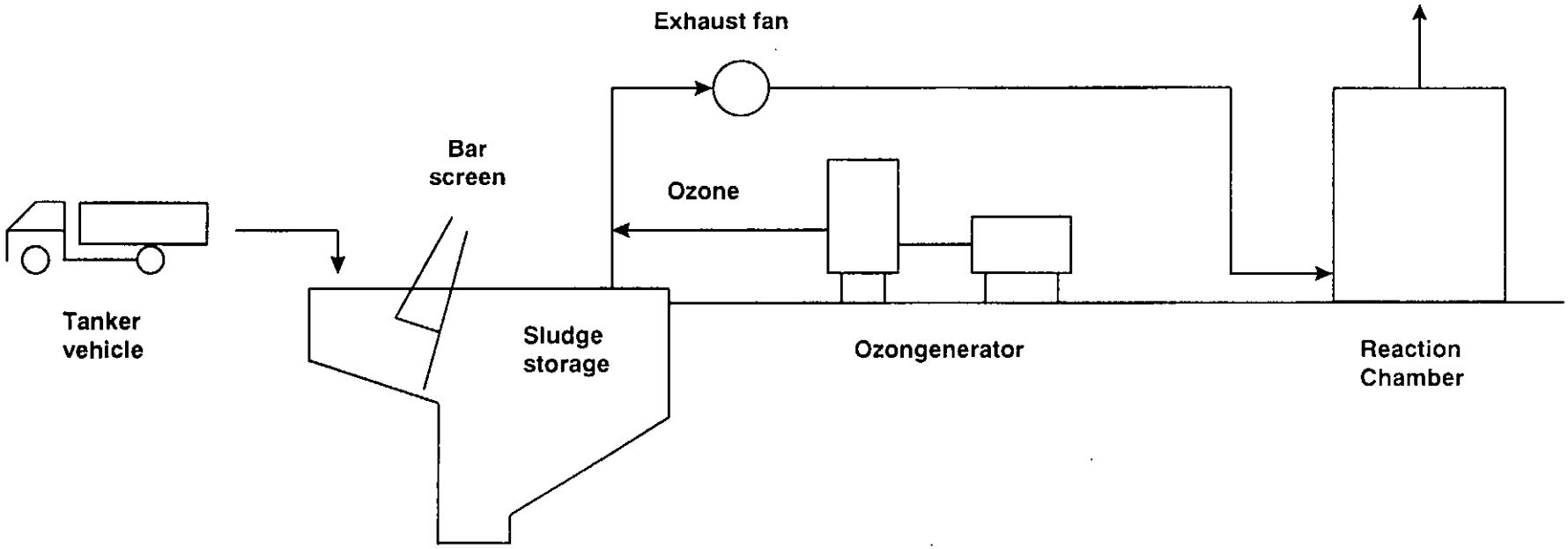

Figure 2.3 Schematic diagram of an ozonation equipment (Eikum and Storhaug, 1986)

2.2.2 Biological Methods

Biological odor treatment technologies have attracted an increasing popularity because of low operational and maintenance cost, good stability and reliability, operational simplicity, along with minimal requirement of energy and raw materials and minimal waste production (Bohn, 1992; Ottengraf, 1986; Van Groenestijn and Hesselink, 1993). In biological treatment systems, odorous compounds are converted by microorganisms, to end products such as water, carbon dioxide, inorganic salts and biomass (Leson and Winer, 1991; Swanson and Loehr, 1997).

There are three groups of biological odor treatment systems that have been developed and applied, namely biofilters, bioscrubbers and trickling biofilters. They can be distinguished and classified (Table 2.3) by the behavior of the liquid phase (continuously moving or stationary in the contact apparatus) and of the microorganisms (freely suspended in the aqueous phase or immobilized on a carrier or packing material) (Ottengraf, 1987).

Table 2.3 Distinctions between biological waste gas purification systems (Ottengraf, 1987)

		Aqueous phase	
		Moving	Stationary
Microbial flora	Dispersed	Bioscrubbers	
	Immobilized	Trickling filters	Biofilters

2.2.2.1 Biofiltration

Biofiltration is the oldest biological method used for the removal of waste gas components. Since the 1920s, biofilters, often in form of soil beds, have been applied to remove odorous compounds such as hydrogen sulfide from wastewater treatment plants (Leson and Winer, 1991). Up to 1980 biofiltration has mainly been used to reduce odor in off-gases (Bohn, 1975). In the 1980s, the field of application was extended to the removal of many other volatile compounds in municipal emissions that are easily biodegraded. Odorous compounds removed by biofilters are primarily volatile organics and reduced sulfur and nitrogen compounds, and are typically degraded either as primary substrates or as co-metabolites (Ottengraf and Van Den Oever, 1983; Swanson and Loehr, 1997; Westmeier and Rehm, 1987).

In a biofilter (Figure 2.4), the odorous gas is forced to rise through a layer of a packing medium of natural origin with a thickness of around 50-100 cm (Ottengraf, 1987), on which microorganisms are attached as a biofilm. Biodegradable odorous compounds are absorbed by the bed material and the biofilm, and subsequently biologically oxidized into water, carbon dioxide and inorganic salts such as nitrates and sulfates. Generally, the packing medium is a mixture of a natural fibrous substance with a large specific area and a coarse fraction (Van Groenestijn and Hesselink, 1993). The first substance is the active fraction that contains most of the microorganisms and nutrients. Peat and compost are broadly used. While the coarse fraction serves as support material,

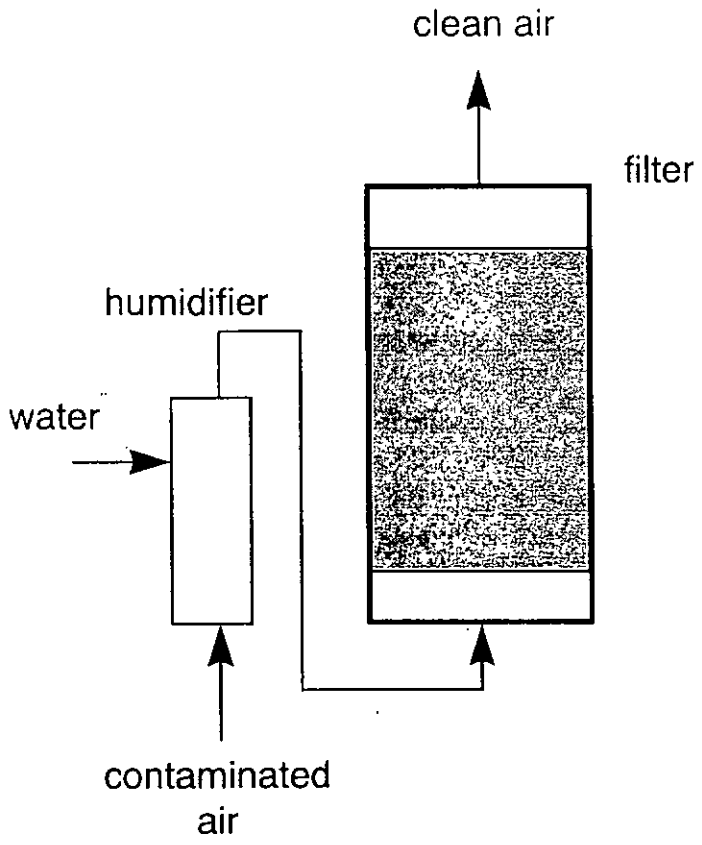

Figure 2.4 Schematic diagram of a biofilter (Edwards and Nirmalakhandan, 1996)

which increases reactive surface and durability, also prevents high pressure drops in the biofilter, it may consist of inert materials like polystyrene or lava particles, or partially active natural material like wood bark, wood chips and heather (Leson and Winer, 1991; Ottengraf and Diks, 1992).

Biofiltration has been applied on a full scale for control of odorous emissions from many industries. Fouhy (1992) listed the compounds which have been treated by biofilters together with their source (Table 2.4). While Leson and Winer (1991) presented a list of successful biofilter applications in Europe (Table 2.5). In addition to control of odorous and volatile organic compounds, in the recent past, Kleinheinz and Bagley (1998) reported that biofiltration can reduce toxicity and mutagenicity associated with volatile organics.

Although high odor removal efficiency can be achieved with biofilters, soil and compost as the biological attachment media have several drawbacks due to their low porosity and high compactness, causing high resistance and channeling flow. These biofilters are also subject to clogging and dehumidification over long-term operation (Leson and Winer, 1991; Ottengraf, 1986). Moreover, control of reaction condition and disposal of excess biomass in the biofilter is difficult (Lau *et al.*, 1996; Edwards and Nirmalakhandan, 1996; Wittorf *et al.*, 1993). Furthermore, the large footprint of conventional biofilters limit their use in small and crowded city areas.

Table 2.4 Biofilter: where they're used (Fouhy, 1992)

INDUSTRY	ODORS	ALIPHATICS	AROMATICS	OXYGEN-CONTAINING ORGANICS	SULFUR-CONTAINING ORGANICS	NITROGEN CONTAINING ORGANICS	HALO-GENATED ORGANICS	H_2S	NH_3	AROMATICS OILS
Used oil	×	×	×		×		×			
Aroma extraction	×									×
Beer yeast drying	×			×		×				
Dump gas removal	×			×	×			×		
Fat processing	×			×	×	×	×	×		
Foundries	×			×	×				×	
Sewage (municipal)	×	×	×	×	×	×	×	×	×	
Sewage (industrial)	×	×	×	×	×	×	×	×	×	×
Composing	×	×		×	×					
Plastics processing	×	×	×	×		×				×
Adhesives	×			×						
Oils and greases	×	×	×		×	×		×	?	
Polyester					×	×				×
Friction linings	×			×	×	×		×	×	×
Rendering	×			×	×					
Tank farms	×	×	×							

Table 2.5 Examples of successful biofilter applications in Europe (Leson and Winer, 1991)

Adhesive production	Coffee roasting	Industrial wastewater treatment plants
Coating operations	Coca roasting	Residential wastewater treatment plants
Chemical manufacturing	Fish frying	Composting facilities
Chemical storage	Fish rendering	Landfill gas extraction
Film costing	Flavors and fragrances	
Investment foundries	Pet food manufacturing	
Iron foundries	Slaughter houses	
Print shops	Tobacco processing	
Waste oil recycling		

2.2.2.2 Bioscrubbers

A bioscrubber consists of two interconnected reactors (Figure 2.5) The first reactor is the contacting unit, where the liquid phase flow countercurrently with the waste gas for mass transfer of the odorous compounds from the gas phase to the liquid phase. The second reactor is the biodegradation unit (usually with activated sludge), where the contaminants are under biodegradation (Edwards and Nirmalakhandan, 1996; Ottengraf, 1986). The liquid phase is continuously recirculated over the two units. In contrast to biofilters, the liquid phase in bioscrubbers is mobile, which allows a better control of the reaction conditions. Nutrient, buffers and titrants can be added and the liquid can be refreshed and discharged in order to remove undesired products. In addition, temperature, pH and ionic strength can be monitored and controlled more easily (Van Groenestijn and Hesselink, 1993).

Bioscrubbers have been successfully employed in several branches of industry, for treating waste gases from enameling ovens, containing alcohols, glycols, ketones, glycolether, aromats and resins. Waste gases from incinerators, foundries containing amines, phenols, formaldehyde, ammonia have been deodorized (Ottengraf, 1987).

A drawback compared to biofilters is the lower specific gas/liquid surface area. This restricts the field of bioscrubber application to compounds with dimensionless Henry's constant lower than 5-10 or even lower than 0.01 if high spray columns and large water flows are not applied (Van Groenestijn and

Hesselink, 1993). Besides, plugging usually occurs in the contacting unit due to excess biomass. Moreover, the capital and running costs are higher than biofilter (Edwards and Nirmalakhandan, 1996).

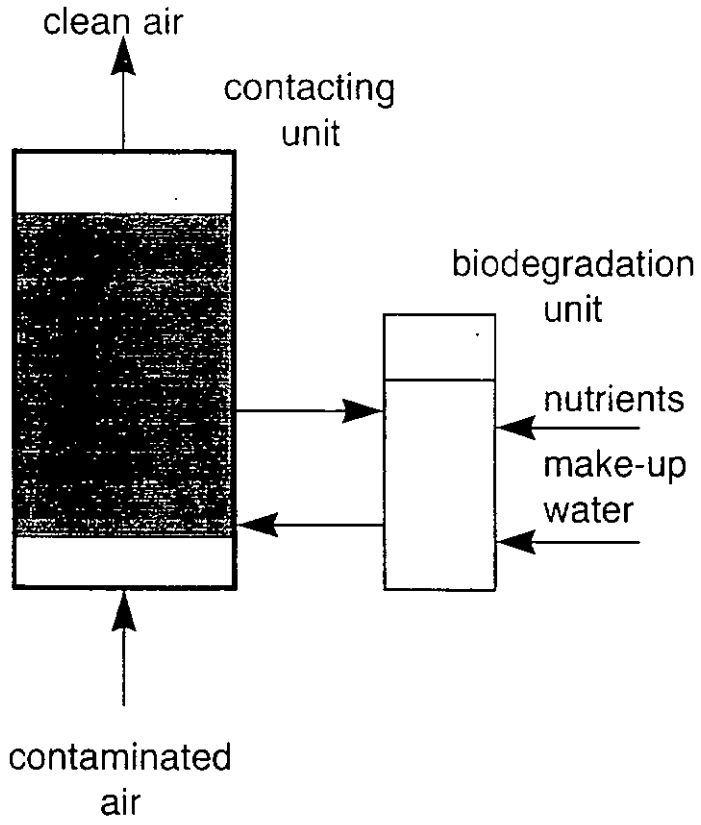

Figure 2.5 Schematic diagram of a bioscrubber (Edwards and Nirmalakhandan, 1996)

2.2.2.3. Trickling Biofilters

Trickling Biofilters can be regarded as an intermediate between biofilters and bioscrubbers. In this system (Figure 2.6), a water phase is continuously recirculated over a packed bed with inert material covered with an active biofilm. The waste gas is forced through the bed where the pollutants are absorbed in the liquid phase and transferred to the biofilm layer and degraded biologically. The waste can be forced through the bed co-currently (Sorial *et al.*, 1997; 1998; Wu *et al.*, 1998) or counter-currently to the liquid phase (Chou and Huang, 1997; Mpanias and Baltzis, 1998).

Different types of packing medium were employed in trickling biofilters, including pelletized earth media (Sorial *et al.*, 1995), steeling pall rings (Arcangeli and Arvin, 1992), ceramic (Diks and Ottengraf, 1991b), polypropylene rings (Apel *et al.*, 1990), and Perlite (Oh and Bartha, 1994; 1997).

The trickling biofilter system avoids some problems of the classical biofilter, such as compaction, channeling and degradation of filter medium (Kirchner *et al.*, 1989; Harmans and Tramper, 1991). Additionally, the metabolites from the biofilm can be easily removed by replacing the recirculation liquid (Chou and Huang, 1997). It also allows pH control which is essential for biodegradation of odorants such as hydrogen sulfide and ammonia, and volatile organics like halogenated hydrocarbons, from which acidic or alkaline metabolites are produced (Diks and Ottengraf, 1991a; Mpanias and Baltzis, 1998).

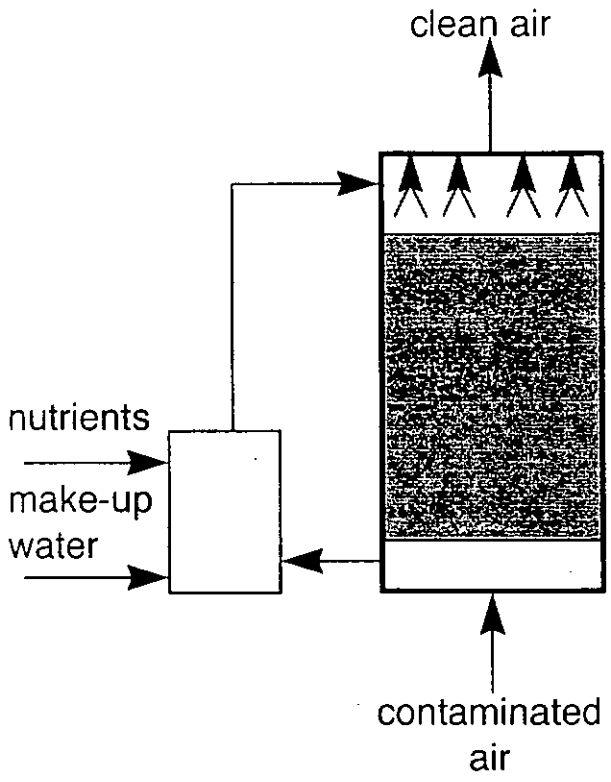

Figure 2.6 Schematic diagram of a trickling biofilter (Edwards and Nirmalakhandan, 1996)

Moreover, larger air/liquid interfacial area in trickling biofilter leads to removal rates which are usually substantially higher than those obtained with conventional biofilters. These high rates, which imply potentially substantial lower sizes and thus capital expenditure for industrial application, have caused a shift in interest from conventional to trickling biofilters in the recent past (Mpanias and Baltzis, 1998). The number of studies concerning the trickling biofilter has increased in the past decade (Chou and Huang, 1997; Sorial *et al.*, 1995; 1997; 1998 Kirchner *et al.*, 1989; Hartmans and Tramper, 1991; Dharmavaram *et al.*, 1995; Wu *et al.*, 1998; Rihn *et al.*, 1997; Mpanias and Baltzis, 1998). The pollutant treated including odorants such as hydrogen sulfide, methly mercaptan, deimethyl thiosulfide and ammonia, and also volatile organics such as BTEX (benzene, toluene, ethylbenzene and xylene), isobutane, isopentane, acetone, methylethylketone, propionaldehyde, ethanol, dichloromethane, monochlorobenzene.

Although trickling biofilters solved most of the drawbacks of traditional biofilters, the disposal of excess biomass from the packing medium is a crucial problem. Accumulation of biomass results in lowered removal efficiency since the specific surface area of microorganisms was decreased (Alonso, 1997). Clogging of the packed bed is another resulting problem. Backwashing is a means to remove the excess biomass, nevertheless, the stable performance of the reactor would be disturbed.

2.3 Fibrous Bed Bioreactor

A fibrous-bed, immobilized cell system that can overcome the problems encountered by biological odor treatment systems has been developed. This bioreactor contains a packed bed of porous fibrous materials in spiral configuration (Figure 2.7) and has been successfully applied in several fermentation and cell culture processes for production of biochemicals (Silva and Yang, 1995; Yang *et al.*, 1992; 1994; 1995; 1996) and treatment of BTEX-contaminated ground water and waste streams (Shim and Yang, 1999).

In the fibrous-bed bioreactor, cells are immobilized in a spiral-wound, fibrous matrix that provides large surface areas for cell attachment and for gas-liquid contacts, and large void spaces for cell entrapment. There are built-in vertical gaps along with the spiral-wound layers of the fibrous matrix to allow excess cell biomass to fall off to the bottom of the reactor, gases such as CO_2 and air to flow upward freely and escape from the top of the reactor. Liquid medium is also allowed to be pumped through the packed bed without substantial pressure drop. Cells are loosely immobilized within the fibrous matrix and there are continual growth of new cells and sloughing-off of aged and dead cells. This continuing cell regeneration process allows the bioreactor to operate continuously for long periods without observable loss in its performance.

The fibrous-bed bioreactor has been used in laboratory studies for organic acids (lactate, acetate, and propionate) production with bacterial cultures. In all cases, superior reactor performance (e.g., three- to ten-fold increases in productivity

and up to 1 year stable continuous operation) was obtained (Silva and Yang, 1995; Yang *et al.*, 1992; 1994; 1995). Moreover, the reactor, after several weeks of adaptation or acclimation period, was able to produce the acidic product at a concentration several times higher than the normal maximum concentration achieved with other types of reactor systems, despite the fact that some of these types of reaction systems even used acid-tolerant mutant strains (Yang *et al.*, 1994). The fibrous-bed bioreactor is thus an effective tool to acquire unusual biological capabilities for processing purposes without going through microbial mutation or genetic engineering procedures. In environmental aspects, this bioreactor has been applied successfully for the treatment of BTEX-contaminated ground water and waste stream. Superior degradation rate and long term stable performance were observed (Shim and Yang, 1999). Therefore, it was of much interest to study this bioreactor and its potential advantageous applications in odor treatment.

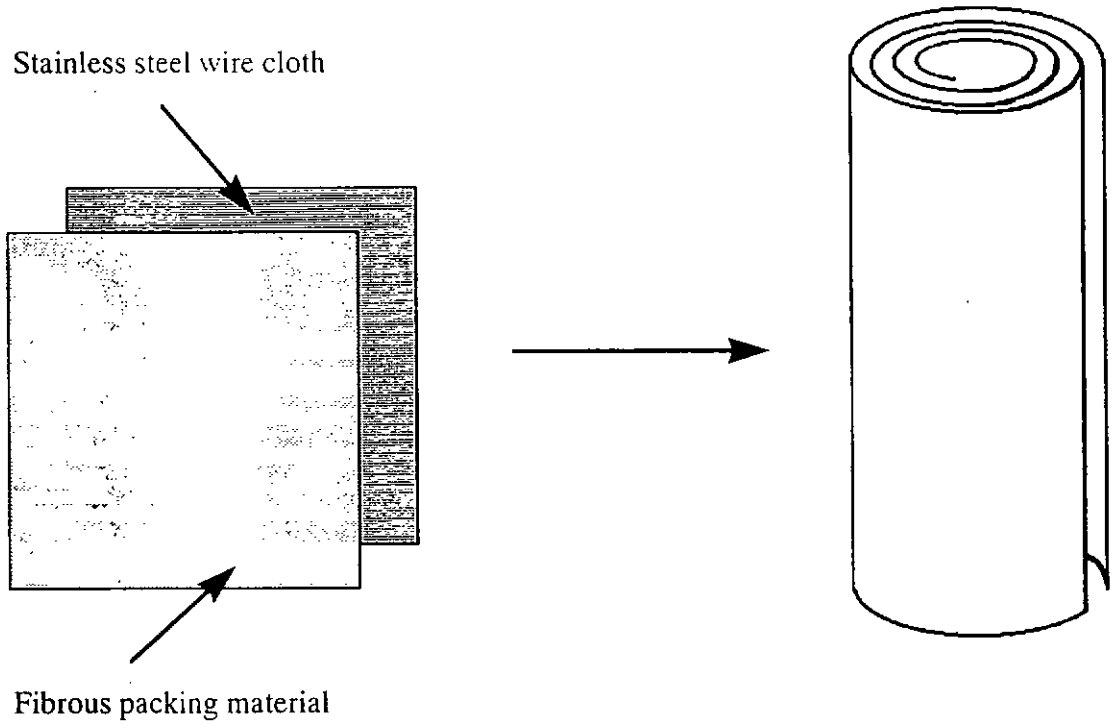

Figure 2.7 The spirally wound configuration of the packing medium.

CHAPTER 3. GROWTH AND ODORANT DEGRADATION KINETICS IN FIBROUS BED BIOFILMS

3.1 Introduction

This preliminary study constituted the first stage of the research. The objective of was to investigate the feasibility of the fibrous bed bioreactor for the treatment of odorous VFAs using microorganisms selected from activated sludge. The microbial growth and VFA degradation kinetics in the selection culture at increasing VFA mass loadings were studied.

3.2 Materials and Method

3.2.1 Odorous volatile fatty acids

Acetic, propionic and butyric acids were used as the odorous components in the simulated fouled air used in this study. Their volatility and molecular weight are inversely related. Generation of the fouled air with desired VFA concentrations will be described in the subsequent sections.

3.2.2 Microorganisms and culture conditions

An Activated sludge (Southerly Waste Water Treatment Plant, Columbus, OH) was used as the initial culture. The desired microorganisms were selected by the three VFAs using shake flask cultures.

The medium for microbial selection contained: 2.5 g/l $(NH_4)_2SO_4$, 1 g/l KH_2PO_4, 1 g/l $MgSO_4.7H_2O$, 1 g/l yeast extract, 6.67 g/l acetic acid, 6.67 g/l propionic acid and 6.67 g/l butyric acid. The total VFA concentration was 20 g/l.

3.2.3 Microbial kinetics and bioreactor start up

One ml of activated sludge was transferred to a 500 ml flask containing 100 ml culture media, incubated at 30 °C and 200 rpm. After a 3 day growth period, the 100 ml cell broth was used to inoculate a stirred tank with 4 l culture medium. The growth condition was controlled at 30 °C and pH was between 7.5 to 8.0 by the stirred tank reactor. This culture was used to study the microbial kinetics. After the cessation of microbial growth, the culture broth inside the stirred tank was trickled on top of the fibrous bed at 200 ml/min for immobilization of the starved microorganisms. After 15 days of liquid recirculation, when the cell concentration in the stirred tank became steady (Figure 3.1), gaseous VFA was introduced into the bioreactor.

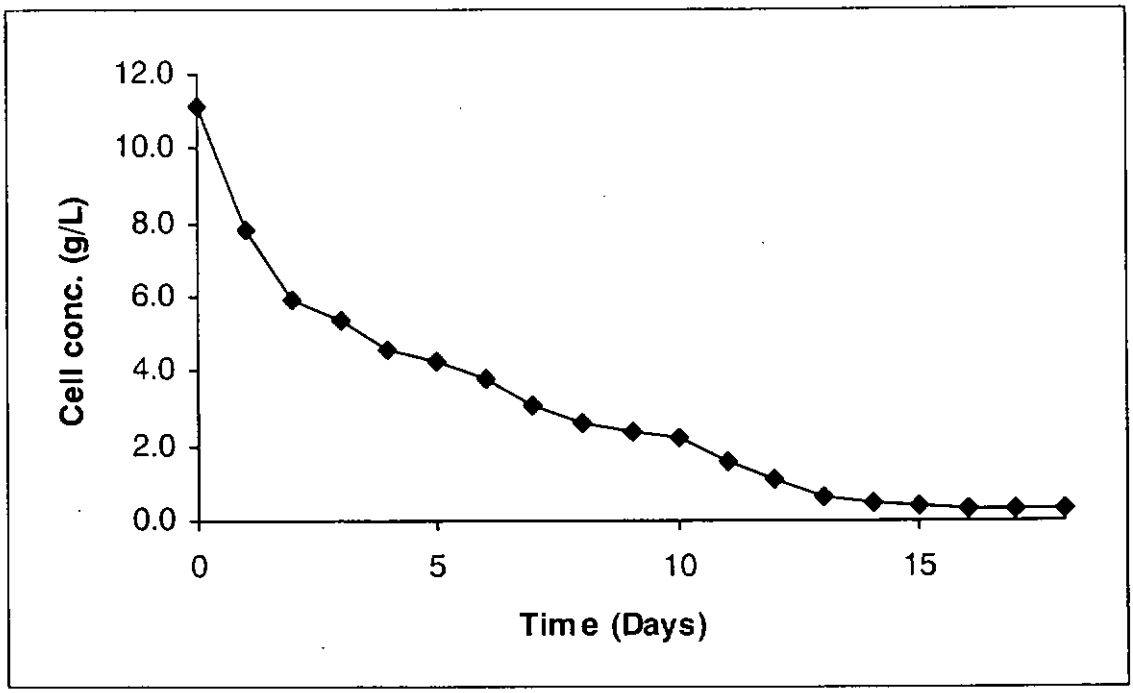

Figure 3.1 Change of cell concentration in stirred tank during immobilization.

3.2.4 Experimental apparatus

An illustration of the experimental biofilter system is shown in Figures 3.2 and 3.3. The reactor system consisted of a cylindrical glass column with internal diameter of 5 cm and height of 73 cm. The cotton fabric packing material with dimensions 52 × 30 cm was spirally wound together with a stainless steel wire cloth with the same dimensions. The empty bed volume was 1 liter and void volume was 900 ml.

The odorous VFA-contaminated fouled air was generated by bubbling air through 25 % (v/v) VFA solution. Different air flow rates were used to vary VFA concentrations in the gas inlet. The odorous gas was introduced at the bottom of the reactor and treated gas was exited from the top.

The stirred tank was used for culture selection and as a recirculation tank during microbial immobilization. After the completion of immobilization, it was disconnected from the column reactor. The fibrous bed packing was totally submerged in liquid which provided a moist condition for the microorganisms.

Gas sampling ports were located at the inlet and outlet of the fibrous bed reactor. Liquid sampling ports were at the bottom of column and also at the stirred tank.

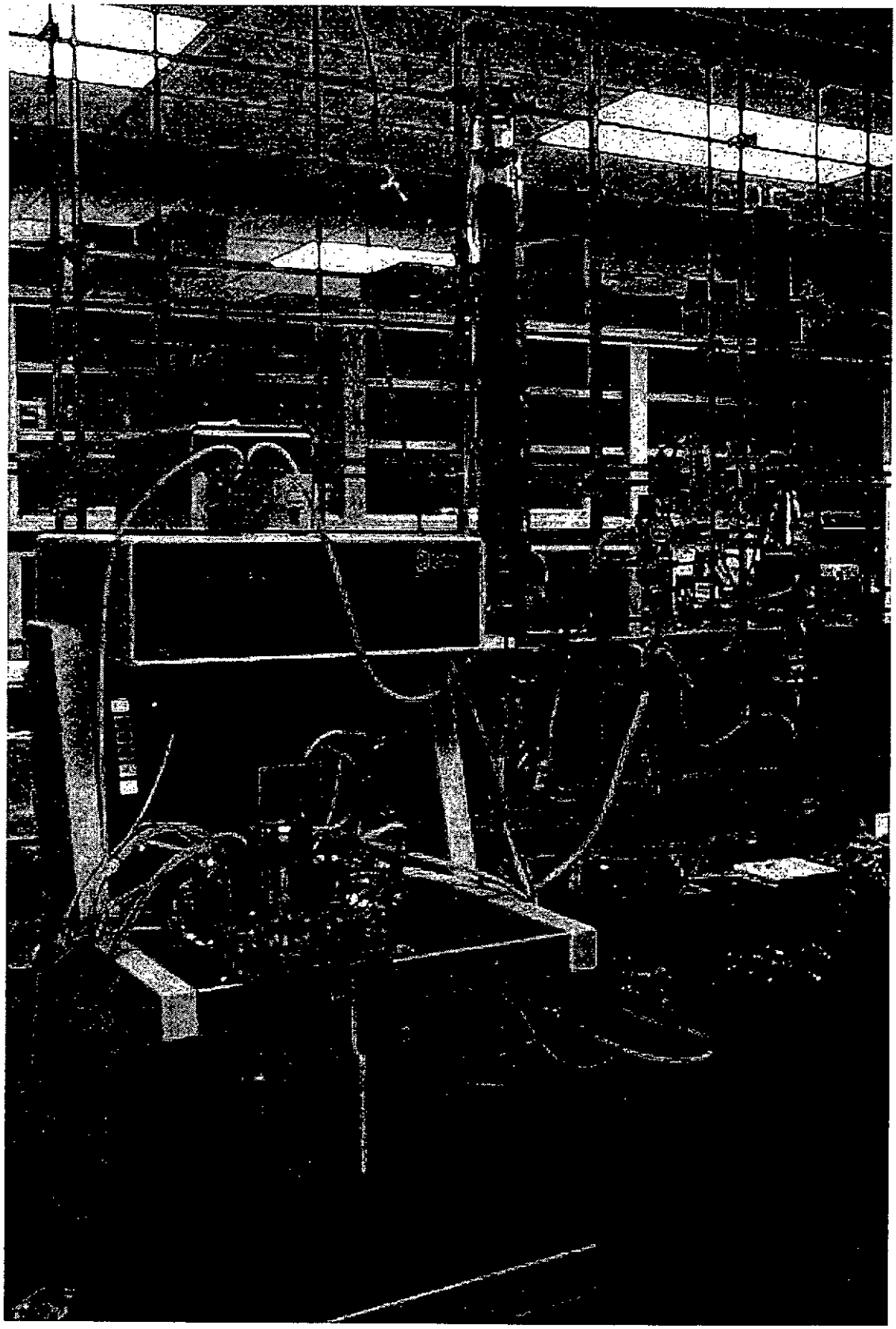

Figure 3.2 The experimental set up

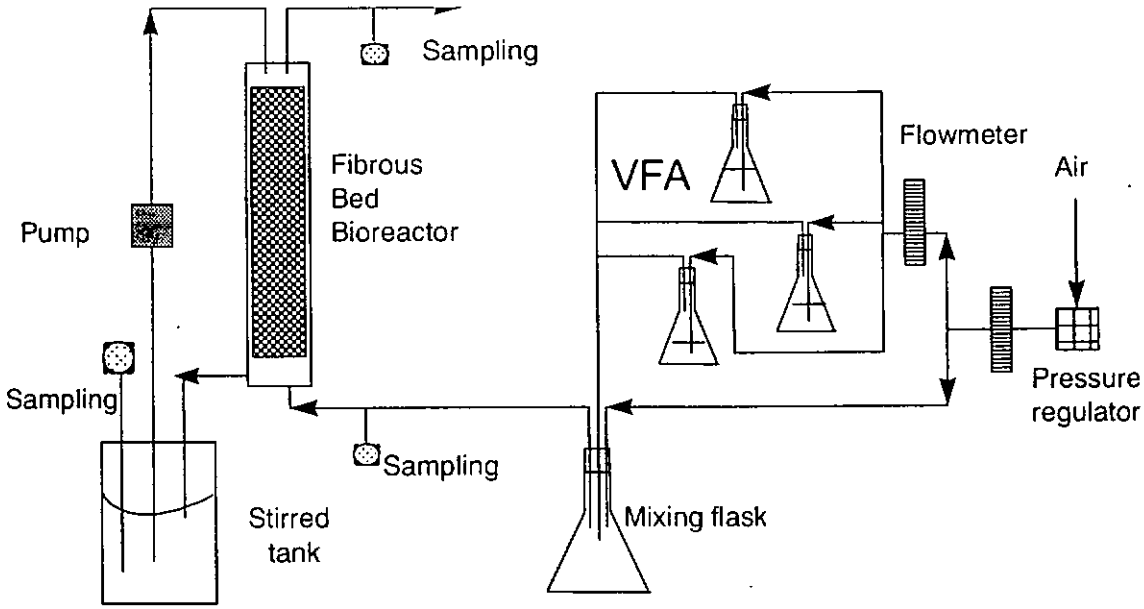

Figure 3.3 Schematic diagram of the experimental set up.

3.2.5 Biofiltration experiments

The effects of VFA mass loading on the bioreactor performance were studied. The flow rate ranged from 1 to 4 l/min, which was equivalent to an empty bed retention time (EBRT) of 15 to 60 seconds. The total VFA concentration ranged from 0.10 to 0.43 g/m^3, and the resulting total mass loading of VFA studied was between 9.7 to 104 $g/m^3/hr$.

3.2.6 Analytical methods

The gaseous VFA concentrations were determined using a Varian gas chromatograph (GC) 3300 system equipped with a DB-WAX capillary column (J & W scientific, 15 m × 0.53 mm i.d.) detected by a flame ionization detector. Nitrogen was used as the carrier gas and the temperature of column, injector and detector was 110, 110 and 160 °C, respectively. Fifty ml of gas sample was taken from the sampling port by using 60 ml air-tight syringe, which was then pre-concentrated by injecting into a 1.5 ml micro-centrifuge tube containing 1 ml deminerialized distilled water and 2 µl of this liquid was then injected into the GC. The error of this pre-concentration step was found to be below 10 %. The VFA concentration from the liquid in the stirred tank and the bioreactor was analyzed with high performance liquid chromatography (HPLC). The liquid sample was first centrifuged at 12000 rpm for 3 minutes. 10 µl of cell-

free sample was then injected into an organic acid analysis column (Bio-Rad, Model PX-87). The eluant used was 0.01 N H_2SO_4 at a flow rate of 0.6 ml/min. The cell density was determined by optical density at 600 nm determined by a spectrophotometer (Model 340, Sequoia-Turner). It was found that 1 unit of OD was equivalent to cell density 0.708 g/l.

3.3 Results and Discussion

3.3.1 Microbial kinetics study

The microbial growth in the stirred tank, the change in pH and VFA concentrations in the culture broth are shown in Figure 3.4. The specific growth rate (rate of cell increase per cell concentration unit) was found to be 0.05 h^{-1} and the maximum cell concentration obtained was 12.6 g/l. The growth of microbes stopped at 100 hour, and continued to grow after 1 g/l yeast extract was added. At 122 hour, the growth ended due to exhaustion of VFA.

Acetic acid was the first VFA depleted in the culture broth. It was consumed at an average rate of 0.13 g/l/hr, and was used up after 48 hours. Propionic and butyric acids were consumed slowly in the presence of acetic acid, only at 0.007 and 0.005 g/l/hr, respectively. The consumption rates of propionic and butyric acids, after the exhaustion of acetic acid, was increased sharply. Finally, both depleted at 122 hour. The maximum VFA consumption rates were found to be 0.30, 0.05 and 0.06 g/l/hr for acetic, propionic and butyric acids respectively. It implied that during VFA treatment, acetic acid would be removed in a higher priority compared with propionic and butyric acids.

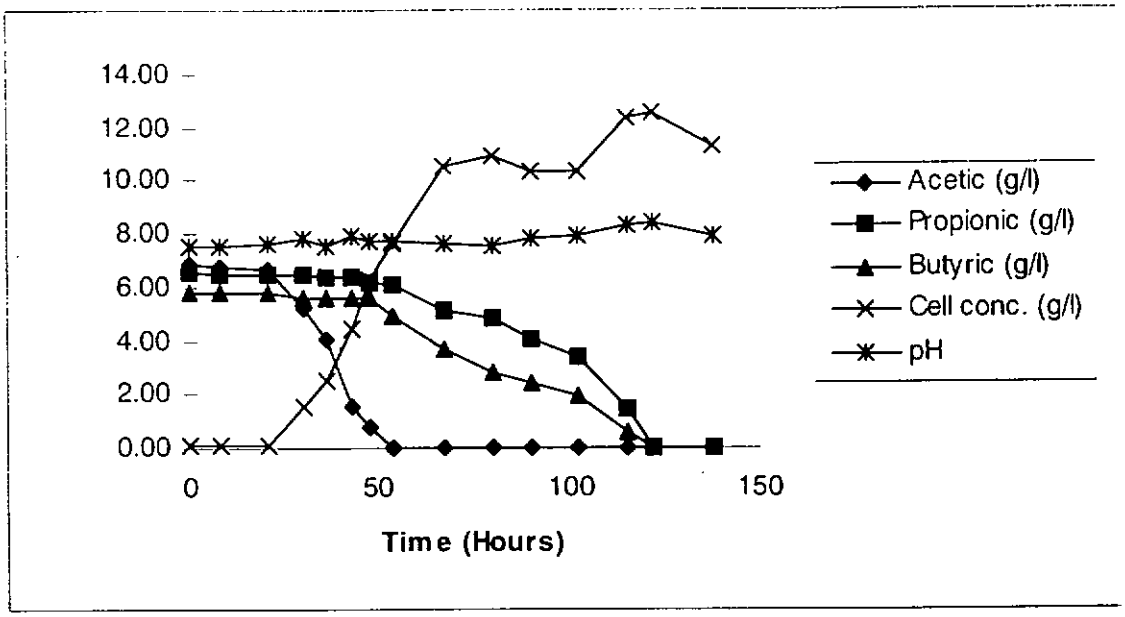

Figure 3.4. Growth kinetic of microorganisms showing cell concentration and VFA concentration in selection culture from activated sludge using VFA as carbon source.

3.3.2 Performance of bioreactor on increasing mass loading

The removal capacities and removal efficiencies at different mass loadings are shown in Figures 3.5 to 3.8. At VFA mass loadings below 22.4 g/m^{3}hr, the VFA concentration from the gas outlet and in the liquid inside the bioreactor was always non-detectable, and a steady pH in the liquid phase was observed. Under this condition, there was no accumulation of VFA inside the bioreactor where the microorganisms was able to degrade all the VFA introduced.

When total mass loading was increased to 22.4 g/m^3/hr, VFAs were still non-detectable in the gas outlet. However, propionic and butyric acids started to accumulate in the liquid phase (Table 3.1). The system was stabilized when the VFA concentration in the liquid phase reached 1.0 g/l.

When total VFA mass loading was raised to 50.3 g/m^3/hr, the outlet VFA concentration started to show, and the removal efficiency was reduced to 91.9 % and the resulting removal capacity was 46.1 g/m^3/hr.

The total VFA mass loading was further increased to 104 g/m^3/hr, with 37.2, 36.6 and 30.5 g/m^3/hr for acetic, propionic and butyric acids, respectively. At a "semi-steady" state, the total VFA removal efficiency was lowered to 87.7 %, with 94.4, 85.3 and 82.7 % for acetic, propionic and butyric acids, respectively. Their respective concentrations in the liquid phase were 0.5, 3.1 and 3.1 g/l (Table 3.1).

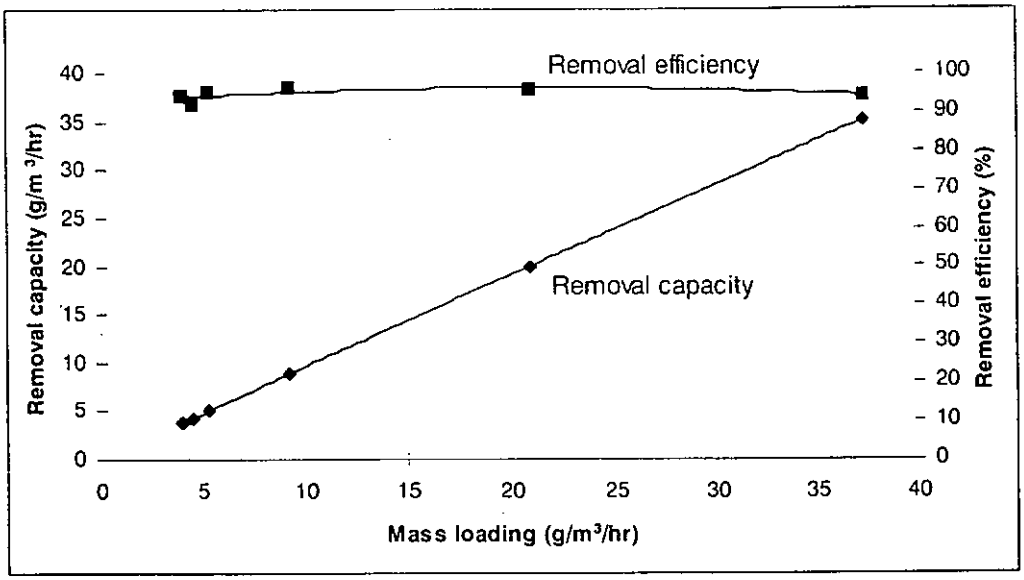

Figure 3.5 Removal profile of acetic acid at increasing mass loading.

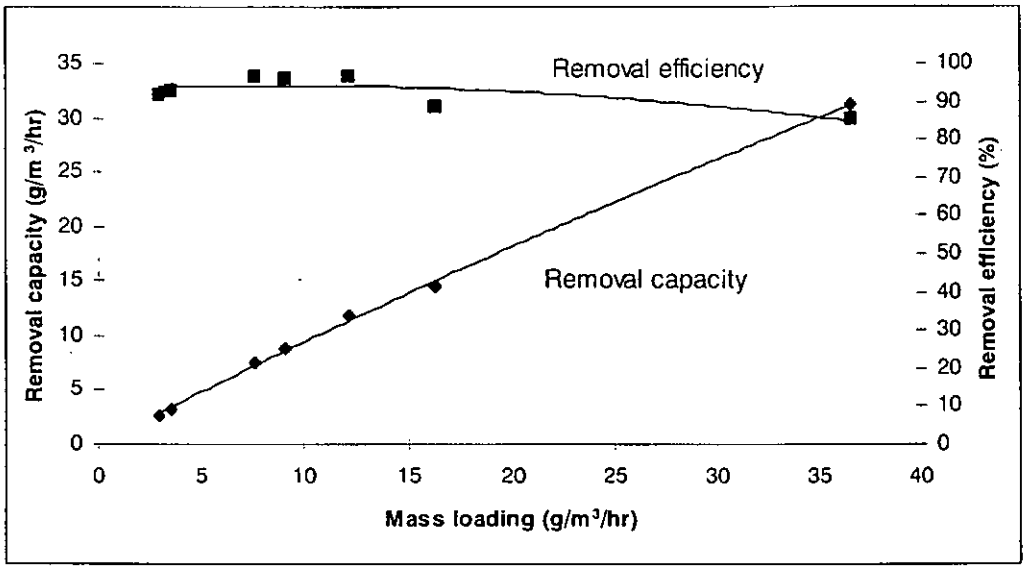

Figure 3.6 Removal profile of propionic acid at increasing mass loading.

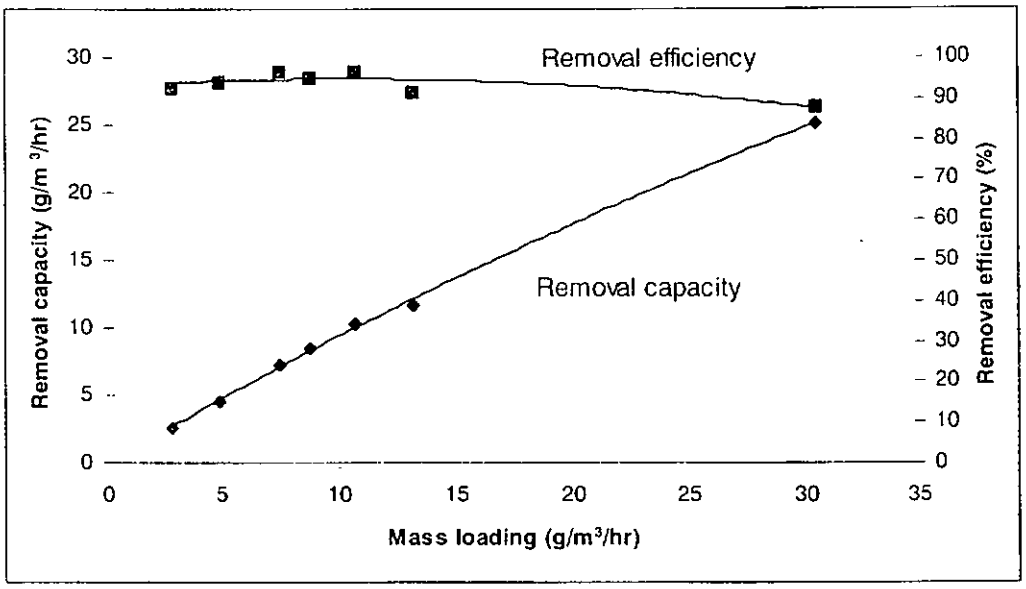

Figure 3.7 Removal profile of butyric acid at increasing mass loading.

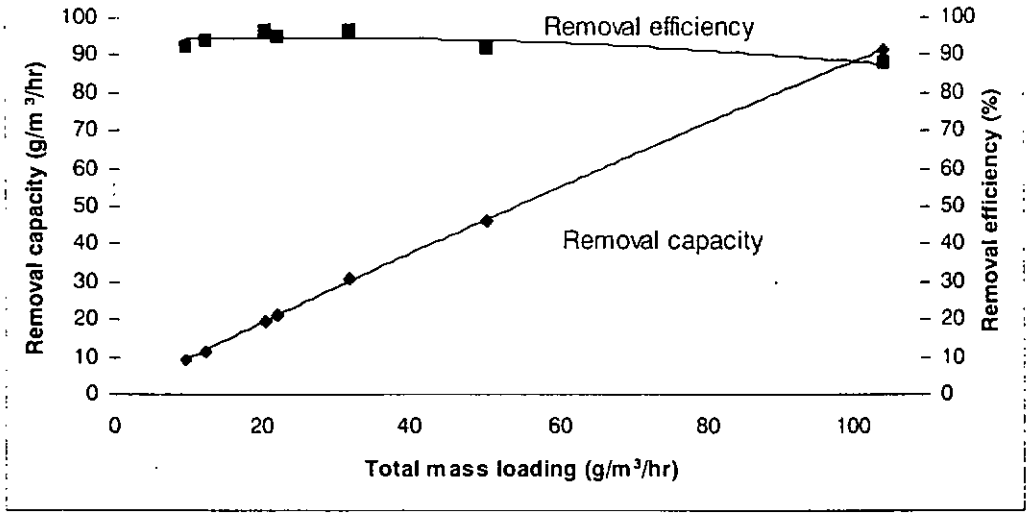

Figure 3.8 Removal profile of total VFA at increasing mass loading.

Table 3.1 VFA concentration (g/l) in liquid at different mass loadings

Mass loadings ($g/m^3/hr$)	Acetic	Propionic	Butyric	Total VFA
104	0.5	3.1	3.1	6.7
50.3	ND	2.8	2.7	5.5
22.4	ND	0.5	0.5	1.0

In the gas phase, the removal efficiency of acetic acid was highest among the three VFAs. In the liquid phase, acetic acid was also at the lowest level compared with propionic and butyric acids (Table 3.1). There was no accumulation of acetic acid at VFA mass loadings of 22.4 and 50.3 $g/m^3/hr$. At total mass loading of 104 $g/m^3/hr$, acetic acid concentration was the lowest compared to other VFAs. This finding was consistent with the microbial kinetics study that acetic acid was preferentially degraded.

CHAPTER 4. DESIGN AND PERFORMANCE OF THE FIBROUS BED REACTOR FOR ODOR TREATMENT

4.1 Introduction

In the preliminary study, the application of fibrous bed biofilter for odor treatment was found feasible. In this second stage, in order to optimize the process, it was scaled up with design and operation considerations. Instead of using cotton fibrous material as packing medium, synthetic fiber was used since cotton was observed to be a biodegradable material which was found unsuitable for long term processes. A biochemically inert material was employed. In addition to submerged bed configuration (the packing medium is totally submerged in the liquid phase) in the preliminary study, trickling biofilter configuration (the packing medium is continuously wetted by the trickling liquid, but not submerged in it) was applied and investigated, and the performance of the two configurations were compared. Moreover, valeric acid was used in place of acetic and propionic acids, because of its lower detection threshold (Williams and Miller, 1992), more unacceptable smell and widespread generation in odorous emissions.

In order to obtain reliable information on the bioreactor performance under realistic operational conditions, the reactor performance under changing loading conditions was studied. Therefore, the effects of inlet VFA concentration and gas empty bed retention time (EBRT) on bioreactor

performance were investigated. The pressure drop and the long term stability of the fibrous bed bioreactor were also monitored.

4.2 Materials and Method

4.2.1 Odorous gas

Butyric and valeric acids were used as the odorous gas. The method of generation of the simulated odorous fouled air was similarly to that described previously.

4.2.2 Microorganisms and culture selection conditions

An activated sludge (Sha Tin Sewage treatment plant, Hong Kong) was used as the seed culture. The VFA degrading microbes were selected by shake flask cultures, from a medium containing VFA as the sole carbon source.

The culture medium contained: 3 g/l $(NH_4)_2SO_4$, 1 g/l KH_2PO_4, 1 g/l $MgSO_4.7H_2O$, 10 g/l butyric acid and 10 g/l valeric acid. 1ml of activated sludge was transferred to a 500 ml flask containing 100 ml culture medium, incubated at 25 °C and 200 rpm. After 3 days of growth period, the culture

broth was used to inoculate another 10 100-ml flasks. The culture media and conditions of these 10 flasks were same as the previous cultures.

4.2.3 Experimental apparatus

The experimental bioreactor system is shown in Figures 4.1 and 4.2. The reactor system consisted of a cylindrical acrylic column with internal diameter of 37 mm and height of 120 cm. The fibrous packing material with dimensions of 60 × 70 cm was spirally wound together with a stainless steel wire cloth with the same dimensions. The microstructure of the fibrous matrix are shown in Figure 4.3. The empty bed volume was 3 L with a porosity of 95 %.

The odorous VFA gas was generated by bubbling air through 10 % (v/v) VFA solution. Different air flow rates were used to vary the inlet VFA concentrations. The process was operated in an air-conditioned room with ambient temperature ranged from 24 - 27 °C.

Two configurations of the bioreactor were employed, namely the submerged biofilter and the trickling biofilter. For the trickling biofilter configuration, the bioreactor was operated under counter-current flow of gas and liquid streams. The odorous gas was introduced at the bottom and treated gas was exited from the top of the reactor, while the recirculation liquid was trickled on top of the fibrous bed at 200 ml/min and exited from the bottom and returned to the recirculation tank. The recirculation liquid provided moisture, as well as

inorganic nutrients, to the microorganisms in the fibrous bed. The recirculation tank also served as a sedimentation tank from which excess biomass from the bioreactor was removed.

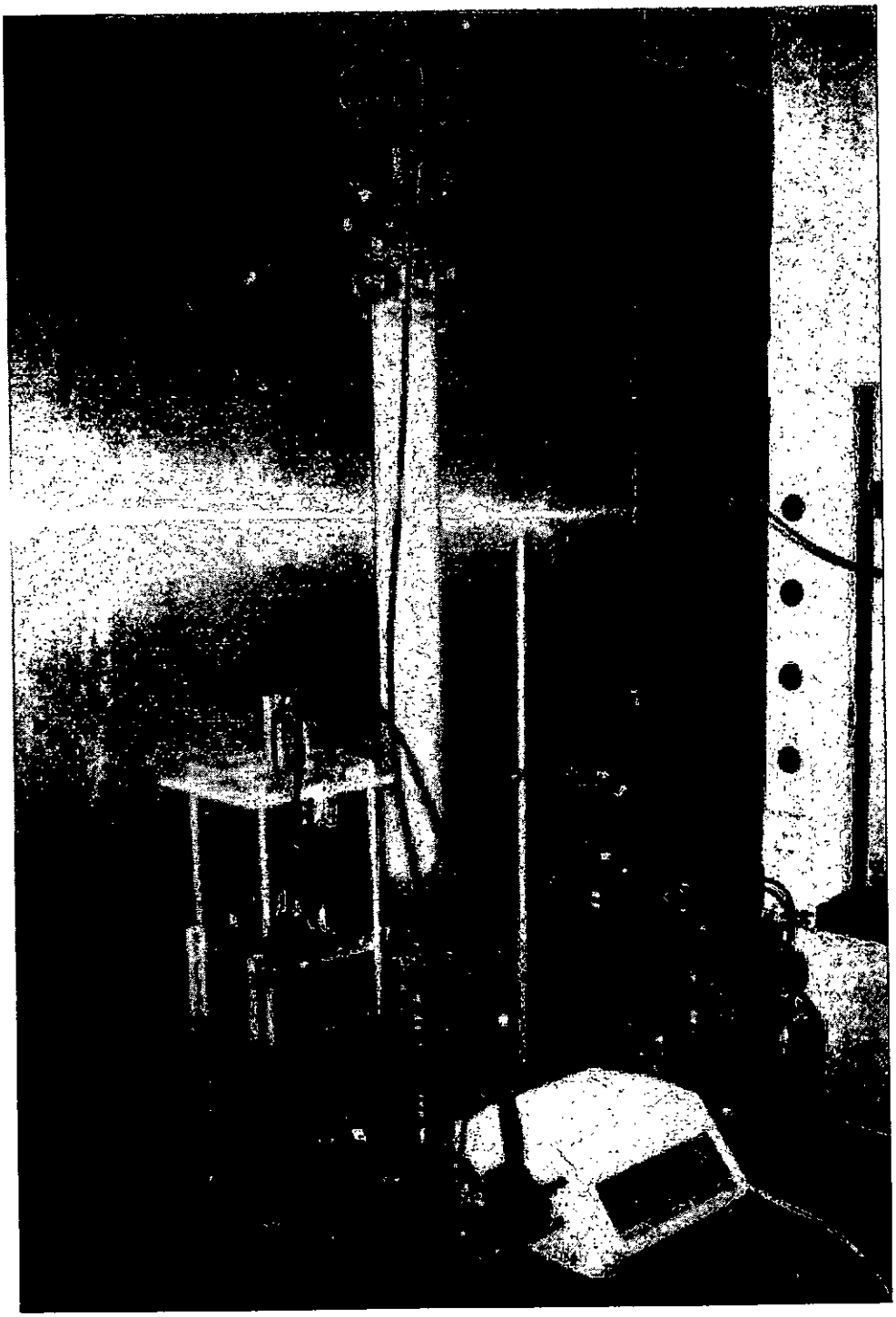

Figure 4.1 The experimental set up.

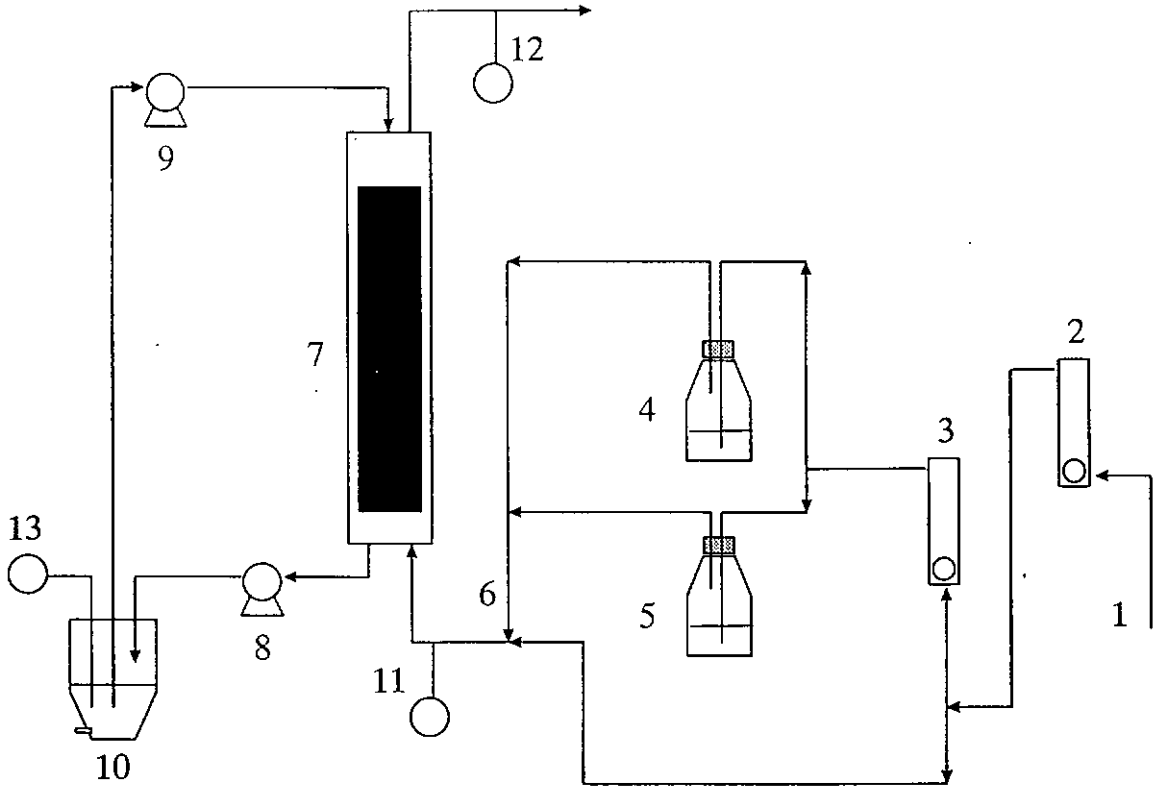

Figure 4.2 Schematic diagram of the experimental set up. 1 Compressed air; 2 Flowmeter controlling the total gas flow rate; 3 Flowmeter controlling VFA concentration; 4 & 5 VFA solution; 6 VFA contaminated gas; 7 Fibrous bed bioreactor; 8 & 9 Recirculation pumps; 10 Recirculation tank; 11- 13 Sampling ports from: gas inlet, gas outlet and recirculation tank respectively.

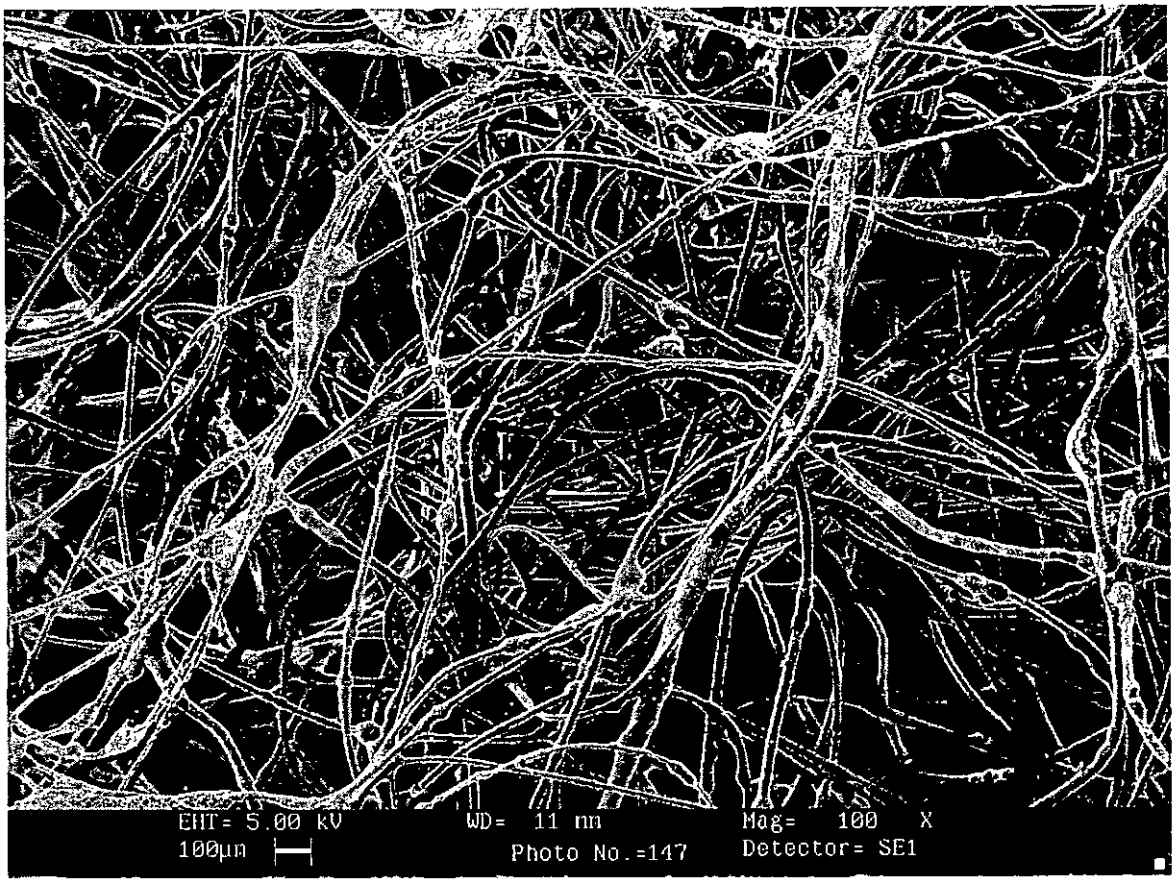

Figure 4.3 The microstructure of the fibrous matrix.

For the submerged bed configuration, the bioreactor was operated under counter-current flow of gas and liquid streams. The odorous gas was introduced at the bottom and treated gas was exited from the top of the reactor, while the a closed loop of recirculation liquid was introduced on top of the fibrous bed at 200 ml/min and exited from the bottom.

Gas sampling ports were located at the inlet and outlet of the reactor. Liquid sampling ports were at the bottom of column and also at the recirculation tank.

4.2.4. Bioreactor start up and operation conditions

In the start up procedure for the trickling bioreactor, the 1 liter culture broth from the flasks, together with 1 liter inorganic nutrient, were filled into the recirculation tank and trickled from the top of the fibrous bed at 200 ml/min for the immobilization of the starved microorganisms.

After recirculation for 7 days, the cell concentration in the recirculation tank became steady. To establish the biofilm in the fibrous bed, gaseous VFA was supplied to the bioreactor at an inlet concentration of 0.2 g/m^3 and gas empty bed retention time (EBRT) of 90 sec.

After the start up period, the odorous gas was supplied to the bioreactor at flow rates that ranged from 2 to 6 l/min (EBRT 30 to 90 sec) and with inlet VFA concentrations that ranged from 0.08 to 0.86 g/m^3.

To start up the submerged bioreactor, the 1 liter culture broth from the flasks, together with 3 liter inorganic nutrient, were added to the bioreactor. The rate of the close recirculated liquid was 200 ml/min selected for microbial cell immobilization. However, after 7 days, the cell concentration in the liquid phase remained high, indicating that the microorganisms had not attached to the packing medium, which was attributed to the shear force generated from the bubbles from the air supply. Thus, the operation of the submerged biofilter configuration was discontinued.

4.2.5 Analytical methods

The inlet VFA concentration was determined using a HP 5890 gas chromatographic system equipped with a HP-FFAP column and a flame ionization detector. Nitrogen was used as the carrier gas at 20 ml/min. The temperature of injector and detector was 280 and 300 °C respectively. The oven temperature profile was programmed and controlled from 80 to 200 °C at 20 °C/min.

The VFA concentration in the recirculation liquid was determined according to Levett (1991), the liquid samples were first centrifuged at 12000 rpm for 5 minutes. Thereafter, the cell-free samples were acidified by 50% aqueous H_2SO_4 and then mixed with diethyl ether, 1 μl of the ether layer was injected into the GC.

The cell density was determined optically at 600 nm by a spectrophotometer (Spectronic Genesys 2). It was found that 1 unit of OD was equivalent to cell density 0.685 g/l.

The pressure drop in the fibrous bed was measured using a manometer (Dwyer Slack Tube).

4.2.6 Scanning electron microscopy

For SEM observations of the fibrous packing medium and the biofilm samples, the samples were coated with a 25 nm layer of gold-palladium mixture (Joel Fine-Coat Ion Sputter Type JFC-1100) and observed with a scanning electron microscope (Joel JSM-T220A) at 5 kV accelerating voltage and 100 - 5000 times magnification.

4.3 Results and Discussion

4.3.1 Bioreactor start up

During the start up period, gaseous VFA was supplied at a concentration of 0.2 g/m^3 and the gas EBRT was set at 90 sec. The bioreactor responded with a high removal efficiency of above 99 %. It revealed that no acclimation time was needed for the microorganisms to be fully active and functional as they have already adapted to the VFA environment during the selection culture period. After 21 days, a biofilm was developed throughout the fibrous bed, as shown in the scanning electron micrograph (Figure 4.4), attaching to the fibrous matrix.

4.3.2 Effect of inlet concentration on bioreactor performance

The effect of inlet VFA concentration on bioreactor performance was studied by increasing the gaseous VFA concentrations at fixed EBRTs of 90, 60, 45 and 30 seconds. As shown in Figure 4.5, at EBRT of 90 s, a high removal efficiency of 99 % was obtained. When the inlet concentration was increased to 0.86 g/m^3, the bioreactor responded with an accumulation of VFA in the recirculation liquid instead of an increased VFA concentration in the outlet gas, while the removal efficiency remained very high (> 99 %).

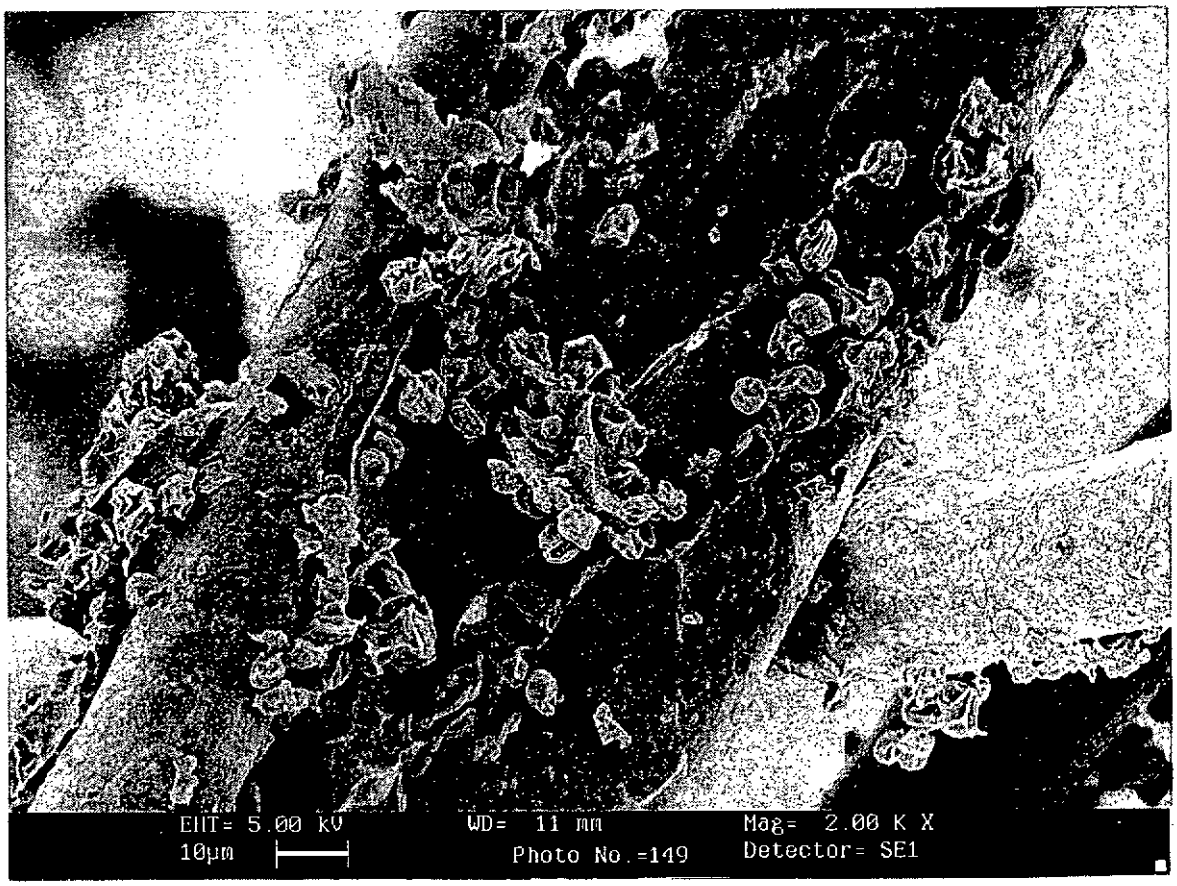

Figure 4.4 The biofilm attached to a fibrous strand in the matrix

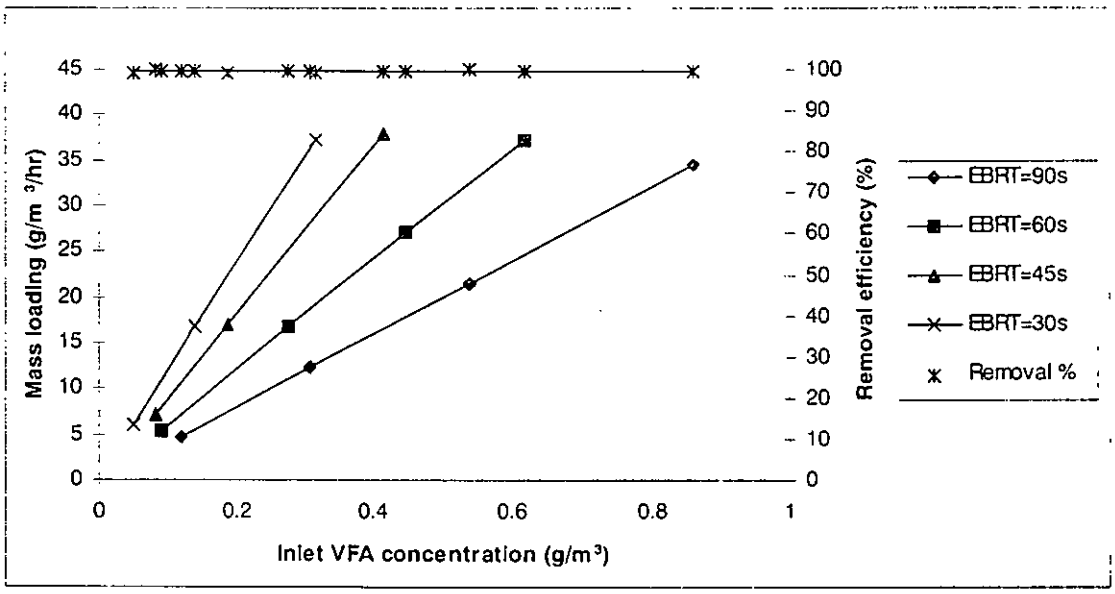

Figure 4.5 The mass loadings and removal efficiencies on increasing inlet concentration at various EBRTs

At a shorter EBRT of 60 s, VFA was found to be accumulating at a lower inlet concentration of 0.62 g/m^3. Similar results were obtained at shorter EBRTs of 45 and 30 s. The accumulation of VFA in the recirculation liquid was found at inlet concentrations of 0.42 and 0.32 g/m^3, respectively.

The accumulation of VFA compounds in the liquid phase indicated that the biofilm was unable to degrade all the VFA introduced. As shown in Table 4.1, among the EBRTs studied, VFA began to accumulate at similar mass loadings between 34.4 to 37.8 $g/m^3/hr$.

Table 4.1 The operation conditions (inlet concentration and mass loading) at which VFA accumulated

EBRT (s)	Inlet concentration (g/m^3) at which VFA accumulated	Corresponding mass loading ($g/m^3/hr$)
90	0.86	34.4
60	0.62	37.2
45	0.42	37.8
30	0.31	37.2

4.3.3 Effect of gas flow rate on bioreactor performance

The effect of gas retention time on bioreactor performance was investigated by increasing the gas superficial velocity or shortening the EBRT, while the inlet VFA concentrations were set at 0.08, 0.2, 0.4 and 0.7 g/m^3. As shown in Figure 4.6, at low inlet concentrations of 0.08 and 0.2 g/m^3, high removal efficiencies of >99 % were obtained and no VFA accumulation was found in the liquid phase even when the reactor was operated at a short EBRT of 30 seconds (superficial velocity of 88.1 $m^3/m^2/hr$).

When the inlet concentration was set at 0.4 g/m^3, accumulation of VFA was found in the recirculation liquid at EBRT of 45 seconds (superficial velocity of 55.8 $m^3/m^2/hr$). When the VFA concentration was further increased to 0.7 g/m^3, VFA showed in the liquid phase at shorter EBRT of 60 seconds (superficial velocity of 41.9 $m^3/m^2/hr$), indicating a longer retention time was needed for complete degradation as the concentration was increased. From Table 4.2, at mass loadings of 32 and 42 $g/m^3/hr$, VFA was found present in the liquid phase. The results reveal that the bioreactor performance was mainly affected by mass loading, which was equal to the inlet concentration divided by EBRT. Whereas the inlet concentration or EBRT could not affect the bioreactor performance alone. It was observed that VFA started to accumulate in the recirculation liquid at a mass loading of 32 $g/m^3/hr$, which was regarded as the critical mass loading.

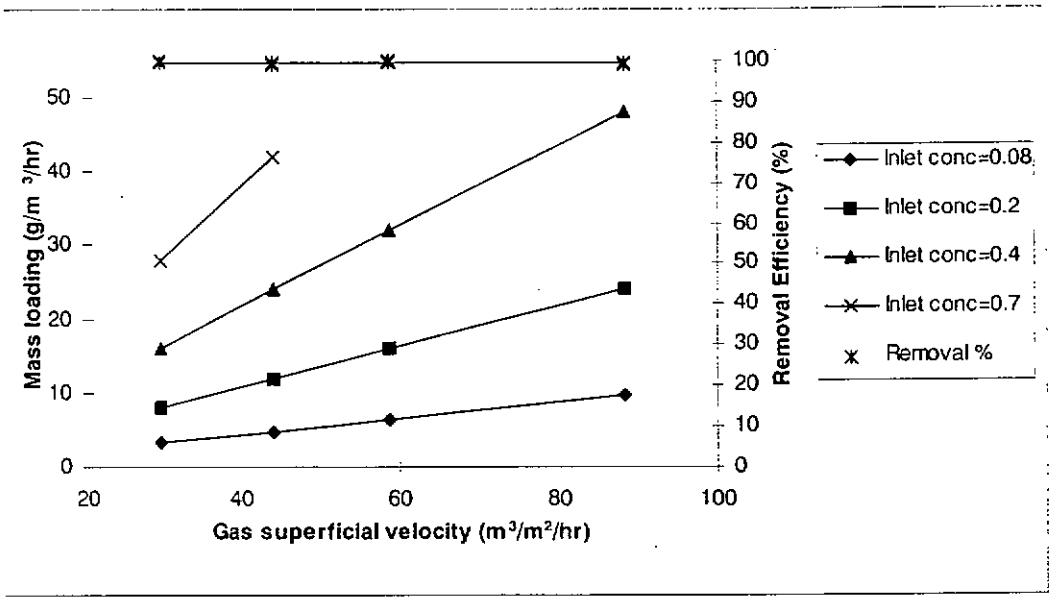

Figure 4.6 The mass loadings and removal efficiencies on increasing gads superficial velocity at various inlet concentrations

Nevertheless, the removal efficiencies remained high (>99%). It implied that the mass transfer of VFA compounds from gaseous phase to liquid phase was not the rate determining step in the process and the VFA removal rate was mainly limited by the biochemical degradation in the biofilm.

Throughout the course of bioreactor operation, although the accumulation of VFA in the liquid phase did not show any effect on the removal efficiency, it was undesirable as the presence of VFA would lead to a decrease in pH of the liquor in the system which in turn adversely affected the biodegradation process. In addition, instead of odor removal, stinking smell would be generated from the outlet gas even at very low VFA concentration in the recirculation liquid. Thus, the optimum operating condition of this process should be zero accumulation of VFA in the liquid phase. The accumulation of VFA in the liquid phase was controlled below 500 mg/L during the experiment, above which only air was supplied to the bioreactor until the VFA in the liquid phase was completely degraded.

Table 4.2 The operation conditions (EBRT and mass loading) at which VFA accumulated

Inlet concentration (g/m^3)	EBRT (s) at which VFA accumulated	Corresponding mass loading ($g/m^3/hr$)
0.08	NA	NA
0.2	NA	NA
0.4	45	32
0.7	60	42

4.3.4 Bioreactor pressure drop and long term stability

Generally, the pressure drop of a packed bed depends on flow properties, the gas velocity, and the nature, composition, and configuration of the packing medium. Packing materials such as coarse bark and compost which used in conventional biofilter usually show aging phenomena resulting from the formation of cell clusters, the shrinkage of the bed and accumulation of cracks in the stack. The aging phenomena can eventually disturb the homogeneous flow distribution of the gas. Consequently, the pressure drop increases considerable with time in the conventional biofilters (Ottengraf, 1986).

As shown in Figure 4.7, the pressure drop in the fibrous bed bioreactor was found between 973 and 2921 Pa/m at gas superficial velocities between 29.4 and 88.1 $m^3/m^2/hr$. Comparing with conventional biofilters, this novel bioreactor had a lower pressure drop (Diks and Ottengraf, 1991a). Additionally, it was observed that the pressure drop was steady at each superficial velocity, and did not increase with time which always occur in conventional biofilters.

Moreover, the fibrous bed bioreactor had a stable long term performance. Over 4-months period of operation, no clogging or aging problems of the packing medium were encountered.

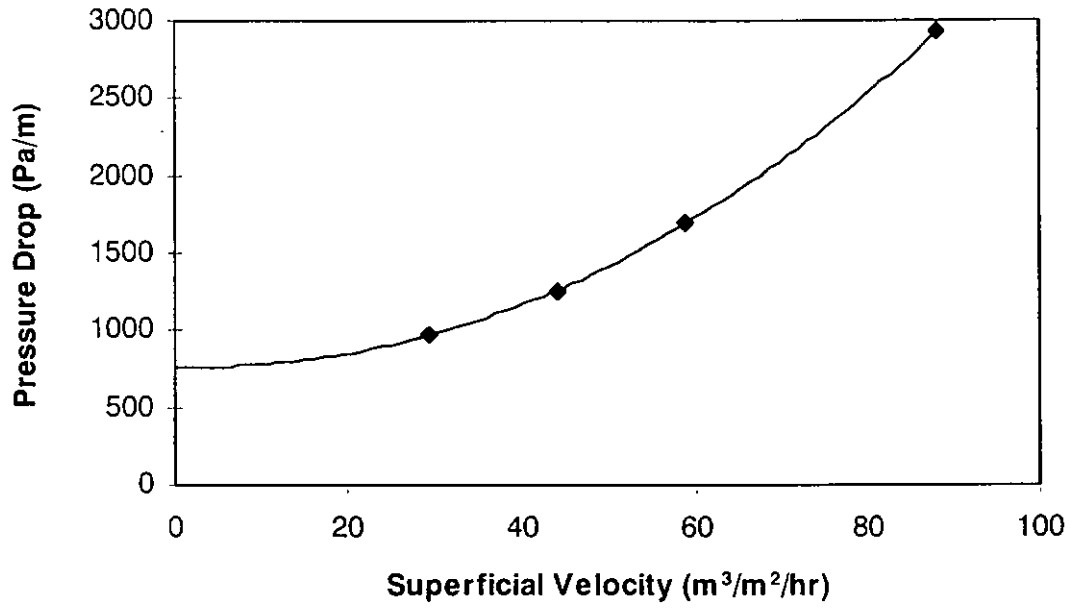

Figure 4.7 The pressure drop of the fibrous bed at increasing gas superficial velocity.

The low pressure drop and long term stability of the fibrous bed bioreactor was attributed to its highly porous fibrous matrix and spirally wound packing configuration, which resulted in an ideal hydrodynamic environment and efficient mass transfer that had prevented the formation of cluster of biomass. Besides, the microbial cells in the fibrous bed were constantly being renewed with news cells, thus avoiding problems such as aging and sloughing of biofilm commonly seen in conventional biofilters.

CHAPTER 5. CONCLUDING REMARKS

The fibrous bed bioreactor was successfully applied as a submerged biofilter to treat odorous VFA, namely acetic, propionic and butyric acids. At VFA mass loadings of 37.2, 36.6 and 30.5 $g/m^3/hr$ (104 $g/m^3/hr$ totally) for acetic, propionic and butyric acid, respectively, the overall removal efficiency was 87.7 %. For total mass loading below 50.3 $g/m^3/hr$, a removal efficiency higher than 90 % was attained. Competitive effect between the three VFAs was elucidated. Acetic acid was most rapidly and preferably degraded among the VFAs, which was consistent with the liquid phase kinetics.

In the process operation study, both submerged biofilter and trickling biofilter configurations were investigated. The operation of the submerged biofilter was unsuccessful due to the shear force generated by the gas bubbles which hindered the attachment of microorganisms on the packing medium. On the other hand, the trickling biofilter was shown to be effective in removing odorous VFAs from the fouled gas streams. The bioreactor performance was affected by mass loading, but not by inlet concentration or EBRT alone. The critical mass loading was found at 32 $g/m^3/hr$, at which VFAs started to accumulate in the liquid phase. High removal efficiencies (>99%) were still obtained, which indicated that the biodegradation process was limited by microbial activity. The bioreactor also showed low pressure drop and long term stability indicating a good potential for industrial scale up.

REFERENCES

Air Noise Administration Division, Department of Environment, U.K (1980) Odours and other nuisances: the legal position in England and Wales, in *Odour control: a concise guide*, Valentin, F.H.H. and North, A.A. eds, Warren Spring Laboratory, Department of Industry, Stevenage, England, 11-16.

Alonso, C., Suidan, M.T., Sorial, G.A., Smith, F.L., Biswas, P., Smith, P.J. and Brenner, R.C. (1997) Gas treatment in trickle-bed biofilters: Biomass, how much is enough? *Biotechnology and Bioengineering*, **54**(6), 583-594.

Anderson, R. (1994) Sewage treatment processes: the solution to the odour problem, in *Characterization and control of Odoriferous Pollutants in Process Industries*, Vigneron, S., Hermia, J., and Chaoki, J., eds, Elsevier Science B.V. Amsterdam, 471-496.

Apel, W.A., Dugan, P.R. and Wiebe, M.R. (1990) Use of methantrophic bacteria in gas phase bioreactors to abate methane in coal mine atmospheres. *Fuel*, **10**,1001-1003.

Arcangeli, J.P. and Arvin, E. (1992) Modeling of toluene biodegradation and biofilm growth in a fixed biofilm reactor. *Water Science and Technology*, **26**, 617-626.

Bohn, H (1992) Consider biofiltration for decontaminating gases, *Chemical Engineering Progress*, April, 34-40.

Bohn, H.L. (1975) Soil and compost filters of malodorant gases, *Journal of the Air Pollution Control Association*, **25**(9), 953-955.

Brandl, J.S., Stover, E.I. (1988) Odorous VOS control and large industrial wastewater treatment plant. *Water Pollution Federation 61st Annual Conference*, 2-6 Oct., Dallas, TX, USA.

Carleton, A.J. (1980) Thermal incineration, in *Odour control: a concise guide*, Valentin, F.H.H. and North, A.A. eds, Warren Spring Laboratory. Department of Industry, Stevenage, England, 51-60.

Carleton, A.J. and Valentin, F.H.H. (1980) Absorption, in *Odour control: a concise guide*, Valentin, F.H.H. and North, A.A. eds, Warren Spring Laboratory, Department of Industry, Stevenage, England, 77-84.

Cheremisinoff, P.N. and Young, R.A. (1975) *Industrial Odor Technology Assessment*. Ann Arbor Science Publishers, Ann Arbor, MI, USA, 509.

Chou, M, and Huang, J. (1997) Treatment of methylethylketone in air stream by biotrickling filters. *Journal of Environmental Engineering*, **123**(6), 569-576.

Diks, R.M.M., and Ottengraf, S.P.P. (1991a) Process engineering aspects of biological waste gas purification, in *Proceedings, International Symposium on Environmental Biotechnology, Part I*, Ostend, Belgium, 353-367.

Diks, R.M.M., and Ottengraf, S.P.P. (1991b) Verification studies of a model for the removal of dichloromethane from waste gases using a biological trickling filter (Part I), *Bioprocess Engineering*, **6** (3), 93-99.

Dorling, T.A. (1980) Carbon adsorption, in *Odour control: a concise guide*, Valentin, F.H.H. and North, A.A. eds, Warren Spring Laboratory, Department of Industry, Stevenage, England, 85-92.

Edwards, F.G., and Nirmalakhandan, N. (1996) Biological treatment of airstreams contaminated with VOCs: an overview. *Water Science and Technology*, **34**(3-4), 565-571.

Eikum, A.S. and Storhaug, R. (1986) Odour problems related to waste water and sludge treatment, in *Odour Prevention Air Control of Organic Sludge and Livestock Farming*, Nielsen, V.C., Voorburg, J.H. and L'Hermite, P. eds., Elseveir Applied Science Publishers, London, 12-20.

Fouhy, K. (1992) Cleaning waste gas naturally, *Chemical Engineering*, December, 41-46.

Harkness, N. (1980) Chemistry of septicinity, *Effluent Water Treatment Journal*, **1**, 16-25.

Hartmans, S., and Tramper, J. (1991)Dichloromethane removal from waste gases with a trickle-bed bioreactor. *Bioprocess Engineering*, **6**, 83-92.

Hellwig, G. (1998) U.S. Federal and state laws, in *Odor and VOC Control Handbook*, Rafson, H.J. ed., McGraw-Hill, New York, 10.11-10.17.

Huismann, B.C., de Nie, L.H., Peters, H.F., Poel, P.W. (1987) Odour emission and control in the Dutch sugar industry. *Zuckerind*, **112**(11), 958-965.

Hwang, Y., Matsuo, T., Hanaki, K., and Suzuki, N. (1994) Removal of odorous compounds in wastewater by using activated carbon, ozonation and aerated biofilter. *Water Science and Technology*, **28**(11), 2309-2319.

Kirchner, K., Schlachter, U., and Rehm, H.J. (1989) Biological purification of exhaust air using fixed bacterial monocultures, *Applied Microbiology and Biotechnology*, **31**, 629-632.

Kleinheinz, G.T. and Bagley, S.T (1998) Biofiltration for the removal and 'detoxification' of a complex mixture of volatile organic compounds, *Journal of Industrial Microbiology and Biotechnology*, **20**(2), 101-108.

Laplanche, A., Bonnin, C. and Darmon, D. (1994) Comparative study of odors removal in a wastewater treatment plant by wet scrubbing and oxidation by chlorine or ozone, in *Characterization and control of Odoriferous Pollutants in Process Industries*, Vigneron, S., Hermia, J., and Chaoki, J., eds, Elsevier Science B.V. Amsterdam, 277-294.

Lau, A.K., Bruce, M.P., and Chase, R.J. (1996) Evaluating the performance of biofilters for composting odor control. *Journal of Environmental Science and Health, part A*, **31**(9), 2247-2273.

LeCloirec, P., Gueux, M., Paillard, H. and Anselme, C. (1994) Sources of volatile organic compounds and study of odorous pollution, in *Odor and Deodorization in the Environment*, Martin, G. and Laffort, P. eds, VCH Verlagsgesellchaft, Weinheim, New York, USA, 213-263.

Levett, P.N. (1991) Identification of clinically important anaerobes, in *Anaerobic Microbiology A Practical Approach* , Levett, P.N. ed., Oxford University Press, New York, USA, 29-49.

Leson, G., and Winer, A.M. (1991) Biofiltration: an innovative air pollution control technology for VOC emissions. *Journal Air & Waste Management Association*, **41**(8), 1045-1054.

Moss R.L. (1980) Catalytic afterburners, in *Odour control: a concise guide*, Valentin, F.H.H. and North, A.A. eds, Warren Spring Laboratory, Department of Industry, Stevenage, England, 61-76.

Mpanias, C.J. and Baltzis, B.C. (1998) An experimental and modeling study on the removal of mono-chlorobenzene vapor in biotrickling filters, *Biotechnology and Bioengineering*, **59**(3), 328-343.

Oh, Y.S. and Bartha, R. (1994) Design and performance of a trickling air biofilter for chlorobenzene and o-dichlorobenzene vapors. *Applied and Environmental Microbiology*, **60**, 2717-2722.

Ottengraf, S.P.P (1986) Exhaust Gas Purification, in *Biotechnology*, vol. 8, Rehm, H.J., and Reed, G., eds., VCH Verlagsgesellchaft, Weinheim, Germany, 426-452.

Ottengraf, S.P.P. (1987) Biological systems for waste gas elimination, *Trends in Biotechnology*, **5**, 132-136.

Ottengraf, S.P.P., and Van Den Oever, A.H.C. (1983) Kinetics of organic compound removal from waste gases with a biological filter. *Biotechnology and Bioengineering*, **25**, 3089-3102.

Pomeroy, R.D. (1982) Biological treatment of odorous air. *Journal of Water Pollution Control Federation*, **54**(12), 1541-1545.

Prokop, W.H., and Bohn, H.L. (1985) Soil bed system for control of rendering plant odors, *Journal of the Air Pollution Control Association*, **35**(12), 1332-1338.

Rix, M. (1998) Odor and VOC regulations in Canada, in *Odor and VOC Control Handbook*, Rafson, H.J. ed., McGraw-Hill, New York, 10.2-10.10.

Roberts, M.C., Johnson, C.E. and Miller, R.C. (1971) Removal of H_2S from waste gases, U.S. Patent No. 2, 104-250.

Shanahan, I. (1993) Odour control in wastewater treatment process, *Institute of Water Officers Journal*, April, 32-37.

Shim, H. and Yang, S.T. (1999) Biodegradation of benzene, toluene, ethylbenzene, and *o*-xylene by a coculture of *Pseudomonas putida* and *Pseudomonas fluorescens* immobilized in a fibrous-bed bioreactor, *Journal of Biotechnology*., **67**(2-3), 99-112.

Silva, E.M. and Yang, S.T. (1995) Kinetics and stability of a fibrous-bed bioreactor for continuous production of lactic acid from unsupplemented acid whey., *Journal of Biotechnology*, **41**(1), 59-70.

Smet, E., Lens, P. and Van Langenhove, H. (1998) Treatment of waste gases contaminated with odorous sulfur compounds, *Critical Reviews in Environmental Science and Technology*, **28**(1), 89-117.

Sorial, G.A., Smith, F.L., Suidan, M.T., Biswas, P., and Brenner, R.C., (1995) Evaluation of trickled bed biofilter media for toluene removal. *Journal of the Air and Waste Management Association*, **45**, 801-810.

Sorial, G.A., Smith, F.L., Suidan, M.T., Pandit, A., Biswas, P., and Brenner, R.C., (1997) Evaluation of trickled bed air biofilter performance for BTEX removal. *Journal of Environmental Engineering*, **123**(6), 530-537.

Sorial, G.A., Smith, F.L., Suidan, M.T., Pandit, A., Biswas, P., and Brenner, R.C. (1998) Evaluation of trickle-bed air biofilter performance for styrene removal, *Water Research*, **32**(5), 1593-1603.

Swanson, W.J. and Loehr, R.C. (1997) Biofiltration: fundamentals, design and operations principles, and applications, *Journal of Environmental Engineering*, **123**(6), 538-546.

Tanaka, H., Kuroda, K., and Osada, T., Yonaga, M., Suzuki M. and Inaba, M. (1991) Aerial VFA in livestock houses and animal waste treatment facilities, *Animal Science and Technology*, **62**(10), 955-962.

Tanaka, H., Kuroda, K., and Yonaga, M. (1992) Biological removal of VFA from animal wastes, *Animal Science and Technology*, **63**(1), 54-59.

Tang, H., Hwang, S., and Hwang, S. (1996) Waste gas treatment in biofilters, *Journal of Air and Waste Management Association*, **46**(4), 349-354.

Terasawa, M., Hirai, M. and Kubota (1986) Soil deodorization systems, *BioCycle*, **27**(6), 28-32.

Tichy, R., Grotenhuis, J.T.C., Bos, P. and Lens, P. (1998) Solid-state reduced sulfur compounds: environmental aspects and bioremediation, *Critical Reviews in Environmental Science and Technology*, **28**(1), 1-40.

Turk, A., Mahmood, K. and Mozaffari, J. (1993) Activated carbon for air purification in New York city's sewage treatment plants, *Water Science and Technology*, **28**, 2545-2552.

Turk, A., Sakalis, E., Lessuck, J., Karamitsos, H. and Rago, O. (1989) Ammonia injection enhances capacity of activated carbon for hydrogen sulfide and methyl mercaptan, *Environmental Science and Technology*, **23**, 1242-1245.

Van Groenestijn, J.W. and Hesselink, P.G.M. (1993) Biotechniques for air pollution control, *Biodegradation*, **4**, 283-301.

Webster, T.S., Devinny, J.S., Torres, E.M., and Basrai, S.S. (1996) Biofiltration of odors, toxics and volatile organic compounds from publicly owned treatment works. *Environmental Progress*, **15**(3), 141-147.

Weckhuysen, B., Vriens, L., and Verachtert, H. (1994) Biotreatment of ammonia-and butanal-containing waste gases. *Applied Microbiology and Biotechnology*, **42**, 147-152.

Westmeier, F. and Rehm, H. J. (1987) Degradation of 4-chlorophenol in municipal wastewater by adsorotive immobilized Alcaligenes sp. A 7-2, *Applied Microbiology and Biotechnology*, **26**, 78-83.

Williams, T.O. and Miller, F.C. (1992) Odor control using biofilters, *BioCycle*, **33**(10), 72-77.

Wu, G., Chabot, J.C., Caron, J.J. and Heitz, M (1998) Biological elimination of volatile organic compounds from waste gases in a biofilter, *Water, Air, and Soil Pollution*, **101**(1-4), 69-78.

Yang, S. T., Zhu, H. and Li, Y. (1994) Continuous propionate production from whey permeate using a novel fibrous bed bioreactor, *Biotechnology and Bioengineering*, **43**(11), 1124-1130.

Yang, S.T. and Shu, C.H. (1996) Kinetics and stability of GM-CSF production by recombinant yeast cells immobilized in a fibrous bed bioreactor, *Biotechnology Progress*, **12**, 449-456.

Yang, S.T., Huang, Y., and Hong, G. (1995) A novel recycle batch immobilized cell bioreactor for propionate production from whey lactose, *Biotechnology and Bioengineering*, **45**(5) 379-386.

Yang, S.T., Tang, I.C. and Hong, G. (1992) A novel fermentation process for calcium magnesium acetate (CMA) production from cheese whey, *Applied Biochemistry and Biotechnology*, **34/35**, 569-583.

RELATED PUBLICATIONS

Refereed journal articles:

1. H. Chua, X.Z. Li, **C.Y. Tam**, Y.L. Huang and S.T. Yang (1998), Biofiltration of VFA using a novel fibrous bed bioreactor. *Journal of the Institute of Engineers, Singapore*, **38**, 51-54.
2. H. Chua, X.Z. Li, P.H.F. Yu, **C.Y. Tam**, Y.L. Huang and S.T. Yang (1999), Performance of fibrous bed bioreactor for treating odorous gas. *Applied Biochemistry and Biotechnology*, **77**, 561-569.
3. H. Chua, X.Z. Li, P.H.F. Yu, **C.Y. Tam**, Y.L. Huang and S.T. Yang, Design and performance of a novel fibrous bed bioreactor for odor treatment. *Applied Biochemistry and Biotechnology*. (In press)
4. H. Chua, X.Z. Li, **C.Y. Tam**, Y.L. Huang and S.T. Yang, Deodorization of contaminated air by immobilized microbes. *Toxicological and Environmental Chemistry*. (In press)

Conference Presentations:

1. H. Chua, X.Z. Li, **C.Y. Tam**, Y.L. Huang and S.T. Yang (1998), Biofiltration of VFA using a novel fibrous bed bioreactor. Presented in IAWQ specialty conference on microbial ecology of biofilms, Illinois, USA, 8-10 Oct 1998.
2. **C.Y. Tam**, H. Chua, X.Z. Li, P.H.F. Yu, Y.L. Huang and S.T. Yang (1999), Biofilter system for odor treatment in industrial fouled air discharge. Presented in Asian industrial technology congress 99, Hong Kong, 26-29 Apr 1999.
3. H. Chua, X.Z. Li, **C.Y. Tam**, Y.L. Huang and S.T. Yang (1999), Deodorization of contaminated air by immobilized microbes. Presented in International conference on urban pollution control technology, Hong Kong, 13-15 Oct 1999.