BIOFILTRATION FOR THE REMOVAL OF REDUCED SULFUR GASES FROM LOW CONCENTRATION AIR STREAMS

by

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A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF
THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

in

THE FACULTY OF GRADUATE STUDIES
(Department of Chemical & Bio-Resource Engineering)

We accept this thesis as conforming
to the required standard

THE UNIVERSITY OF BRITISH COLUMBIA

August 1999

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Vancouver, Canada

Date _August 25, 1999_

DE-6 (2/88)

ABSTRACT

In the work reported here, media effectiveness, bioelimination rates and the operational features of aerobic biodegradation of reduced sulfur gases (hydrogen sulfide, methyl mercaptan, dimethyl sulfide and dimethyl disulfide) in compost, hog fuel, and the mixture of compost and hog fuel biofilters have been investigated. Specific consideration was given to the biofilter media characterization, the elucidation of phenomena occurring during the transient conditions in biofilters, and the evaluation of media effectiveness in removing reduced sulfur gases both singly and in mixtures to illustrate the inhibitory effects, if any, of one contaminant on the removability of another.

Biofilter media characterization identified the significant role of filter material C/N ratio on biofilter media degradation and the length of media useful life. Stage-wise first order kinetics proved appropriate in describing the mineralization of media carbon. Compost filter media was found to be easily degradable with a loss of 17% media carbon within 127 days of incubation with ambient air in comparison to 6 and 12% carbon loss in hog fuel and the mixture (50:50 compost:hog fuel) biofilter media, respectively. Media decomposition was significantly enhanced in the presence of reduced sulfur gases as a result of increased bioactivity by sulfur-oxidizing bacteria and other microorganisms thereby decreasing the media half-life by more than 50%.

Evaluation of the transient response of biofilters exposed to abrupt changes in contaminant concentration and/or waste airflow rate highlighted the key role of sorption/desorption process during the transient state operation. Biofilters recovered to their initial removal capacities rapidly and, in general, the steady states were re-established within 2 to 12 hours after perturbations occurred. Contaminant concentration spikes in the waste air stream demonstrated major substrate inhibition that occurred with short-term exposure of biofilters to methyl mercaptan concentrations of 158 ppmv, however, in case of hydrogen sulfide similar inhibitory effects were observed at concentrations above 615 ppmv. Biofilters were found to be capable of withstanding downtime periods with rapid recovery to full performance when starvation ceased, and the re-

acclimation times for the biological activity after different periods of non-use were significantly shorter than the initial startup times.

A Michaelis Menten type kinetic model modified for plug flow behavior of biofilters, with the assumptions of steady state, negligible dispersion, and rapid contaminant transfer between phases very well described the bioelimination rates in the three biofilter media materials investigated. Hydrogen sulfide biodegradation was found to be independent of the coexistence of organic sulfur gases with the maximum bioelimination capacities of 136.1, 136.8 and 138.3 g m^{-3} h^{-1} in compost, hog fuel and the mixture biofilter, respectively; and there were no noticeable differences amongst the three biofilters in their capacities for the bioelimination of hydrogen sulfide. However, the bioremovability of dimethyl sulfide and dimethyl disulfide was significantly reduced in presence of other reduced sulfur gases, and the filter materials significantly varied in their capacities for the removal of methyl sulfides. The maximum elimination capacity of the compost, hog fuel and the mixture biofilter for dimethyl sulfide, as a single pollutant, was reduced by a factor of 1.4 to 2 from its initial values of 5, 3.8 and 4.6 g m^{-3} h^{-1}, respectively, with the co-supply of methyl mercaptan and dimethyl disulfide. But, the presence of hydrogen sulfide had no adverse effects on the biodegradation of dimethyl sulfide. Instead it slightly improved the dimethyl sulfide bioelimination. Dimethyl disulfide maximum elimination rates of 16.9, 12.3 and 13.6 g m^{-3} h^{-1}, as a single contaminant, in compost, hog fuel and the mixture biofilter respectively, were significantly reduced to 10.8, 8.4 and 9.6 g m^{-3} h^{-1} in presence of hydrogen sulfide, and to 7.5, 6.1 and 7.4 g m^{-3} h^{-1} with the co-supply of dimethyl sulfide.

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ACKNOWLEDGEMENTS

Dedicated

to

My Parents (Mr. & Mrs. G.A. Wani)
In Deep Appreciation of Their Love

and

My Academic Supervisor (Prof. R.M.R. Branion)
As a Gratitude for His Encouragement and Guidance

PREFACE

This thesis is based on the following manuscripts that have either been published or submitted for publication in refereed journals:

1. Wani A.H., Branion R.M.R., Lau A.K. Biofiltration: A promising and cost-effective control technology for odors, VOCs and air toxics. *J. Environ. Sci. & Health.* **32A**, 2027-2055, 1997.

2. Wani A.H., Branion R.M.R., Lau A.K. Degradation kinetics of biofilter media materials treating reduced sulfur odors and VOCs. *J. Air & Waste Mgmt. Assoc.* **48**, 1183-1190, 1998.

3. Wani A.H., Branion R.M.R., Lau A.K. Effects of periods of starvation and fluctuating hydrogen sulfide concentration on biofilter dynamics and performance. *J. Hazardous Materials.* **60**, 287-303, 1998.

4. Wani A.H., Lau A.K., Branion R.M.R. Biofiltration control of pulping odors – Hydrogen sulfide: Performance, macrokinetics and coexistence effects of organo-sulfur species. *J. Chem. Technol. Biotechnol.* **74**, 9-16, 1999.

5. Wani A.H., Lau A.K., Branion R.M.R. Performance of compost and hog-fuel biofilters: Impact of periods of non-use and varying methyl mercaptan loading. *Environ. Technol.* 1999. (*in press*).

6. Wani A.H., Lau A.K., Branion R.M.R. Transient behavior of compost and hog-fuel biofilters: Initial start-up, re-acclimation and impact of fluctuating dimethyl disulfide loading. *Environ. Technol.* (*submitted* 1999).

7. Wani A.H., Lau A.K., Branion R.M.R. Biodegradation of dimethyl sulfide in compost and hog-fuel biofilters: Removal characteristics, macrokinetics, and interaction with other reduced sulfur gases. *Environ. Sci. Technol.* (*to be submitted*).

8. Wani A.H., Lau A.K., Branion R.M.R. Biofiltration of air polluted with dimethyl disulfide: Media performance, removal characteristics, and bioelimination macrokinetics. *Ind. Eng. Chem. Res.* (*to be submitted*).

CHAPTER I

GENERAL INTRODUCTION

Odor from chemical pulp mills is one of the major public perception problems facing the pulp and paper industry. There are no technology gaps that prevent achieving relatively large reductions in odorous gas emissions, however, the achievement of "odor free" operations is a difficult goal for fugitive emission sources. Area and fugitive sources, such as from effluent treatment systems, are the cause of a great deal of the odor problems associated with kraft pulp mills.

Atmospheric emissions from the kraft pulping process include both gaseous and particulate materials. The major gaseous emissions are malodorous reduced sulfur compounds such as hydrogen sulfide, methyl mercaptan, dimethyl sulfide, and dimethyl disulfide commonly referred to as "total reduced sulfur (TRS)"; oxides of sulfur, and oxides of nitrogen. Other gaseous pollutants include alcohols, ketones, terpenes, phenols and acids. The concentration of these malodorous pollutants ranges from traces to about 1% by weight. Most of the sulfur bearing compounds are by-products from the chemical pulping reaction between sodium sulfide, a pulping chemical and the lignin in wood, while the presence of terpenes depends on the wood species being pulped. The odor threshold of these TRS gases is very low and can be detected by the human nose at concentrations of only a few parts per billion (ppb). The major sources of TRS emissions are the digester blow and relief streams, vacuum washer hoods and seal tank vents, multiple-effect evaporation hot well vents, recovery furnace flue gases, smelt-dissolving tanks, slaker vents, black liquor oxidation tanks, lime kiln exit vents and wastewater treatment operations. The largest sources of potential emissions are the recovery furnace, followed closely by the digester blow gases and the washer hood vents, while the most concentrated emissions come from the digester blow and relief gases.

In the kraft pulping process caustic soda and sodium sulfide are the basic chemicals used in the cook, and the resulting product is termed kraft or sulfate pulp. Some of the sulfide reacts with the lignin giving rise to the odors characteristic of kraft mills. The amount of odorous materials

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released in the kraft pulping process is dependent upon wood species, pulping conditions, the nature of subsequent processing, and the relative flow rates of the various streams.

Gas scrubbers, adsorption, condensation, oxidation, and other air pollution control systems have been used to remove the majority of air pollutants from these off-gas streams, however, despite these efforts, significant quantities of odorous and toxic volatile organic compounds are still released from many pulp and paper mills. These releases include residuals in already treated off-gas streams and fugitive emissions e.g., from wastewater treatment facilities. The concentration of these odorous gases required to be cleaned from waste gas streams generally makes the use of conventional control systems difficult and expensive.

An innovative approach for dealing with these low concentration waste gas streams is via biological means such as biofilters, bioscrubbers and biotrickling filters, collectively known as biological gas cleaning (BGC) technologies. Biofilters are microbial systems incorporating microorganisms grown on a porous solid media like compost, peat, soil, activated carbon or a mixture of these materials, surrounded by a thin film of water called the biofilm. Waste-gases containing biodegradable volatile organic compounds and inorganic air pollutants are vented through this biologically active material, where soluble contaminants partition into the liquid film and are biodegraded by the resident microorganisms in the biofilm into carbon dioxide, water, additional biomass and innocuous metabolic products. Biofiltration is suitable for the control of dilute air streams of biodegradable compounds. The adsorptive capacity of the filter bed plays an important role in damping the fluctuating contaminant concentrations, and in the removal of less water soluble compounds.

Biofiltration is an attractive air emission control technology for the pulp industry for several reasons. First, it is a cost (in terms of both capital and operating costs) effective approach for treating moist, dilute streams; second, it breaks down compounds thereby preventing the cross media transfer of pollutants; third, it is simple in operation and requires only minimal operational control; and fourth, it has the potential to use normally wasted materials such as bark/hog fuel, etc. as the filter medium. Nevertheless, the main limitation of biofiltration is a large land area requirement in comparison to other two types of BGC technologies bioscrubbers and trickling filters.

Although the biofiltration process has been shown to be an effective, practical and simple biological waste air technology that is increasingly being used around the world, a knowledge gap does exist in biofiltration control of these reduced sulfur odors. Design and operational parameters as well as the microbiological processes involved have not been very well defined. A systematic compilation of data from an operational view point is also lacking. The performance of biofilter systems, therefore is not readily predictable and sometimes these systems are not operated under suitable conditions, as a result the desired elimination efficiency is not achieved. The main reasons for channeling (short-circuiting) of untreated gases are usually compaction and drying of the filter media, and acidification of the filter material due to sulfate accumulation. The ease of biodegradability, chemical bonding, solubility of organo-sulfur compounds and inhibition of various enzymatic reactions also play pivotal roles. Differences in the composition of a gas stream result in different types of inhibition of enzyme-catalyzed reactions and reduce the overall removal efficiency. In order to overcome the uncertainties and disadvantages encountered in the full-scale application of biofiltration technology it would be desirable to document biofiltration performance in terms of the operational parameters and maintenance procedures.

The overall objective of this thesis project, therefore, is to obtain a quantitative understanding of the fundamental principles and operation of a biofiltration unit for the control of TRS odorous gases from waste gas streams typical of kraft pulp mills. Emphasis was placed on evaluating the basic removal mechanisms and appropriate filtering media essential for optimization of biofiltration performance.

This thesis is presented in six chapters. A brief introduction to the subject presented in this chapter is followed by a review of literature on biofiltration technology in Chapter 2, wherein individual steps involved in biofiltration and its overall advantages are presented in detail. Chapter 3 deals with the evaluation of degradation phenomena of biofilter materials while treating reduced sulfur gases and the influence of TRS gases on biofilter media half-life. Results of the investigations on the dynamics and transient response of biofilters are presented in Chapter 4. The effect of important operational parameters such as downtime periods, contaminant load, waste gas residence time, and step changes in concentration and flow are discussed. In Chapter 5 steady state operating data for biofilters degrading single and multiple contaminants are reported.

The evaluation of biofilter media effectiveness and the bioelimination macrokinetics[*] for TRS gas degradation are presented. Finally, in Chapter 6 the overall findings are placed in perspective with consideration for further research on the biofiltration of TRS gases.

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[*] macrokinetics means not separating the effects of gas-liquid mass transfer rates from biological degradation rates

CHAPTER II

REVIEW OF BIOFILTRATION TECHNOLOGY

2.1. ABSTRACT

Biofiltration, a relatively recent air pollution control technology, has been identified as a promising method of odor, VOC and air toxic removal from waste-gas streams because of its low capital and operating costs, low energy requirements and an absence of residual products requiring further treatment or disposal. Biofiltration units are microbial systems incorporating microorganisms grown on a porous solid media like compost, peat, soil or mixture of these materials. The filter media and the microbial culture are surrounded by a thin film of water called a biofilm. Waste-gases containing biodegradable VOCs and inorganic air toxics are vented through this biologically active material, where soluble contaminants partition into the liquid film and are biodegraded by the resident microorganisms in the biofilm. The technology has been successfully applied to a wide range of industrial and public sector sources for the abatement of odors, VOCs and air toxics, often with an elimination efficiency of more than 90%. Owing to its economic advantages over conventional air pollution control methods, coupled with environmental benefits like low energy requirements and the avoidance of cross-media transfer of pollutants, biofiltration is becoming more popular and practical in meeting the statutory emission regulations. This study presents an overview of the historical development and present status of biofiltration and summarizes its basic requirements, engineering fundamentals, operating principles, applicability, cost-effectiveness and potential failures.

2.2. INTRODUCTION

Biodegradation is a natural phenomenon, occurring continuously in water, air and soil as a result of decomposition action of microorganisms on organic/inorganic compounds. These natural processes are presently being exploited in managing our environment. Biofiltration of waste gases is an example of the emerging application of biodegradation processes, utilizing microorganisms that are capable of oxidizing many compounds and thus having potential for being used for the abatement of odors, volatile organic compounds (VOCs), and air toxics[1]. The concept of biofiltration is actually not new, it is an adaptation of the process by which the atmosphere is cleaned naturally[2],

however, biofiltration is in its infancy for application to gas purification under controlled conditions.

Biofiltration is analogous to the biological treatment of wastewater or in-situ bioremediation of contaminated soils and hazardous sludge[3]. It is becoming more popular as new processing twists are explored and stringent emission regulations are implemented. The acceptance of biofiltration has followed from biotechnological advances that provide an increasingly thorough knowledge of the system and how the process can be optimized not only to achieve high removal efficiencies with low energy consumption but importantly, to achieve these elimination efficiencies over long periods of time with minimal operator intervention and/or need for maintenance[4]. VOC emissions have become a substantive issue for industrial operators as a result of the implementation of the US 1990 Clean Air Act Amendments and similar regulations in Europe, and thus a major driving force for the exploration of cost effective control options. Biofiltration could be a promising control technology for processes such as kraft pulp manufacture that emit large off-gas volumes with relatively low concentrations of contaminants. With respect to the purification of polluted air, biofiltration is a frequently applied technique to odor abatement, where it is an established control method. It has also demonstrated limited success in controlling VOCs[5].

Biofiltration uses naturally occurring microorganisms immobilized in the form of a biofilm on a porous substrate such as soil, compost, peat, bark, synthetic substances or their combination. The substrate provides the microorganisms with both a hospitable environment in terms of oxygen, temperature, moisture, nutrients, pH and a carbon source of energy for their growth and development. As the contaminated air stream passes through the filter bed, contaminants are transferred from the vapor phase to a thin biofilm containing the microorganisms and water, which covers the surface of the packing particles. The microorganisms utilize these favorable conditions to metabolize carbon based compounds to their primary components - carbon dioxide and water, plus additional biomass and innocuous metabolic products[1,3-5]. The absorption and/or adsorption capacity of the filter media is thus continuously renewed by the biological oxidation of the sorbed contaminants[6,7].

Biofiltration has the advantage that the pollutants are not transferred to another phase and therefore, new environmental problems are not created or are only minimal i.e., air pollution problems are not

converted to water pollution problems[1,8,9]. Moreover the process is said to be cheap and reliable, and does not usually require complex process facilities[1]. Unfortunately, its inexpensiveness has resulted in the cynical perception that "if it's cheaper, it can't be any good". The low cost of biofiltration is associated with its use of natural rather than synthetic sorbents and microbial rather than thermal or chemical oxidation[2].

2.3. HISTORICAL DEVELOPMENT

Biofiltration has been used to control odors for many years in Germany, the Netherlands, the UK, Japan and to a limited extent in the USA, but the use of biofilters to degrade more complex air emissions from chemical plants has occurred only within the last few years[4,10-12]. Because of its technical and economic advantages this vapor-phase biological treatment is rapidly gaining acceptance as an abatement technology for use in the treatment of VOCs, including odorous chemicals and air toxics[12]. The process has been tested technically for about 30 years[13]. It was initially applied to odor abatement in composting works, waste water treatment plants and similar situations. It is known that in 1953 a soil biofilter system was used for the treatment of odorous air in Long Beach, California[14]. In Europe the first attempt with a soil bed was made in Geneva for deodorization at a composting facility[8]. Around 1959 a soil bed system was used at municipal sewage treatment in Nuemberg, Germany[10,15]. In early 1960s Carlson and Leiser[16] started systematic research on biofiltration in the USA and used biofilters to treat hydrogen sulfide emissions from sewage. After that biological gas cleaning made considerable progress, but is still in its developing stages for application to the control of VOCs and air toxics in industrial use.

During the last two decades research activities, especially on the soil bed systems, have intensified in USA with the installation of some full scale operations[17-19]. Excellent reviews of the historical development of biofiltration have been presented by Ottengraf[8], Leson and Winer[10], and Shimko et al[15]. Having proven its success in deodorization, recent research and application of biofiltration has been focused on the removal of VOCs and air toxics from the chemical and other process industrial exhausts. Current research activities are aiming at understanding the practical behavior of the biofiltration process, optimizing its operational parameters and modeling the system on the basis of reaction kinetics for single as well as multiple contaminant gas streams. More detailed discussions on these issues has been presented by various researchers[8,20-37].

2.4. PROCESS ENGINEERING FUNDAMENTALS

This section briefly introduces the theory and process engineering fundamentals of biofiltration. More theoretical descriptions of the processes involved in the operation of a biofilter can be found in several publications[1,8,20-23,38].

Biofiltration is based on microbial degradation. The operation of a biofilter, then, has a rather complex microbiological and physical basis. Waste gas is fed to a fixed bed of soil, compost, peat or plastic beads, to which the microorganisms and nutrients are attached, where unwanted contaminants are oxidized by microorganisms to mineral compounds such as carbon dioxide, water and mineral salts. In some recent designs microorganisms have been immobilized on carrier materials like porous polypropylene pellets, Ca-alginate, etc. to enhance the viability of microorganisms[39,40]. VOCs in the waste gas serve as the source of energy and/or carbon for the heterotrophic microbial metabolism, while oxidizable inorganic compounds like hydrogen sulfide and ammonia are treated directly by autotrophic microorganisms. Both the contaminants to be degraded and the oxygen required for degradation must enter the liquid phase, because water is the habitat for microorganisms[8,13,41]. Because the component interchange surface is very large, the solubility of the contaminants can be very small[4,23]. The transformation process can be expressed in simplified form as follows:

$$\text{UNDESIRED GASEOUS POLLUTANT} + O_2 \xrightarrow{\textit{BACTERIA}} \text{CELL MASS} + CO_2 + H_2O + \text{HEAT}$$
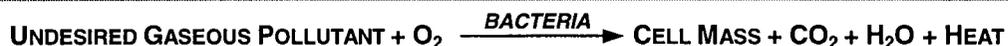
In addition to these products, mineral salts and acid metabolic byproducts are also produced depending upon the type of the contaminant treated.

In a nutshell, biofiltration can be divided into two consecutive processes as: (1) absorption/ adsorption of the waste-gas components into or on the biofilm, and (2) bacterial regeneration of the biofilm as a result of microbial transformation of the sorbed substances with the consumption of oxygen.

2.4.1. Kinetics and Modeling

To calculate the necessary dimensions for a biofilter it would be desirable to have a complete set of mathematical tools available or, in other words, to have a mathematical model of the process[23]. To optimize a biofilter, process kinetic analyses are important. Preliminary laboratory and pilot tests

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have shown positive results using predictive modeling for biofilter designs[8,12,20-37,43]. In a simplified model, mass transfer of the contaminant in the waste gas is assumed to take place in a wet biolayer, situated around each packing particle. The contaminants diffuse through the biolayer and are simultaneously degraded, and the total elimination rate is dependent on diffusion and degradation (reaction). While the reaction rate can be expressed as zero-order, first-order or pseudo-first-order; the diffusion rate is dependent on physical phenomena such as the concentration gradient, physical properties of the gas and liquid, and the solubility of the contaminant[1,8,42].

Figure 2.1 illustrates a simplified biophysical model of the biofiltration process. Biodegradation rates tend to be independent of pollutant concentration levels (i.e., are zero-order) at high concentrations and at low concentrations the degradation rate is proportional to the concentration of the substrate present (i.e., first-order)[43]. At low gas phase concentrations or low water solubilities of the contaminants the elimination rate in the filter bed becomes diffusion-controlled[1,8], and the energy available becomes insufficient to support the microbial population[45]. In the case of hydrophobic or poorly water soluble contaminants the limitation can be overcome by a pretreatment such as photochemical oxidation that on one occasion caused a three-fold increase in the biodegradation of styrene[46].
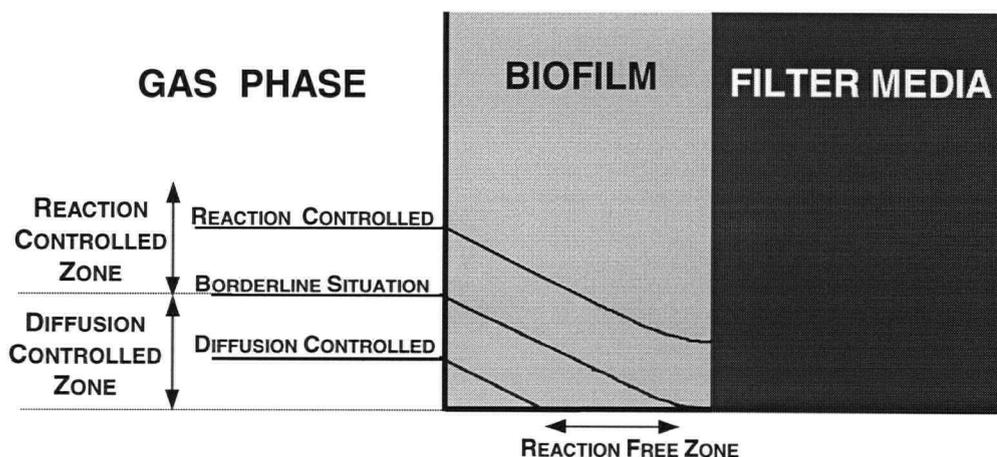
Figure 2.1. Simplified biophysical model of biofiltration

The biodegradation kinetics of organics are significantly affected by the concentration of the compound itself and the presence of other compounds in the gas stream, due to interactions between the compounds present in the gas stream[45,47]. In the case of cometabolism a second substrate is required to induce the necessary enzymes before metabolism of the target compound can take place[45]. Sometimes inhibition can occur when two or more compounds are present because

of the preferential uptake of one compound (diauxy) or because of the toxic interactions of compounds[23,45]. van Langenhove et al[48] reported the inhibition of aldehyde biofiltration by sulfur dioxide, with a reduction in removal efficiency from 85 to 40% at 40 ppmv SO_2. Similar coexistence effects have been observed in the biodegradation of odorous reduced sulfur compounds with inhibitive effects of H_2S and methyl mercaptan on methyl sulfides[49-52].

Biofilter kinetics and theoretical design criteria have been addressed in detail by various researchers[8,12,20-37,43,44]. A number of simple mathematical models have been developed to help explain and predict biofilter performance as a function of residence time and the inlet contaminant concentration. Elimination rates have been approximated by zero order kinetics[20-23], first order kinetics[26-34], and saturation kinetics (Monod kinetics)[24,25,35-37,52]. Ottengraf's model incorporating both diffusion as well as reaction limitations allows quantitative description of the basic processes involved in biofiltration and accurate sizing of the biofilter for a single contaminant off-gas. Its applicability to a multi-component waste gas stream, that is often encountered in industrial application, is limited by the increasing mathematical complexity needed for multiple components and because individual components would be biodegraded independently[10]. However, recent attempts have been made to account for the multiple gas streams by Deshusses et al[35-37] and somewhat encouraging results have been obtained.

2.5. DESIGN AND OPERATIONAL FEATURES

Proper design of a biofilter requires consideration of a number of technical issues from biocatalysts (the microorganisms) to their living space (the packing/filter media) through various environmental factors vital for the biological activity. Besides a proper selection of microorganisms and their support media, the components needed for pre-conditioning of the waste gas stream, its transport to and uniform distribution throughout the filter bed are the other main elements of a biofilter design[10]. The incoming air must be evenly distributed over/under the bed depending upon the flow direction, with no bypassing around the edges, and its velocity through, or residence time in the bed must be sufficient for complete destruction of the contaminant[15]. There are several ways of uniformly distributing the waste gas stream into the filter bed depending on flow direction and these have been addressed in detail elsewhere[2,6,13,19,54-57]. A conceptual design of a typical downflow biofilter is shown in Figure 2.2.
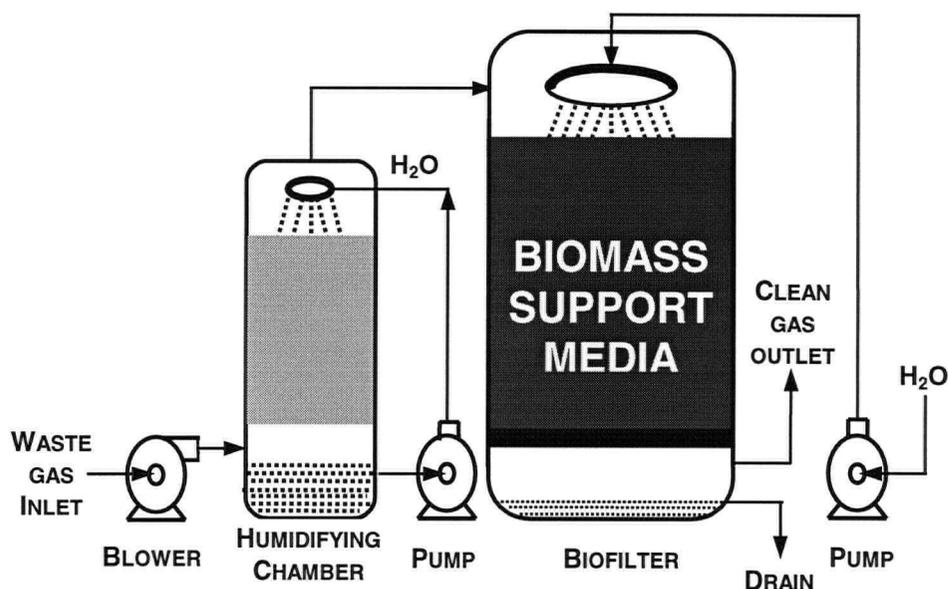
Figure 2.2. A conceptual design of a typical biofilter

The design of a biofilter bed required for maximum removal of the target contaminant depends primarily upon the pollutant load per unit time ($g\ m^{-3}\ h^{-1}$) and the degradation capacity of the filter material under optimal condition for the specific off-gas contaminant ($g\ m^{-3}\ h^{-1}$). These degradation rates vary widely from contaminant to contaminant and are predominantly dependent on the type of pollutant, and the biological and physical characteristics of the filter material. An excellent summary on the biodegradability rating of VOCs has been published elsewhere[58]. For common air pollutants 10 to 100 $g\ m^{-3}\ h^{-1}$ is a typical range[10] and for specific compounds the degradation rates can be found from the published literature[22,23,49,59-63].

The large mass of the filter bed often provides sufficient damping capacity to prevent breakthrough during peak loads and allows for dimensioning based on the hourly averages rather than instantaneous peak loads. However, the buffering capacity of the filter material varies with the filter material itself owing to its adsorption capacity, the pollutant type due to its water solubility, and the surface loading[10]. These buffering capacities of the filter media can allow for the rapid changes in contaminant concentrations as demonstrated by Tonga et al[12], Ergas et al[45], and Deshusses et al[47]. Specific surface loads up to 300 $m^{3}\ m^{-2}\ h^{-1}$ are usually feasible without excessive pressure losses and can go to around 500 $m^{3}\ m^{-2}\ h^{-1}$ for an optimized filter bed mixture of compost and bark[10,64]. According to Werner et al[65] the guide values for the specific filter load range from 80 to 150 $m^{3}\ m^{-2}\ h^{-1}$, depending on the biodegradability of the waste gas component. For deodorization specific gas flow rates have ranged between 18 to 570 $m^{3}\ m^{-2}\ h^{-1}$ with typical values at 18 to 96 m^{3}

m^{-2} h^{-1}. A contact time of 30-60 s is recommended[67]. The lower residence time range applies to beds formed from compost owing to their open structure. Higher values apply to soil biofilters. For VOC removal residence times ranging between 20 and 60 s are desirable[68].

2.5.1. Filter Media

Filter media are the key components of a biofilter[69]. Filter media not only support the sorption effects, thereby ensuring adequate residence time for metabolic destruction, but also serve as a living space and reserve substrate for the microorganisms, a humidity reservoir, and as the mechanical support for the maintenance of the internal structure of the filter bed[4,65,66]. This last function is the key for maximum porosity and minimum pressure drop in the filter bed. Media particles usually are of a size that provides both a reasonable adsorbing surface and an acceptable flow resistance. Too small an adsorbing surface necessitates an overly large and consequently uneconomical filter volume, whereas too large a filter resistance requires an excessive energy consumption[1].

Theoretically, biodegradation of contaminants can occur on all substrates that are biologically active i.e., most surfaces can form a supportive medium for a wide range of microorganisms. These media do not differ much in their intrinsic biological activity as compared to their physical and mechanical properties. The key property of an intrinsically active filter media for biological oxidation is its structure. This must be and must remain at all times open enough to allow a uniform flow of air throughout the bed, with no blockages and/or bypassing[55]. Non-homogenous media cause channeling and air passes only through the most permeable sections of the filter. This enhances drying of the more permeable zones, reduces the detention time within the filter bed and eventually decreases the treatment efficiency[30].

Biofilter systems for gas cleaning mainly depend on the choice of packing media that have a large reactive surface, limited pressure drop, and that provide a suitable attachment surface for the biofilms. These media include peat, compost, wood bark, soil, carbon particles, inert synthetic packing materials or a combination[72]. The use of soil beds for odor control has been known for a long time. Soil beds are effective and safe because soil both adsorbs and oxidizes the odorous contaminants with removal efficiency of up to 99%[19,73]. However, soils are limited in effectiveness because they are prone to clogging and short circuiting.

Compost has been more widely used than soil[69]. The useful properties of compost are its high surface area, high air permeability, high water permeability, high water holding capacity, high microbial population and low cost[73,74]. However, compost does suffer from aging effects because of microbial mineralization. As a result compost beds settle over time, creating short circuiting and consequently should be replaced every few years[23,69]. Compost aging and subsequent compaction can be prevented to a large extent by using fully mature and stable compost.

Peat is preferred as a support media for microorganisms because of its absorption/adsorption properties, high cellulose content, large moisture retention capacity, buffering capacity and easy availability[68]. Martin[75] has presented a detailed analysis of peat as a medium for biofilters and other biological degradation.

Wood bark has also been used as packing material because of its excellent air permeability, easy availability and low cost[76]. Granulated activated carbon (GAC) as a sole support medium has demonstrated superior performance to soil and diatomaceous earth, because of its higher adsorptive capacity[7,29], however, the improvement was not so much better than compost as to justify the price difference[69]. Besides, some microorganisms can not easily acclimatize with the GAC, as observed by Graham[78] while treating non-BETX (benzene, ethylbenzene, toluene and xylene) reactive organic compounds (ROCs).

In recent years the composition of packing materials has undergone tremendous improvements to retard aging effects and to maintain bed porosity[1,64]. Pelletized compost is more stable both under moist as well as dry conditions than simple compost with higher elimination rates and lower pressure drops thereby reducing both investment as well as the operating costs[79]. Inorganic inert materials like polystyrene spheres, perlite, or ground scrap tires can be added to the organic media in order to maintain the bed porosity, and to prevent compaction and the development of lumps[8,77]. GAC is often mixed with the compost to provide a buffering capacity against shock loads because of its high adsorptive capacity[69]. GAC has also been reported to be useful in the biofiltration of hydrophobic contaminants. Mohseni and Allen[70] reported that a compost/wood chip filter medium amended with GAC gave higher elimination rates of 30-35 g α-pinene m^{-3} bed h^{-1} as compared to 0.75-2 g α-pinene m^{-3} bed h^{-1} obtained by Apel et al[71] with other filter media. With these optimized filter media the useful life of a filter bed can be up to five years[10,64].

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Biofilter medium depth ranges between 0.5 and 2.5 m. A depth of approximately 1 m appears to be most common, allowing sufficient residence time while minimizing filter land area requirements[67]. Multi-layer biofilters are used to deal with higher loading rates with less land area used[10]. Biofilter units even up to 5 m high in one section can be designed with the pelletized media without gas channeling[68]. Table 2.1, adapted from Bohn et al.[81], gives a comparison of soil, compost, and peat as filter media.

Table 2.1. Comparison of biofilter media types

| Parameter | Biofilter Media Type | |
	Soil	Peat & Compost
Removal efficiency	Medium	Low
Permeability to gas flow	Low	Medium
Initial Cost	Low	Medium
Maintenance requirements	Low	High
Space requirements	High	Medium
Substance adaptability	Medium	Low

These packing materials also supply the inorganic nutrients necessary for microbial life, therefore, need to be renewed after several years, depending upon the type of operation[1]. Finally, the choice of the packing material is determined by the structure, the porosity, the area per unit volume, the specific flow resistance and the ability of the filter media to hold water, both at the beginning as well as over the extended period of operation[8]. A good packing material should have high water retention capacity without becoming saturated, low bulk density, structural integrity, capacity to buffer acidification of the filter material, and the ability to buffer high peak concentrations of the contaminants[4].

2.5.2. Microorganisms

Several groups of microorganisms are known to be involved in the degradation of air pollutants in biofilters including bacteria, actinomycetes and fungi[1]. The microbial population is generally made up of autotrophic microorganisms - feeding directly from inorganic compounds, and heterotrophic microorganisms - utilizing organic compounds as sources of energy and carbon[4,41]. The composition and survival of microorganisms on the filter bed are key process parameters. Their

growth and activity depend on the physical and chemical conditions in the packing material viz., water, oxygen, mineral nutrients, carbon source, energy source, pH and the temperature[80]. The diversity of the active microorganisms is a function of the inlet gas stream composition[1].

Some packing materials of natural origin, like compost, contain a sufficient number of different microorganisms to initiate the reactions for the elimination of simple contaminants. The efficiency of the purification process is generally enhanced following the growth of active strains during the adaptation time after the start up of the biofilter. For easily biodegradable organic compounds acclimatization can typically take about ten days[8], and for less biodegradable and, those contaminants for which the microorganisms are less likely to be initially present in the biofilter material, the period can be longer[10]. Sinitsyn et al[82] reported that the acclimatization period for oxygen bearing substances like alcohols and ketones was very short, 2-3 days, in comparison to more than a week for reduced sulfur compounds such as hydrogen sulfide, methyl mercaptan and methyl sulfides in their biofilter treating kraft mill emissions. It has become a common practice to inoculate the filter bed with pure cultures of microorganisms capable of biodegrading more complex contaminants to reduce the adaptation time of the biofilter[22]. However it is not only the inoculum but the source of inoculum that makes a difference to the biofilter performance[83]. For instance, inoculation of a biofilter with a laboratory grown culture of microorganisms drastically reduced the acclimatization period for biodegradation of dichloromethane from 10 weeks to 10 days[53]. Similar results of very short or no acclimatization periods were observed for biofilters treating reduced sulfur gases, inoculated with *Thiobacillus* species[51,74,84-88]. In addition a six-fold increase in the removal rate of hydrogen sulfide was observed. Microbial breakdown pathways for different gaseous contaminants, like reduced sulfur compounds, have been studied for better understanding of their fate during biofiltration[89-92].

Microorganisms can survive for fairly long periods when the biofilter is not loaded with hardly any loss of microbial activity[20], and can go for up to two months if sufficient nutrients are available from the filter material[10]. This is important to know because it means that a filter bed can be quickly reactivated after an idle period. Tonga et al[12] reported that a biofilter treating styrene worked extremely well, without any reduction in the elimination efficiency, with discontinuous daily and weekly waste gas feeds, coupled with occasional extended plant shutdowns. Similar dynamic behavior of biofilters treating other organics like ketones and benzenes has been reported by

Deshusses et al[47], Martin et al [93] and Tang et al[94].

After selection of the proper filter media and the active microorganisms, to maximize the biodegradation of air-borne contaminants the following conditions, each of which significantly impacts microbial growth, must be optimized[3]:

- ◆ moisture content;
- ◆ temperature;
- ◆ oxygen content;
- ◆ pH levels;
- ◆ nutrients;
- ◆ waste gas pretreatment; and
- ◆ maintenance

2.5.3. Moisture Content

Moisture content of the filter bed is the single most critical factor for the biofilter effectiveness because microorganisms require water to carry out their natural metabolic reactions[4,8,15,48]. Variations in the moisture content within the filter bed have been shown to be the biggest single factor contributing to deterioration in its elimination performance[23]. Although water is essentially fixed in the reactor, it can leave the filter media through evaporation[23,68]. Besides being essential for microbial growth, moisture level also plays a vital role in the biodegradation of hydrophobic compounds like α-pinene[71], wherein a low moisture content could cause substrate toxicity due to higher contaminant concentration in the biofilm[95]. In the case of biofilters there is a target envelope for moisture content, which must be determined by pilot tests[3]. Too little moisture content causes drying of the filter bed, depriving microorganism of water and as a result biological activity is significantly reduced or even stopped completely. The bed material contracts, creating fissures that cause channeling and short circuiting, decreasing the retention time and eventually reducing the removal efficiency. On the other hand too much water inhibits the transfer of oxygen to the biofilm, limits the reaction rate and is typically referred to as "blinding" of the biofilm. This promotes development of anaerobic zones within the filter bed, resulting in foul smelling emissions, increasing back-pressures and reduced efficiency[3,7,21,23].

Optimal water levels vary with different filter media, depending on media surface area, porosity and other factors[7]. Filter moisture content for optimal operation of the biological filter should be within

30-60% by weight depending upon the media used[1,8,23,42,68,96]. For a compost bed a moisture level of 40-50% is recommended[2] and for peat moss it should be 40-60%[19].

In a biofilter moisture can be added through the pre-humidification of the inlet gas stream or by direct application through a sprinkler system at the top of the bed. Most biofilters rely on a steady stream of fine mist to ensure adequate moisture. More advanced controls include the use of load cells that sense the weight of the filter bed[3,23]. Load cells can be connected to sprinkler controls to automatically increase moisture levels in the bed by feeding water directly. Although an inlet gas stream saturation level of greater than 95% is sufficient, drying will continue to occur within the filter bed unless the humidity of the inlet gas is raised above 99% to make it fully saturated[4,6,67].

In addition, to pre-humidification of inlet gas stream, supplemental moisture adjustments may be required through direct application, because bio-oxidation is an exothermic reaction. The actual temperature increase depends upon the nature and concentration of the contaminant to be oxidized, and ranges between 2 - 4 °C with occasional hikes of up to 10 °C or more. Auria et al[97] reported a temperature increase of 4.2 °C within a filter bed during the active microbial growth phase with increased toluene consumption. Metabolic heat production dries the packing material and promotes the development of heterogeneous zones, ultimately resulting in non-uniform gas distribution and reduction in microorganism density. Waste gas flow direction also can help in maintaining the moisture in a filter bed. van Lith[23] recommended downward flow operation because most of the drying results at the entrance to the filter bed, due to the unsaturated gas stream being coupled with exothermic reactions that are strongest where the pollutants are in highest concentration. These problems can be dealt with easily by direct moisturization, which is clearly easier and convenient at the top of the filter bed. For direct application, at the top of the filter bed, water droplet diameters should not be greater than 1 mm because the impact of the falling droplet increases as a fifth power of the diameter and the specific feed rate should be as low as 20-30 $L\,m^{-2}\,h^{-1}$ to avoid destruction of the packing structure and compaction[23]. A general recommendation for water feed rate is between 7 and 14 L for 1,000 m^3 of gas treated[10,67]. A detailed analysis of the optimum moisture content of biofilters has been presented elsewhere[98,99].

2.5.4. Temperature

Temperature is another key concern in all biological treatment systems. Temperature control is a

vital factor for efficient biofilter operation, and in many practical applications temperature controls are added to the biofilter systems to prevent thermal shocks[3,23]. There are three general temperature classes of aerobic microorganisms: psychrophilic microorganisms that grow best below a temperature of 20 °C; mesophyllic microorganisms that achieve highest growth rates between 20-40 °C; and thermophilic organisms that grow best at temperatures above 45 °C[3]. Biological activity roughly doubles for each 10 °C rise in temperature, up to an optimum of about 37 °C for mesophyllic bacteria[54,67]. Operating temperatures between 15 and 40 °C are recommended as optimal for biofiltration[2,10,23,42,55,60,68,96]. If the inlet gas temperature exceeds 40 °C, cooling of the off-gas stream is necessary which can be easily achieved through dilution with ambient air or in a pre-humidification chamber[4]. Similarly for cold air streams below 10 °C the heating of gas stream to a desirable temperature is needed, because microorganisms are relatively inactive at low temperatures. This can be attained by the injection of steam[4,23,85]. Bio-oxidation is an exothermic reaction that may allow for adequate performance even with below freezing ambient temperatures[19]. Giggey et al[100] reported that biofilters treating reduced sulfur gases and terpenes, performed well in winter conditions at ambient temperatures below 0 °C with snowfall. To minimize the operating costs, if possible, influent streams should be treated at the temperatures they are generated. For successful operation the temperature of the system should remain relatively constant. Large changes in temperature disrupt the biological system and decrease overall system performance[3].

2.5.5. Oxygen Content

Oxygen is vital to the operation of biofilters because the predominant microorganisms used in biofiltration are aerobic, and require oxygen to metabolize organic constituents. Aerobic heterotrophic bacteria present in a filter bed require at least 5-15% oxygen in the inlet gas stream to survive[64]. Generally for most air pollution control systems oxygen supply is not an issue because it is abundant in the incoming waste air stream and the active biofilm is relatively thin, however, in overloaded biofilters it may be a limitation resulting in the formation of acidic and other intermediaries[47]. High concentration industrial exhaust air streams, with VOC concentrations in the "percent" rather than the "ppm" range, may reveal that there is not enough oxygen in the incoming stream to sustain the biomass. In such situations ambient air should be mixed in to avoid oxygen-limiting conditions in the biofilter[3]. A minimum of 100 parts of oxygen should be provided for each part of oxidizable gas to ensure sufficient supply exists[54].

2.5.6. pH Control

pH control is an important parameter in biofiltration, because most of the microorganisms have a specific optimum pH range. Any change in the pH of the filter material strongly affects the microbial activity[96]. Recently it has been observed that a reduction in bed pH has more adverse effects on the inoculated microbial consortia than on the indigenous microorganisms[101]. pH within biofilters is controlled by the addition of a solid buffering agent to the packing material at the beginning of the operation, and once this buffering capacity is exhausted, the filter bed is removed and replaced with a fresh material[102]. Compost beds generally have a pH between 7 and 8, a range mostly preferred by bacteria and actinomycetes[10]. Biological treatment systems tend to operate best in the pH range of roughly 6.5 to 8.0[3,8,23,42,60,68]. The metabolic reactions of aerobic microorganisms evolve carbon dioxide that has a tendency to depress the system pH. Therefore, if the waste gas or its intermediate byproducts do not provide sufficient buffering capacity, additional pH control may be necessary. This can be typically accomplished by the addition of chemicals such as sodium hydroxide or magnesium hydroxide[3]. Also biodegradation of reduced sulfur compounds and chlorinated organics generate acid byproducts that result in severe drops in filter pH. Although H_2S can be removed at low pH because the *Thiobacilli* that oxidize sulfide can survive high acidic concentrations[96], other odorous gases like methyl sulfides may not be removed effectively or at all[14,39]. In such cases chemical buffers such as lime should be added to neutralize the acid[10,42,50,60,61,85,86,103]. Jager et al[99] reported that the application of 1% dolomitic lime to a biofilter treating H_2S not only prevented pH lowering but also increased the useful life of the bed material. Sometimes watering of the bed also solves the problem (by leaching out acids), especially if there is much hydrogen sulfide in the air[14,28,85,96].

2.5.7. Nutrients

The degradation of a contaminant generally results in the growth of biomass. Besides carbon and energy derived from the degradation of the contaminant, nutrients such as nitrogen, phosphorous, sulfur and trace elements are required for microbial growth. For good performance of a bioreactor sufficient levels of these nutrients have to be available. In biofilters this is often realized by using nutrient rich compost as the packing material or part of it. Materials used for bed formation may contain sufficient nutrients to support microbial growth on polluted air components, but this may not be always possible especially when synthetic substances are used as filling materials.

Addition of nutrients to biofilters has shown significant improvement in the degradation rates of toluene[9,10,97] and other chemicals[10,103]. Weckhuysen et al[104] reported that the biodegradation of butanal increased with nutrient supplementation due to better nutrient balance for microorganisms and pH stabilization. Similar results were reported by Barnes et al[105] in that addition of an external carbon and energy source (sodium lactate) enhanced the bio-elimination of nitric oxide. Morgenroth et al[106] found that application of a concentrated solution of KNO_3 increased the bio-removal efficiency of hexane from 50% to >99% at an inlet concentration of 200 ppmv. An additional effect of nutrient supplementation is a higher elimination capacity by removing a higher pollutant concentration under the same operating conditions, thus reducing the biofilter area and the cost of installation[104].

2.5.8. Waste Gas Pretreatment

In order to meet the basic requirements for the optimal operation of biofiltration, waste gas conditioning is mandatory. Biofilters being biological systems can be poisoned by the presence of toxic contaminants, the excessive concentrations of the contaminants in the raw gas stream, and excursions in environmental conditions like temperature and moisture content. A sufficient supply of oxygen and humidity, and an acceptable range of temperature and pH levels in the filter bed are indispensable for the survival of the microbial flora, therefore, strongly acidic gases like HCl and HF must not be present in the waste gas in noticeable quantities[65]. Depending on the specific waste gas contaminant, VOC concentrations in the raw gas should not exceed 3-5 g m^{-3}, otherwise pretreatment of the gas stream becomes necessary[4,10].

High particulate loads in the waste gas can adversely effect the operation of a biofilter by clogging the air distribution system and the filter material itself[9,10,67]. Bed temperature and moisture maintenance, as described separately, are the key parameters for successful biofilter operation. In the case of hot waste air streams temperature sensors and alarms are necessary to regulate the fan and/or open the bypass duct in order to prevent the pasteurization of the filter material. In the case of humidification with steam it is necessary to maintain the gas stream temperatures optimal for microbial growth[23]. Inlet gas humidity of > 99% is recommended for efficient biofilter operation[68].

2.5.9. Maintenance

Efficient operation of biofilters is only achieved when there is a uniform distribution of the waste

gas over the entire filter media, besides having uniform moisture content, optimum temperature and the pH within the filter bed[15]. Routine/periodic monitoring of a biofilter includes consideration of a number of factors like waste gas temperature and relative humidity, filter bed moisture content, temperature, pH and pressure drop[10,96]. Monitoring of media alkalinity serves as a warning of impending process upsets[107]. Moisture control is more critical in compost beds because once dried, they become hydrophobic and can only be re-wetted with great difficulty[2,9]. Fully engineered enclosed systems with optimized packing reduce the maintenance requirements. This is typically accomplished by controlling the moisture in the filter bed automatically and by selecting the optimized filter materials, with a useful life of up to five years, that compact more slowly[10]. However, no matter how carefully a biofilter system is engineered, aging due to bio-oxidation of organic substrates in the media and build-up of salts (SO_4^{2-}, Cl^-, NO_3^-, HCO_3^-) will occur in most systems. This phenomenon may occur within six months for pure compost materials or may not become problematic for several years in optimized filter materials[67].

From past experience, biofilters can fail to achieve their designed removal efficiencies for various reasons e.g., inadequate assessment of the waste gas stream for its contaminants and the concentration levels, variations in temperature, pH, moisture and oxygen contents within the filter bed[10,108-110]. The following problems are usually encountered in the use of biofilters[1,8,10,109-114].

- Uniform gas distribution within the filter bed is often difficult to realize, and flow channels may be either present in the filter media (especially if they are non-homogeneous) or may develop with aging of the filter material;

- Moisture content of the packing is usually difficult to regulate, resulting either in bed drying, especially at the entrance, due to insufficient supply of water or in the development of anoxic zones due to excessive water levels;

- Generation of acid metabolites as a result of bio-oxidation of reduced sulfur compounds and chlorinated organics decreases the media pH and eventually affects biological activity; and

- Improper waste gas conditioning prior to entering the biofilter leads to system upsets due to air borne particulates or as a result of large temperature excursions.

In addition to these potential system failures, recently Devinny et al[107] and Yang et al[115] have demonstrated that similar to incomplete combustion, biofilter overloading can also lead to

incomplete biodegradation and formation of more toxic intermediates, however, this can be overcome by providing sufficient residence time within the filter bed. Accumulation of biodegradation metabolites also inhibits the bio-removal of odorous contaminants[116].

2.6. SUCCESSFUL APPLICATION OF BIOFILTERS

Originally applied to the treatment of odorous gases from sewage treatment plants, rendering and composting facilities, biofiltration is adding to its list of applications rapidly as a result of continuous efforts to expand the useful domain of this cost effective and environmentally friendly gas cleaning technology. The ability of biofilters to act as a dual control technology for both VOC and odor control makes it appealing for its application at publicly owned treatment works (POTWs)[117] where large volumes are combined with low concentrations. There biofiltration represents the most economical way to satisfy statutory regulations[4].

Biofilters have also been used to treat a wide variety of organic and inorganic pollutants in industrial and municipal exhaust streams. Among those are odorous gas (ammonia, hydrogen sulfide, mercaptans, disulfides, etc.) control from food processing wastes, wastewater treatment facilities, composting operations and others, and VOC (propane, butane, styrene, phenols, methylene chloride, methanol, etc.) destruction from industrial activities[3]. Biofilters have been shown to be effective for treating aromatics such as benzene, toluene, styrene, phenols, etc.[8,12,20-23,27,33,45,62,66,68,102,118-121]; aliphatics such as dichloromethane, propane, isobutane, etc.[18,24,45,53]; more easily biodegradable organics such as alcohols, ketones and esters[20,29-37,68,118]; hydrophobic terpenes like α-pinene[70,71,95] and odorous reduced sulfur gases such as carbon disulfide, hydrogen sulfide, mercaptans, and methyl sulfides[49-52,61,76,82,85-88,115,122-128]. Besides these contaminants biofiltration has also achieved >90% removal efficiency for odorous nitrogenous pollutants[103,105,117,129,130]. A detailed summary of biofiltration applications, according to the type of industrial activity and nature of contaminant emitted, can be found elsewhere[58,131]. In response to the 1990 US Clean Air Act Amendments, bench/pilot-scale research has shown that 60 out of 189 hazardous air pollutants (HAPs) can be successfully treated with biofiltration[58,132].

In Europe more than 600 chemical process industries are using biofilters for deodorization and treatment of VOCs from the waste gas[58]. In Germany about 80% of wastewater treatment plants are using biological processes for VOC and odor control, out of which biofiltration covers 59% of the

installations[133]. Bohn[2] has presented an excellent list of successful full-scale biofilter installations treating air toxics and VOCs at chemical processing industries in North America. Table 2.2, adapted from Leson et al[10,11], provides a list of sources where biofiltration is an established control technology for odors, VOCs and air toxics. The new areas of application for this established biological gas cleaning technology are pulp and paper mills, petrochemicals, petroleum processing and transportation, wood processing, and site remediation.

Table 2.2. Examples of successful biofilter applications in Europe

Adhesive production	Coffee roasting	Industrial wastewater
Coating operations	Coca roasting	treatment plant
Chemical manufacture	Fish frying	Residential
Chemical storage	Fish rendering	wastewater
Film coating	Flavors & Fragrances	treatment plant
Iron foundries	Pet food manufacturing	Composting facilities
Print shops	Slaughter houses	Landfill gas extraction
Waste oil recycling	Tobacco processing	

Some of the recently reported successful installations are briefly summarized here. In the USA several biofilters installed at different composting facilities for the control of odors and VOCs are working successfully with removal efficiencies of up to 99% for odors, 52-99% for VOCs and more than 80% for reduced sulfur compounds[134]. At a landfill operation an elimination efficiency of 89-96% has been achieved for ammonia concentrations ranging from 468 to 866 ppmv, and 84-86% for non-methane hydrocarbons with inlet strength of 39-41 ppmv[135]. Exclusively for VOCs (benzene, toluene, alcohols, aldehydes and organic acids) and other air toxics, a full-scale biofilter at a wood products industry has attained a removal efficiency of 93% for treating a gas flow rate of 40,800-91,800 m^3 h^{-1} with VOC concentration of about 500 ppmv[137]. A similar full-scale biofiltration system treating odors from a hardboard plant with a removal efficiency of >95% at an operating cost of US$ 4.8 scfm^{-1} treated has been reported by Allen et al[114]. Biofiltration serves the pharmaceutical industries too. A two stage biofilter system using bark compost as filter media at a pharmaceutical industry has achieved more than 99% elimination efficiency for VOCs[139]. However, to list all the biofilter installations is beyond the scope of this study and in any event can be found elsewhere[5,12,100,131-144].

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2.7. COMPARISON WITH OTHER APC TECHNOLOGIES

Biofiltration is a promising technology for controlling odors, VOCs and air toxic emissions and has several advantages over traditional air pollution control (APC) technologies including: low capital and operating costs, low energy requirements, no additional chemicals or fuel requirements, minimal maintenance requirements (for well engineered systems with optimized filter media), the absence of residual products requiring further treatment or disposal (with recirculation of any leachate), and above all public acceptance as a "natural" process[1-5,8,12,13,20,53,65-68,93,134]. Another advantage of biofiltration is its ability to deal simultaneously with several contaminants[9,117,145].

APC technologies that are available to tackle the VOCs and air toxics in gas streams can be broadly grouped as thermal or catalytic incineration, physical or chemical treatment, and biological degradation, wherein contaminants are either destroyed by oxidation or removed from an air stream by absorption/adsorption for further recovery/ treatment. Incineration of organic vapor laden gas stream often guarantees 99+% destruction of organic contaminants, however, large amounts of fuel are needed to attain such high destruction rates which in turn may produce noxious byproducts like NO_x. Although the use of catalysts and heat recovery systems can reduce fuel costs, these gains may be offset by calls for greater capital and maintenance costs[3,7,146]. Chemical oxidation, besides changing the contaminant from a gas to a liquid phase, is typically ineffective for hydrocarbons and other slow reacting compounds, and also needs further treatment of the wastewater produced[3,7,102]. Table 2.3, adapted from Ostojic et al[123], summarizes the removal efficiencies of wet scrubbing and biofiltration for organic contaminants.

Adsorption on activated carbon is also costly and the saturated carbon is a hazardous waste, requiring either regeneration or transportation to a hazardous waste landfill[3,7,146]. These processes can treat a wide variety of pollutants at higher concentrations, however, for treating air with low pollutant concentrations these approaches become unsatisfactory[7]. Table 2.4, adapted from *Air Poll. Consultant*[146], summarizes the features of the available VOC emission control technologies. Recent advances in biotreatment systems have broadened the appeal and the practicability of microbial treatment for vapor streams.

The attractiveness of biofiltration is related to its utilization of microbial reactions at ambient temperatures and pressures[7,13], thus making it an inherently safe and energy saving process in

comparison to conventional chemical reactions that generally require elevated temperatures and pressures[9]. However, one must accept the trade-off in terms of longer residence times of up to 60 seconds in comparison to 2-3 seconds in wet scrubbing and even lower in incineration[9]. Site specific requirements may dictate whether these two drawbacks rule out the use of biofiltration[3,5].

Table 2.3. Removal efficiencies of wet scrubbing and biofiltration

Compound	Wet Scrubbing		Biofiltration	
	Inlet (ppb)	Efficiency (%)	Inlet (ppb)	Efficiency (%)
Methyl mercaptan	75	>95	550	>99.3
Dimethyl sulfide	31	>87	294	>98.6
Dimethyl disulfide	8	>53	266	>98.5
Carbonyl sulfide	-	-	47	93.0
Acetone	67	0	2450	99.6
2-Butanone	16	0	545	>99.6
α-pinene	-	-	460	99.8
β-pinene	-	-	240	99.6
D-Limonene	300	67	53	95.7

Capital and operating costs of biofiltration can vary significantly depending upon the level of sophistication in system design. The operating costs for biofiltration are 10-20% less than thermal oxidizers while installation costs are roughly the same. Moreover biofilters do not produce any NO_x[132]. The cost of the biofilter process depends on the total volume flow rate of the waste gas to be treated, the concentration and nature of the pollutants concerned, and the cost of servicing the filter with piping, dust-filters and humidification[1]. Werner et al[65] have presented an excellent cost estimation analysis of biofilter including real estate and other operational costs. Table 2.5 (taken from Bohn[2]) and Table 2.6 (adapted from Vaith et al.[141]) summarize the comparative costs for different gas cleaning technologies. Further details on biofilter cost estimation and system cost comparisons have been addressed by a number of researchers[1,2,6,10,42,64,65,99,118,123,141,147,148].

Table 2.4. Volatile organic compound emission control technology ratings

Parameter	Condensation	Absorption	Adsorption	T&R incineration	Regenerative oxidation	Catalytic oxidation	Flameless oxidation	BIF combustion	Bio-filtration	Flares
I. Chemical category										
Organic gases:										
- Hydrocarbons	F	B	D	A	A	A	A	A	B	A
- Halogenated or sulfonated	F	B	D	B	A	D	A	C	B	D
- Aminated organics	F	B	D	C	C	C	B	C	B	D
Organic condensables:										
- Hydrocarbons	A	A	A	A	A	A	A	A	B	A
- Halogenated or sulfonated	A	A	A	B	A	D	A	C	B	D
- Aminated organics	A	A	A	C	C	C	B	C	B	D
- Polyelemental organics	A	A	A	C	C	D	C	C	C	C
2. Flow rate/concentration										
Low flow/low concentration	B	A	A	B	D	A	B	A	C	F
High flow/low concentration	C	A	A	C	A	A	C	A	C	B
Low flow/high concentration	A	D	D	A	D	D	A	C	B	F
High flow/high concentration	A	D	D	A	D	D	A	C	B	B
3. Process type										
Continuous process	A	A	A	A	A	A	A	A	A	A
Batch or variable process	A	A	A	D	D	D	B	D	C	A
4. Technology characteristics										
High destruction and removal efficiency (DRE)	C	B	B	B	C	C	A	B	B	D
High reliability	A	B	B	A	B	B	A	B	A	A
Low pressure drop	B	C	C	A	C	C	B	A	C	A

T&R = Thermal & recuperative; **BIF** = Boiler & Industrial Furnaces; **A** = Excellent; **B** = Good; **C** = Satisfactory; **D** = Poor; **F** = Unacceptable

Table 2.5. Cost comparison of VOC control technologies

Control Technology	Total Cost (US$ 10^6 ft^{-3} air)
Incineration	130
Chlorine	60
Ozone	60
Activated carbon (with regeneration)	20
Biofiltration	8

Table 2.6. Cost comparison of odor control technologies

Parameter		Control Technology		
		Packed Tower Wet Scrubber	Mist Scrubber	Biofilter
Capacity	*(scfm)*	15,500	3,000	400
Construction cost	*(US$)*	454,000	140,000	10,000
	(US$ scfm^{-1})	29.29	46.67	25.00
Operating cost	*(US$ yr^{-1})*	74,000	22,000	280
	(US$ scfm^{-1} yr^{-1})	4.77	7.33	0.70
H$_2$S removal efficiency	*(%)*	>99.66	>90.0	>99.5

2.8. SUMMARY

Biofiltration has proven to be a valuable means of cleaning up waste gases with its initial application as an odor control technology at composting facilities, sewage treatment plants and similar situations. The control and removal of VOCs from contaminated air streams became a major air pollution concern with the enactment of the 1990 amendments of Clean Air Act in USA. As a result biofiltration emerged as a promising air pollution control technology for controlling odors, VOCs and air toxics. It has several advantages over traditional APC alternatives such as low capital and operating costs, low energy requirements, no additional chemicals or fuel requirements, minimal maintenance requirements, the absence of residual products requiring further treatment or disposal, and above all public acceptance as a "natural process".

Contacting the contaminated air stream with a moist film of microbes attached to stationary support material of compost, peat, soil or mixture, biofiltration harnesses the natural degrading abilities of

microorganisms to biochemically oxidize waste gas contaminants into environmentally benign end products like carbon dioxide, water and mineral salts. Conventional APC technologies like carbon adsorption, incineration, etc., can treat a wide variety of pollutants at higher concentrations, however, for treating waste air with low pollutant concentrations these approaches become unsatisfactory and economically prohibitive. In comparison biofiltration is more cost-effective particularly for treatment of large volumes of waste air with low concentrations of biodegradable contaminants. The low cost of biofiltration is associated with its use of natural, rather than synthetic, sorbents and microbial, rather than thermal or chemical, oxidation. However, one must accept the trade-off in terms of longer residence time that is partially compensated by lower operating cost. The popularity and acceptance of biofiltration has followed from advances in biotechnology that provide in-depth knowledge about the system and how the process can be optimized, not only to achieve high removal efficiencies with low energy consumption, but importantly, to achieve these elimination efficiencies over long periods with minimal maintenance. However, further research is required for the development of a good understanding of the metabolic degradation pathways for single and multiple contaminant waste gas streams, efficient mass transfer from gas to liquid phase, and improved modeling techniques incorporating better kinetic data.

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CHAPTER III

DEGRADATION KINETICS OF BIOFILTER MEDIA

3.1. ABSTRACT

A lab-scale study was conducted to determine the rate and extent of decomposition of three biofilter media materials - compost, hog fuel, and a mixture of the two in 1:1 ratio - used in biofiltration applied to removal of reduced sulfur odorous compounds from pulp mill air emissions. The rate of carbon mineralization, as a measure of biofilter media degradation, was determined by monitoring respiratory CO_2 evolution, and measuring the changes in carbon and nitrogen fractions of the biofilter materials over a period of 127 days. Both ambient air and air containing reduced sulfur compounds were used, and the results compared. After 127 days of incubation with ambient air, about 17% of the media carbon was evolved as CO_2 from compost as compared to 6 and 12% from hog fuel and the mixture, respectively. The decomposition showed sequential breakdown of carbon moieties and three distinct stages were observed for each of the biofilter media. First-order rate kinetics was used to describe each decomposition stage. Decomposition rates in the initial stages were at least twice those of the following stages. Carbon mineralization showed close dependence on the C/N ratio of the biofilter material. Media decomposition was enhanced in the presence of reduced sulfur gases as a result of increased bioactivity by sulfur-oxidizing bacteria and other microorganisms, thus reducing the media half-life by more than 50%. At higher concentrations of reduced sulfur gases, the CO_2 evolution rates were proportionally lower than those at the low concentrations because of the limited acid buffering capacity of the biofilter materials.

3.2. INTRODUCTION

Emission of volatile organic compounds (VOCs) is becoming of increasing regulatory concern. Biofiltration is an attractive technique for elimination of VOCs and odors from low concentration high volume waste air streams because of its simplicity and cost-effectiveness[1-4]. General experiences with the technique are satisfactory, but major problems with filter bed compaction as a result of microbial mineralization are often reported[5-7]. The support medium for the microbial population is the key component of a biofilter reactor. Biofilter media, besides contributing to

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sorption effects, thereby ensuring an adequate residence time for metabolic destruction of gaseous pollutants, also serves as living space and reserve substrate for the microorganisms, as a humidity reservoir, and as the mechanical support for the maintenance of the internal structure of the filter bed[8,9]. The last function is crucial to ensuring an intrinsically active biofilter media with maximum effective filter surface, minimum pressure drop, and uniform air distribution throughout the bed without blockages and bypassing. However, some packing materials, being organic in nature, also undergo mineralization as a result of resident microbial activity, and eventually suffer from aging effects. Consequently, the biofilter bed settles and becomes compacted over time reducing the component interchange surface, increasing the flow resistance and decreasing the removal efficiency, finally needing replacement with a fresh material[7]. To prevent bed compaction as a result of aging effects and to optimize the purification process over extended periods of use, investigations on biofilter media degradation are needed. Until now we know of no study that has exclusively addressed this problem except an effort by Corsi and Seed[10] to account for basal CO_2 evolution in carbon balancing during the biofiltration of BETX compounds.

The ability to evaluate the rate of filter media decomposition from microbial mineralization has the potential to improve the biofilter performance by avoiding compaction, channeling and gas by-passing, through predicting the medium's useful life before it has to be replaced. The organic materials commonly used as biofilter media contain a broad spectrum of carbon species and biodegradation of each depends on the degree of stabilization of the material used in the medium. Generally, in the overall cycling of carbon, various substrates like readily oxidizable soluble organic carbon, proteins, hemicellulose, cellulose, lipids, and lignin have approximately the same order of biodegradability[11,12].

A number of investigations have been carried out to study the decomposition of anaerobically digested sewage sludge[13-15], and fresh and anaerobically digested plant biomass in soils[16]. However, limited information is available on the degradation of compost. Mineralization of compost is not only related to the physical and chemical characteristics of the material but also is a function of the particle size[15]. Decomposition is affected by a number of environmental factors like temperature, pH, moisture, oxygen content, and the presence or absence of foreign chemicals. Oxygen and moisture concentration, pH, temperature and substrate specificity are important population determinants[11,14]. Moreover, in biofiltration the filter materials are subject to conditions that are

quite different from those that prevail in land application. In biofiltration the media are exposed to gas streams that may contain a variety of chemicals in various concentrations. The presence of xenobiotics in the gas stream may either change the population and composition of microorganisms in the filter bed or may significantly affect their metabolic processes thereby altering the degradation of biofilter media.

Various methods can be used to quantitatively determine the biodegradation of organic matter by microbial activity, however respiration, measured as CO_2 evolved, is probably the most reliable, convenient and frequently used[17]. It has been used by various researchers[13,14,16] as a measure of the rate and extent of decomposition of various organic materials added to soils.

In this study three biofilter media materials were investigated for their degradation characteristics. The objective of this study was to determine the extent and kinetics of filter media degradation in biofilters intended to treat reduced sulfur containing odorous gases viz., hydrogen sulfide [H_2S], methyl mercaptan [CH_3SH], dimethyl sulfide [$(CH_3)_2S$] and dimethyl disulfide [$(CH_3)_2S_2$] from pulp mill emissions, and to evaluate the effects of the biofilter media characteristics and the presence of reduced sulfur gases on the useful life of the biofilter media. Hydrogen sulfide and methyl mercaptan were used as the representative of inorganic and organic reduced sulfur odorous compounds, respectively.

3.3. MATERIALS AND METHODS

3.3.1. Experimental Setup

A schematic diagram of the equipment used is shown in Figure 3.1. The incubation columns were made of clear Plexiglass with a total height of 290 mm and inside diameter of 56 mm. The bottom end of each column was closed with a Plexiglas plate leaving a 5 mm gas exit while the top end was plugged with a Teflon stopper and sealed with joint sealant of PTFE.

Constant aeration, wherein incubation vessels are continuously aerated with a stream of water saturated air (air which was close to saturation – relative humidity >98%) from which CO_2 had been scrubbed, was used because it overcomes the limitations of other aeration methods by continuously flushing out the evolved CO_2 and maintaining relatively constant O_2 levels essential for microbial metabolism. A compressed air stream was passed through a dual stage, gas washing
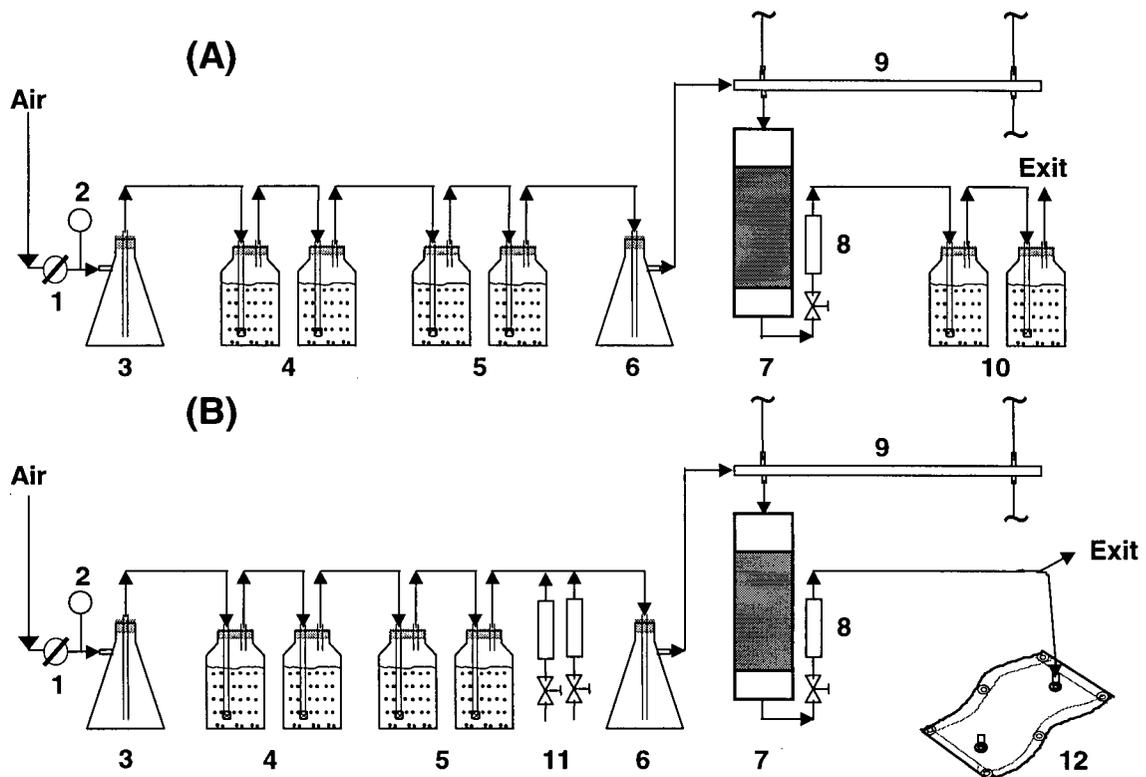
Figure 3.1. Experimental Setup: (1) gas flow regulator; (2) pressure gauge; (3) pressure stabilizing impinger; (4) gas washing scrubbers; (5) humidification vessels; (6) gas mixing impinger; (7) incubation column; (8) gas flow meter; (9) gas distribution manifold, (10) CO_2-collectors; (11) reduced sulfur gas cylinders; (12) Tedlar bag

scrubber containing 4N sodium hydroxide to remove the atmospheric CO_2 and then to a dual stage humidification vessel containing distilled water for saturating the incoming air stream from which CO_2 was removed. Although hereafter referred as to as CO_2-free air stream, small quantities of the atmospheric CO_2 were left over in the air stream as shown in Figure 3.2, and this background CO_2 concentration was deducted from the respiratory CO_2 evolved from the media (Equation 1). The gas washing scrubbers and the humidification vessels were, 250 mL in size, made of Pyrex glass. After removing the larger entrained water droplets by passing through an empty glass impinger (250 mL), the CO_2-free saturated air stream was delivered to a Plexiglass gas distribution manifold, 10 mm in diameter, with four, 2 mm diameter, outlets leading to four different incubation columns, three containing the biofilter media and the fourth one, with no medium, serving as control. The exhaust gas stream from each incubation column was passed to a dual-stage CO_2-collector for the absorption of respiratory CO_2 into a sodium hydroxide solution. The CO_2-collectors were made of

Pyrex glass and had a capacity of 125 mL. Air flow to each incubation column was regulated by high precision rotameters (Cole Parmer, USA) with measuring ranges of 5 to 165 mL min^{-1}. A down flow direction was chosen to ensure that all the media were aerated and to prevent any dead spaces. All the tubing used was 2 and 5 mm ID Teflon.

To investigate the effects of reduced sulfur gases on media degradation, the experimental setup, described above, was modified to allow the feeding of reduced sulfur gases into the CO_2-free saturated air upstream of the incubation columns, and the collection of unreacted reduced sulfur gases and respiratory CO_2 downstream of the incubation columns (Figure 3.1B).

Desired concentrations of hydrogen sulfide and methyl mercaptan were produced by mixing known volumes of compressed 10% hydrogen sulfide and 3% methyl mercaptan into the CO_2-free saturated air stream before the gas distribution manifold.

3.3.2. Biofilter Media

Three different biofilter media materials: compost because of its universal application as a biofilter media owing to its inherently diversified microbial communities, hog-fuel because of its easy availability as on-site waste material from pulp and paper mills, and a mixture of compost and hog fuel (in 1:1 ratio) as an attempt to combine the advantages of both the materials, were investigated. Compost was obtained from a local composting facility (Consolidated Enviro Waste, Aldergrove BC) and was mainly composed of yard waste and some animal manure. Hog fuel (raw bark, wood waste and other extraneous materials that are pulverized and used as a fuel for power boilers in a pulp mill) was obtained from Western Pulp's Mill at Squamish BC. Biofilter media materials were analyzed for their physical and chemical characteristics at the beginning and at the end of the incubation, using standard methods for soil analysis[18,19] (Appendix B). These physical and chemical characteristics are summarized in Table 3.1. Media materials were stored at room temperature (25 °C) in sealed bags to prevent moisture loss.

3.3.3. Reactor Conditions

The compost, hog fuel and mixture (1:1) - 163, 136 and 153 g, respectively - were incubated under controlled conditions in three incubation columns. The initial moisture contents were 59.9, 53.4 and 56.7% for compost, hog fuel and the mixture, respectively. The incubation reactors were

maintained at room temperature (25±1 °C). Compressed air was constantly fed to the incubation columns at a volumetric flow rate of 60±2 mL min^{-1}, equivalent to a renewal rate (air exchange rate) of about 5 h^{-1}.

In the incubation test with reduced sulfur polluted air, 100 g of each biofilter media were incubated at a desired reduced sulfur gas concentration continuously for 5 days and gas sample collected on the 5th day (last 24 hours). About 10% of the exhaust gas stream from each of the incubation columns was sampled continuously over a period of 24 hours in 10 L Tedlar bags, separately, for gas phase analysis. After the incubation, media samples were replaced by fresh ones for incubation at the next reduced sulfur gas concentration level. Reduced sulfur gases were continuously supplied in the CO_2-free saturated air stream at desired reduced sulfur concentrations between 0 and 1000 ppmv. The concentration range was chosen to cover the concentrations typical of various industrial emissions that can be treated with biofilters.

3.3.4. Analytical Techniques

Wet chemistry was used to analyze the CO_2 evolved as a result of media mineralization under controlled conditions (in absence of reduced sulfur gases). The reagents used were 1 N sodium hydroxide, 1 N hydrochloric acid, 10% barium chloride and phenolphthalein indicator. For higher accuracy and complete CO_2 absorption the concentration of sodium hydroxide solution was adjusted such that no more than two-thirds of the alkali was neutralized by the respiratory CO_2.

Gas phase concentration of CO_2 evolved during incubation in the presence of reduced sulfur gases was analyzed by gas chromatograph (HP 5890 Series II). A thermal conductivity detector (TCD) was utilized. The gas chromatograph was equipped with a 3 ft by 1/8 inch stainless steel packed column containing 80/100 Propack Q packing. The analysis was carried out isothermally at 75 °C. The carrier gas (helium) flow rate was 25 mL min^{-1}. Gas samples (20 µL) were injected by a gas-tight syringe (Hamilton Co., USA).

Reduced sulfur gas phase concentration was analyzed by GASTEC detector tubes (Gastec Corp., Japan) after sampling the gas in 1 L Tedlar bags. GASTEC detector tubes of various detection ranges from 10 to 1600 ppmv were used.

3.3.5. Respiratory CO_2 Measurement

The contents of the two CO_2-collectors for each incubation column were mixed and concomitantly titrated with standard 1N hydrochloric acid to a phenolphthalein endpoint. The amount of CO_2 (as mg C) evolved was calculated from the titrimetric data using the following equation[17]:

$$CO_2 = (B - M) * N * E \tag{1}$$

where B and M are the volumes of hydrochloric acid used to titrate sodium hydroxide in CO_2-collectors from the blank and the media, respectively (mL); N is the normality of hydrochloric acid; and E is the equivalent weight (E = 6).

At steady state the growth rate of the microorganisms due to biodegradation is balanced by its own decay, resulting in no net growth and eventually biological equilibrium is achieved[20-21], so under these conditions with no net gain in cell mass[22] and complete oxidation of reduced sulfur gases, the amount of CO_2 evolved from media mineralization in presence of reduced sulfur gases (CO_{2M}, mg C g^{-1}C d^{-1}) was estimated as follows:

$$CO_{2M} = (CO_{2T} - CO_{2RS})/(W_M * C_M) \tag{2}$$

$$CO_{2T} = \{(C_{CO2M} - C_{CO2B}) * 10^{-6}\} * Q * 44/(24.45 * 3.667) \tag{3}$$

$$CO_{2RS} = \{(C_{inRS} - C_{outRS}) * 10^{-6}\} * Q * (M/24.45) * C_f \tag{4}$$

where CO_{2T} is the total amount of CO_2 evolved (mg C d^{-1}), C_{CO2M} and C_{CO2B} are the concentrations of CO_2 in gas samples from media and blank, respectively (ppmv), Q is the total gas flow through the incubation column (mL d^{-1}); CO_{2RS} is the amount of CO_2 evolved from biodegradation of reduced sulfur compounds (mg C d^{-1}), C_{inRS} and C_{outRS} are the inlet and outlet concentrations of reduced sulfur gases to and from the incubation column (ppmv), M is the molecular weight of the reduced sulfur compound, C_f is the carbon fraction of the reduced sulfur compound, and W_M and C_M are the dry weight (g) and dry carbon fraction of the media sample.

In the chromatographic measurements for CO_2, no unidentified peaks that could indicate partial degradation of media to intermediates like organic acids were seen.

3.3.6. Estimation of Degradation Kinetics

Decomposition of a complex carbon substrate can be usually described by a multistage first-order decomposition sequence because the original waste carbon is largely insoluble, thus the rate limiting factor and the overall decomposition is largely determined by individual reaction rates for

different carbon fractions[11,12]. The individual rate constants (k_i) were estimated using the conventional decay equation[11,12,16].

$$- dC_i / dt = k_i C_i \qquad (5)$$

integrated this becomes

$$C_{ti} = C_i \exp(- k_i t) \qquad (6)$$

that gives the equation for half-life as:

$$t_{1/2} = 0.693 / k_i \qquad (7)$$

where C_i and C_{ti} are the carbon contents present at the beginning and the end of a particular decomposition stage (g), t is the duration of the decomposition stage (d), and k_i is the first order reaction rate constant (d^{-1}), $t_{1/2}$ is the half-life of biofilter media (d).

3.4. RESULTS AND DISCUSSION

3.4.1. Physical and Chemical Characteristics of Biofilter Media

The results of standard soil analysis techniques as used on the biofiltration media are presented in Table 3.1. After 127 days of incubation, media pH was reduced in the compost and the mixture beds, while it increased in the hog fuel bed. There was also an apparent increase in the media bulk density because of the increase in media moisture content as a result of moisture accumulation in the biofilter bed. A small increase in the nitrogen content of the media materials was observed after 136 days of incubation. This probably could be as a result of biomass buildup or for other unknown reasons. The carbon content was reduced due to respiratory CO_2 evolution, consequently resulting in a reduction in the media C/N ratio. The porosity of the media also decreased mainly because of increased moisture content of the media. The initial particle size distributions of the three media were very similar. Thus any rate of decomposition effects observed in this study would not be due to particle size *per se*, but there could be differences in the composition of some particles having the same size in the different media. These were not investigated. No significant changes in other physical and chemical properties (see Table 3.1) of the biofilter materials were observed during the period of incubation.

3.4.2. CO_2 Evolution under Controlled Conditions

The respiratory CO_2 evolution rate varied significantly amongst the various biofilter media, as shown in Figure 3.2, because of their different composition. After 127 days of incubation 17.6, 6.4 and 12.3% of the C originally present in the medium had evolved as respiratory CO_2 from the
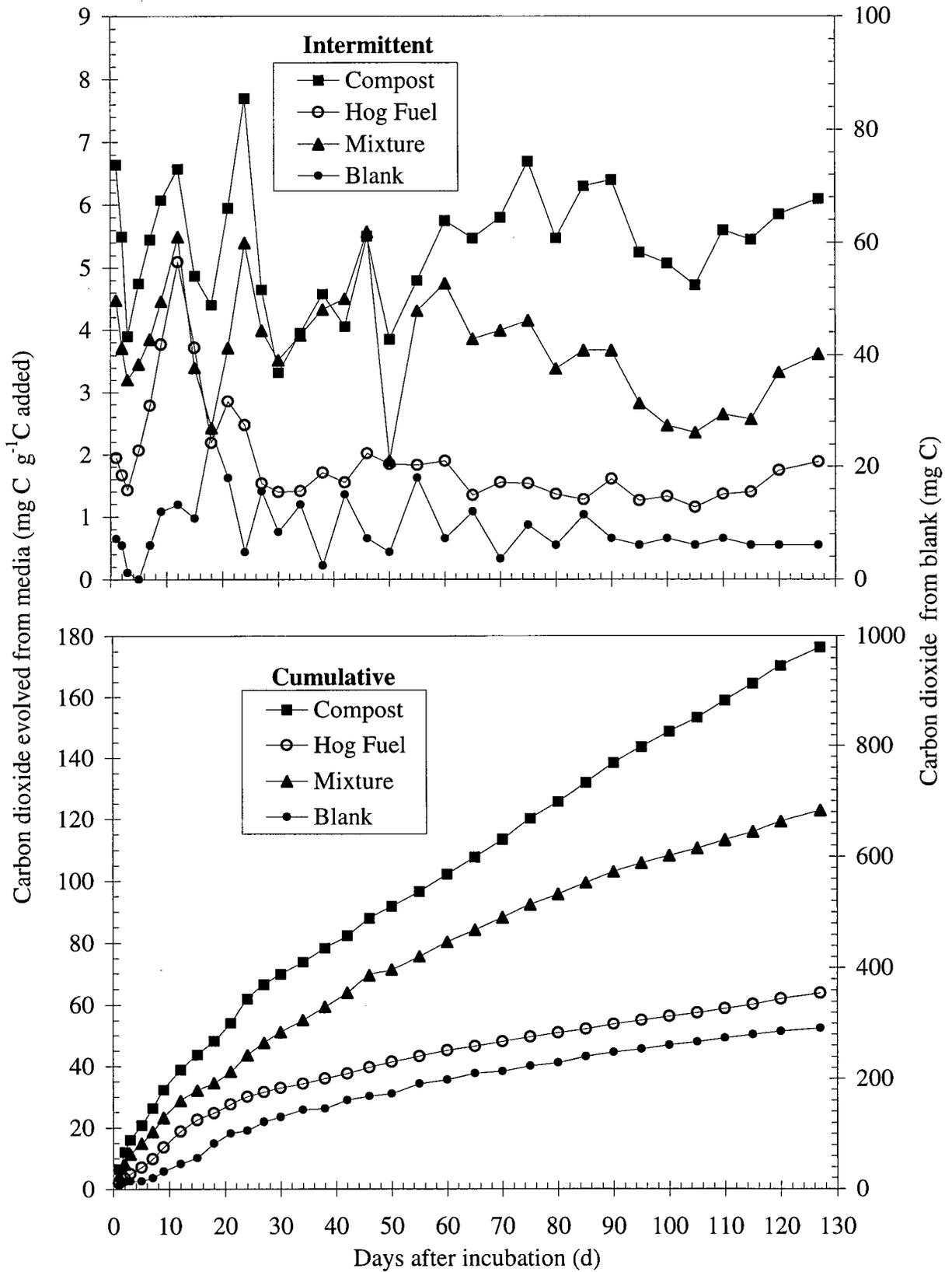
Figure 3.2. Carbon dioxide evolution rates from biofilter media materials.

compost, hog fuel and the mixture, respectively, as a result of media mineralization. During the first 12 days the CO_2 evolution was rapid and almost at the same rate for all three media. After that, CO_2 evolution from compost and the mixture increased linearly but the evolution rate was higher for compost than for the mixture. Contrarily the CO_2 evolution rate from hog fuel declined after the first 12 days indicating an inverse dependence of C-mineralization on the media C/N ratio (Table 3.1). Half the total respiratory CO_2 evolved from hog fuel was produced during first 30 days of incubation as compared to 46 days in the case of compost.

Table 3.1. Characteristics of biofilter media materials before and after incubation

Physical and chemical characteristics	Unit	Compost		Hog fuel		Mixture	
		Before Incubation	After Incubation	Before Incubation	After Incubation	Before Incubation	After Incubation
pH_w	-	8.95	8.13	4.32	5.36	7.89	7.82
Water content	%	59.91	61.33	53.43	67.05	56.67	60.99
Organic matter$_{dry}$	%	53.14	52.76	90.82	93.43	71.98	74.24
Total carbon$_{dry}$	%	36.75	35.07	54.53	53.81	45.64	45.97
Total nitrogen$_{dry}$	%	1.340	1.443	0.168	0.170	0.754	0.823
C/N ratio	-	27.42	24.30	325.01	316.30	60.54	55.86
Bulk density	g/mL	0.514	0.558	0.251	0.358	0.351	0.401
Particle density	g/mL	1.479	1.368	1.428	1.201	1.511	1.300
Porosity	%	65.24	59.20	82.43	70.16	76.76	69.11
Initial Particle Size Distribution*							
> 4.76 mm	wt. %	23.41		22.81		23.11	
4.00 - 4.76 mm	wt. %	8.09		9.37		8.73	
2.83 - 4.00 mm	wt. %	18.21		14.95		16.58	
2.00 - 2.83 mm	wt. %	20.83		17.25		19.04	
1.40 - 2.00 mm	wt. %	13.85		14.80		14.33	
0.85 - 1.40 mm	wt. %	9.95		13.93		11.94	
< 0.85 mm	wt. %	5.67		6.88		6.28	

*obtained by sieving

Decomposition stages and the corresponding reaction rate constants, obtained by the regression fitting of equation 6 for the three biofilter media are presented in Figure 3.3. Each biofilter media
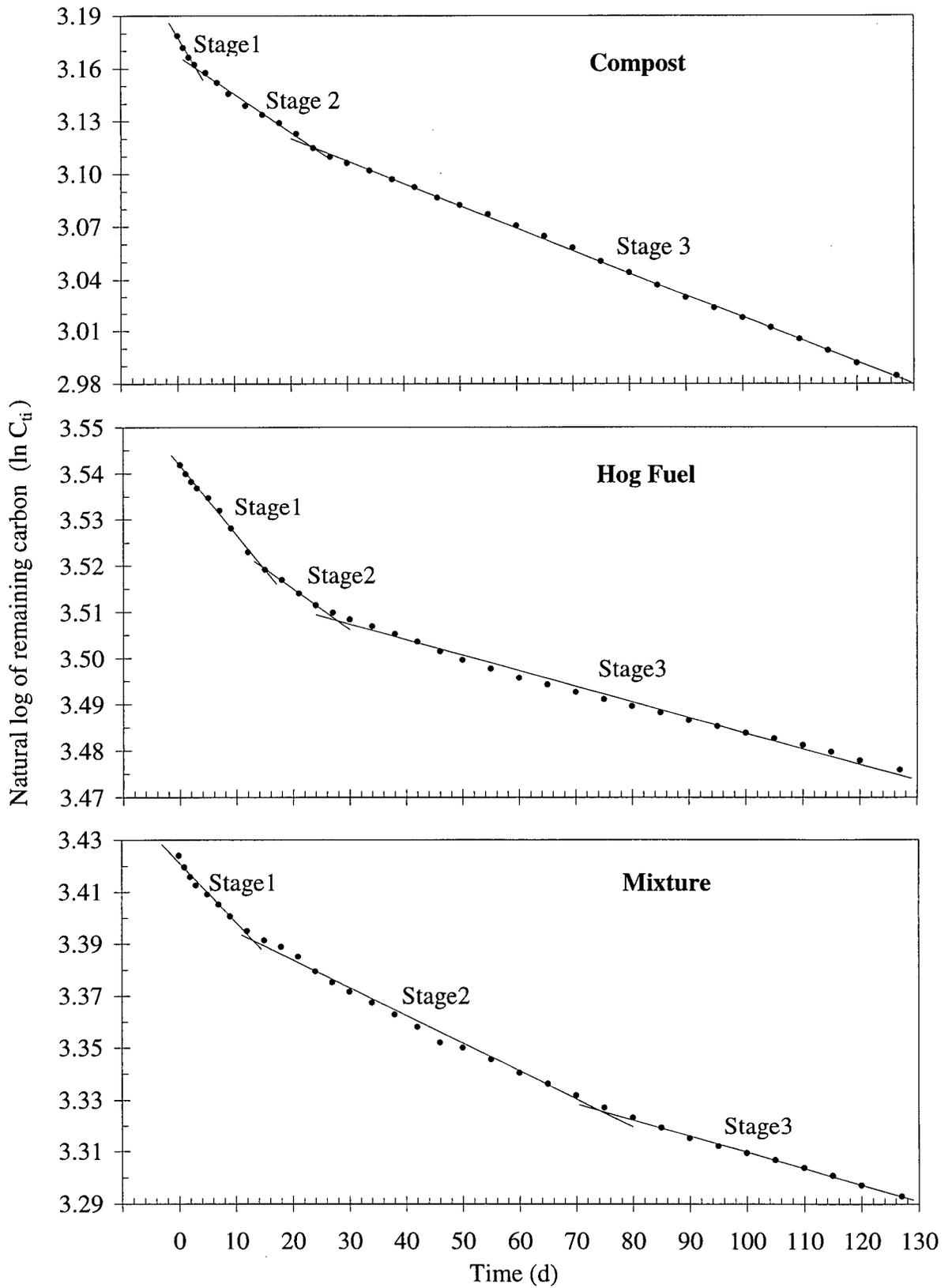
Figure 3.3. Degradation stages and reaction rate constants for biofilter
media materials.

showed three distinct degradation stages of different duration and decomposition rates (Table 3.2). The duration of each stage in the three biofilter media materials was selected in order to maximize the R^2 value. The first stage was the shortest (3 d) for compost, but with the highest rate constant (0.0054 d^{-1}) and the second stage was shortest (3 d) for hog fuel with lowest rate constant (0.0009 d^{-1}). The rate constants for the mixture were approximately equal to the average of those of the compost and hog fuel. Rate constants for the final (third) stage of decomposition were 0.0013, 0.0003 and 0.0006 d^{-1} for compost, hog fuel and the mixture, respectively; and if these are assumed to be representative through the remaining life of the biofilter media, correspond to half-lives of 533, 2310, 1155 d, respectively. Although no comparable study is available to which to compare the results of this work, incubation of compost in soil has given similar results with 20% of the organic carbon being evolved over 6 months[16].

Table 3.2. Biofilter media degradation stages and their reaction rate constants

Biofilter Media Material	Stage I		Stage II		Stage III		Carbon Lost
	Duration (d)	k_1 (d^{-1})	Duration (d)	k_2 (d^{-1})	Duration (d)	k_3 (d^{-1})	(%)
Compost	3	0.0054 (0.99)	21	0.0022 (0.99)	103	0.0013 (0.99)	17.62
Hog Fuel	24	0.0015 (0.99)	3	0.0009 (0.99)	100	0.0003 (0.99)	6.38
Mixture	23	0.0023 (0.98)	17	0.0011 (0.99)	87	0.0006 (0.99)	12.28

Values in parenthesis are the R^2 values for the linear regression of Equation 6 in each case

3.4.3. Effects of Reduced Sulfur Gases on CO_2 Evolution

CO_2 evolution from compost significantly increased with increasing hydrogen sulfide concentration up to 400 ppmv while it did so only up to 100 ppmv in the case of hog fuel and the mixture. Similar effects were observed with methyl mercaptan, but the CO_2 evolution rate increased up to 150 ppmv for hog fuel and the mixture. CO_2 evolution rate was higher in presence of methyl mercaptan as compared to hydrogen sulfide.

The effects of exposure to reduced sulfur gases on biofilter media degradation are illustrated in Figure 3.4. The respiratory CO_2 evolution rate (R_{CO2}, mg C $g^{-1}C$ d^{-1}) in the presence of reduced sulfur gases was linearly correlated to the square root of the reduced sulfur gas concentration (ppmv) in all three biofilter media as follows:

$$\text{Compost} \Rightarrow R_{CO2} = 0.0663[H_2S]^{0.5} + 0.5408 \qquad (R^2 = 0.95) \qquad (8A)$$

$$R_{CO2} = 0.0667[CH_3SH]^{0.5} + 0.5466 \quad (R^2 = 0.94) \qquad (8B)$$

$$\text{Hog Fuel} \Rightarrow R_{CO2} = 0.0133[H_2S]^{0.5} + 0.4627 \qquad (R^2 = 0.88) \qquad (9A)$$

$$R_{CO2} = 0.0164[CH_3SH]^{0.5} + 0.4631 \quad (R^2 = 0.87) \qquad (9B)$$

$$\text{Mixture} \Rightarrow R_{CO2} = 0.0303[H_2S]^{0.5} + 0.4938 \qquad (R^2 = 0.94) \qquad (10A)$$

$$R_{CO2} = 0.0333[CH_3SH]^{0.5} + 0.4996 \quad (R^2 = 0.94) \qquad (10B)$$

The above equations are valid within the concentration range of reduced sulfur gases investigated in this study.

In the case of compost, using Equation 8A, CO_2 evolution rates of 0.54 and 1.69 mg C $g^{-1}C$ d^{-1} were obtained at hydrogen sulfide concentrations of 0 and 300 ppmv, respectively. The ratio of these CO_2 evolution rates is equal to the ratio of the first order rate constants for media degradation at these hydrogen sulfide concentrations, i.e., $CO_{2,300}/CO_{2,0} = k_{300}/k_0 = 1.69/0.54 = 3.12$, that corresponds to a half-life ($t_{1/2,300}$) of 170.7 d at hydrogen sulfide concentration of 300 ppmv as compared to 533.1 d in absence of hydrogen sulfide. Similarly for hog fuel (Eq. 9A) and the mixture (Eq. 10A) the half-lives at 300 ppmv of hydrogen sulfide were estimated at 1542.2 and 559.9 d, respectively. The reduction in the half-lives of the biofilter media was more pronounced in the presence of methyl mercaptan than hydrogen sulfide, because of higher evolution rates of respiratory CO_2. At the same 300 ppmv methyl mercaptan concentration the half lives ($t_{1/2,300}$) were reduced to 169.5, 1431.8 and 536.1 d for compost, hog fuel and mixture, respectively. The results are summarized in Table 3.3. To our knowledge no prior studies of similar effects have been reported, with which to compare the results.

Table 3.3.   Half-life of biofilter media materials

Biofilter Media	Ambient Air	H_2S 300 ppmv	CH_3SH 300 ppmv
Compost	533.2 d	170.7 d	169.5 d
Hog fuel	2310.4 d	1542.2 d	1431.8 d
Mixture	1155.2 d	559.9 d	536.1 d
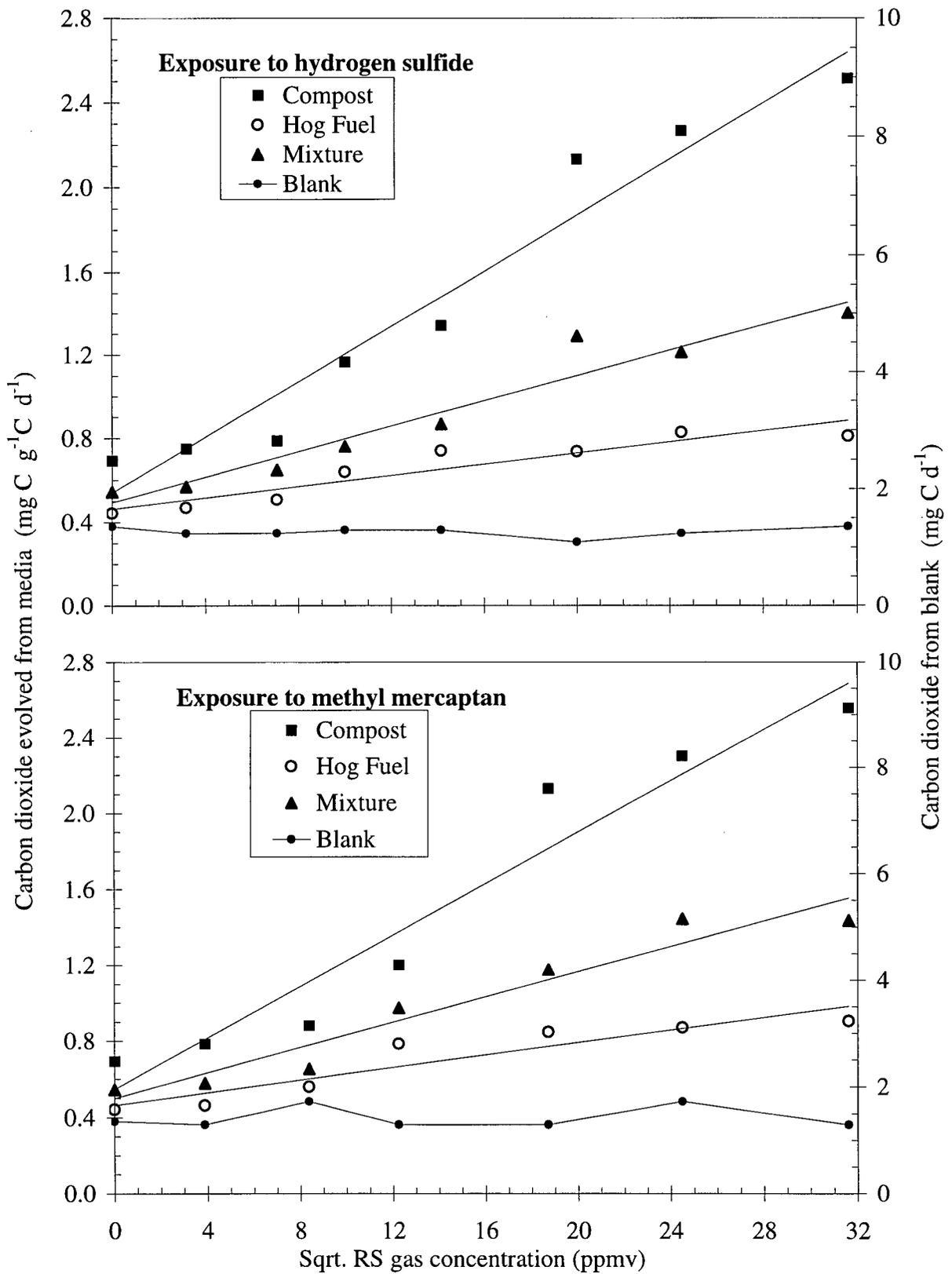
Figure 3.4. Effects of reduced sulfur gas exposure on biofilter media degradation.

3.5. CONCLUSIONS

Media pH was reduced slightly in case of compost and the mixture probably because of the formation of carbonic acid as a result of CO_2 absorption in the biofilm, while it increased in the hog fuel bed possibly due to breakdown of organic and resin acids. The decrease in media C/N ratio was due to loss of soluble carbon moieties as a result of microbial mineralization. Bulk density was apparently increased due to moisture accumulation in the biofilter bed. Sieve analysis for particle size distribution could not be done after the incubation because of the very small size of the media samples. Other physical and chemical properties (see Table 3.1) of the biofilter media materials were not changed significantly during 127 days of incubation with ambient air.

The decomposition patterns for the three biofilter media were significantly different owing to their different constituents. In all the biofilter media, the initial respiratory CO_2 evolutions were rapid and almost at the same rate, because of the abundance of easily degradable soluble carbon compounds. As the soluble carbon fractions were exhausted the CO_2 evolution rate declined. The effect was very noticeable in hog fuel as compared to compost and the mixture where the CO_2 evolution increased linearly over the rest of the incubation period. The reason probably being that lignin and cellulose are the main constituents of hog fuel in addition to small quantities of readily soluble sugars as compared to compost that contains all the sequential carbon moieties thus resulting in a steady evolution of CO_2 over the entire incubation period. This was also confirmed in Figure 3.3 wherein hog fuel showed a very short second stage of degradation as compared to compost and the mixture because of the lack of moderately hard to degrade carbon substrate.

The CO_2 evolution rate was significantly increased in the presence of reduced sulfur polluted air presumably as a result of increased bioactivity of sulfur-oxidizing bacteria and other resident micro-organisms. In all of the biofilter materials the CO_2 evolution rate increased with increasing reduced sulfur gas concentration, but the rate was much higher in the case of compost than hog fuel and the mixture (Figure 3.4). The probable reason may be reduced bioactivity caused by the lower pH of hog fuel and the mixture beds. This was proved with a further increase in reduced sulfur concentration that caused a reduction in CO_2 evolution rates from all the three biofilter media as a result of the saturation of the medium's acid buffering capacity. CO_2 evolution rates were higher in the presence of methyl mercaptan as compared to hydrogen sulfide, probably

because of the availability of another carbon-source (methyl mercaptan) that enhanced the bioactivity in the incubation columns, as a result of higher energy output from carbon-oxidation than sulfur-oxidation. After 24 hours incubation period, the color of the compost was changed to whitish especially at higher hydrogen sulfide concentrations, possibly indicating larger amount of sulfur buildup in the media. Such effects were moderate for the mixture and almost non existent for the hog fuel. Color changes due to the possible accumulation of elemental sulfur were not observed with methyl mercaptan.

Amongst the three biofilter media materials investigated, hog fuel was found to be harder to degrade thus having a longer useful life in biofilters as compared to compost and the mixture of compost and hog fuel (1:1). The half-life of compost was about a quarter of the hog fuel, because of its low C/N ratio. The mixture behaved somewhat in-between compost and hog fuel with its half-life approximately equal to the average of those of the compost and hog fuel. Bioactivity of the sulfur-oxidizing bacteria and other microorganisms was stimulated as a result of sufficient supply of reduced sulfur gases, resulting in an increase in microbial population and a corresponding increase in the CO_2 evolution rate. Consequently the media half-life was reduced to about one-half because of the increased media mineralization.

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CHAPTER IV

DYNAMICS AND TRANSIENT BEHAVIOR OF BIOFILTERS DEGRADING REDUCED SULFUR GASES

4.1. ABSTRACT

The work reported here describes the aerobic biodegradation of reduced sulfur odors from waste air streams in biofilters. Results of a series of three studies, with different reduced sulfur gases, of the transient behavior of biofilters are presented. Experiments were conducted in three bench-scale biofilters packed with the mixtures of compost/perlite (4:1), hog fuel/perlite (4:1), and compost/hog fuel/perlite (2:2:1). The biofilters were exposed to variations in contaminant concentration, fluctuating waste airflow rate, and periods of non-use to evaluate the effects of changes in contaminant mass loading and starvation on biofilter dynamics and performance. The response of each biofilter to variations in contaminant mass loading was studied by abruptly changing the concentration and/or flow rate of the inlet waste air stream.

The starvation period comprised two stages: the "no-contaminant-loading phase" when only humidified air was passing through the biofilters, and the "idle phase" when no air was passing through the biofilters. Concentration spikes were applied to study the effects of shock loading on the biofilter removal efficiency. Hydrogen sulfide, methyl mercaptan and dimethyl disulfide, the malodorous gases produced from kraft pulping processes, were used as the test contaminants.

Proper inoculation of the filter materials with pulp mill wastewater sludge significantly reduced the initial start-up time. The initial acclimation times for methyl mercaptan and dimethyl disulfide were about 5-6 days. Step changes in the contaminant concentration and waste airflow rate demonstrated that the biofilters acclimatized rapidly to the new operating conditions, and responded effectively to these imposed changes. The biofilters responded effectively to hydrogen sulfide concentration variations (up to 370 ppmv) and shock loading by rapidly recovering to the original % removals within 2-8 hours. The re-acclimation times to reach full capacity were very short, ranging between 15 and 120 hours depending upon the duration of downtime. In the case of methyl mercaptan an inlet concentration of about 104 ppmv caused a measurable decrease in the removal efficiency and

so did a waste airflow rate of 2.9 m^3 h^{-1}. A massive reduction in the removal efficiency was observed at a methyl mercaptan inlet concentration of about 141 ppmv, and the biofilters could not recover to their initial removal levels. For dimethyl disulfide a substantial decrease in biofilter removal efficiency was observed at an inlet concentration of 54 ppmv and the biofilters could not regain their original removal efficiency, however, an increase in the waste airflow rate, that eventually reduced the inlet concentration caused an immediate recovery in the removal efficiency. Nonetheless, in most cases a recovery time of about 8-16 h was required, after the step changes, to regain the original removal levels for either methyl mercaptan or dimethyl disulfide. As expected, the extended periods of starvation resulted in longer re-acclimation periods and so did the idle phase as compared to a no-contaminant-loading phase. The re-acclimation time, for methyl mercaptan or dimethyl disulfide, to reach its full capacity after the longest starvation period of one week was significantly shorter, about a day, in comparison to the initial start-up time of about 5-6 days.

4.2. INTRODUCTION

Odor from chemical pulp mills is one of the major public perception problems facing the pulp and paper industry. Reduced sulfur odorous gases, hydrogen sulfide, methyl mercaptan, dimethyl sulfide and dimethyl disulfide, emitted from pulp mills represent some of the most malodorous compounds known to man. These odors can seriously lower real estate property values and there are indications that odor causing stress-induced illnesses can result in lower worker productivity and lost workdays[1]. These reduced sulfur compounds are toxic chemicals and are listed under the Toxic Substances Control Act (TSCA) promulgated by the US EPA[2]. Due to public health concerns and personal comfort of neighboring residential communities, the industry is facing increasingly stringent regulations. Hence, a growing awareness and concern for air quality is driving a search for economical and efficient abatement technology to reduce the impact of the industry on the environment.

Existing odor and air toxics control technologies viz., thermal oxidation and incineration produce undesirable products such as oxides of nitrogen. Physical adsorption to activated carbon requires an expensive regeneration process and can generate hazardous wastes. Low pollutant concentration further hinders the application of these technologies. Other commonly used odor control technology such as chemical scrubbing results in cross-media transfer of pollution,

presents safety concerns due to chemical transportation and handling, and is ineffective in controlling organo-sulfur compounds. Moreover, these conventional control technologies are usually uneconomical if large flow rates and low contaminant concentrations characterize the waste air streams. Biofiltration of off-gases contaminated with odors and air toxics has a potential application to the pulp and paper industry. It has a very low operating cost and is very effective for treating large volumes of moist air streams with low concentrations of the pollutants. Also it has the potential for using on-site materials such as wood chips and bark as biofilter media[3]. Biofiltration, a relatively new application of biotechnology in environmental engineering, instead of transferring contaminants from one medium to another, or using large amounts of energy to destroy or remove pollutants, utilizes the efficiency of microorganisms to degrade the pollutants[4-9]. Biofiltration is a viable and potentially cost-effective alternative for the treatment of low-concentration polluted air streams. The low operating cost results from the utilization of microbial oxidation at ambient conditions instead of oxidation by thermal or chemical means. Under the proper conditions, high removal efficiencies can be achieved and the process is environmentally friendly.

Biofiltration involves passing the contaminated air stream through a moist bed of compost, peat, soil or other permeable material that acts as an attachment for a rich microbial population. After the contaminants have been sorbed from the air stream while passing through the bed, the microorganisms utilize the sorbed contaminants as a food source and convert them into carbon dioxide, water vapor and inorganic salts. As the contaminants are metabolized, the binding site to which they were attached again becomes available to sorb additional contaminant molecules from the incoming air stream. Thus biofilters reach a steady state in which sorption, biological destruction and release of innocuous gaseous products are in balance. If designed properly, these systems combine the advantages of high biomass concentration with high specific surface area for contaminant mass transfer.

Owing to the variable nature of industrial operations, full-scale biofilters are generally exposed to a multitude of changing conditions as a result of fluctuating loads during process condition changes and/or discontinuous loads during shutdowns for retooling or equipment repair. Gaseous emissions from certain pulping processes such as brownstock washers, tank venting, and process vents are neither consistent in concentration nor continuous and thus the pollutant concentrations

vary with time. Fluctuations in the contaminant concentration can be the result of seasonal changes in operation, daily and even hourly variations in operating conditions, due to changing process conditions and operation. Fluctuating concentrations can have a significant impact on a biofiltration process because the short residence time in the biofilters and the concentration fluctuations can have the same time scale. This highlights the significance of obtaining reliable data on the transient behavior of biofilters under the conditions that will be encountered in field operation, in order to ascertain whether a biofilter could respond effectively to sudden changes in operating conditions, shutdowns and restarts, and contaminant shock loading.

The major features of biofiltration have been described in recently published reviews of available literature[8-10]. The steady state performance of biofiltration processes treating reduced sulfur compounds and their mixtures has been extensively documented in both lab-scale studies[11-23], and pilot systems[24-28]. Only a few studies[29-33] have addressed the transient state operation of biofilters and the changes occurring during shutdowns and interruptions. Moreover, minimal attention has been given to the characterization and mitigation of such transient loading response in biofilters, treating reduced sulfur gases, which occur when the concentrations of flow-streams vary over time[34-36]. However, observations of field installations, laboratory systems and industrial sources have shown that adequate process monitoring will require improved knowledge of transient response characteristics[33]. Obviously, based on the same observations, in-depth investigation of the unsteady state behavior of biofilters is required to understand the complex phenomena occurring in the biofiltration process under real world conditions, and to develop the operational protocols and design methods that can mitigate breakthrough of contaminants resulting from transient loadings.

To address these issues a series of three studies was performed to study the transient behavior of three biofilter materials degrading reduced sulfur gases. This report describes the results of these bench-scale studies to examine the effects of changes in airflow rate and contaminant concentration, under constant and variable loading conditions, on biofilter performance treating reduced sulfur odors. Initial acclimation and re-acclimation of three biofilter media materials, for reduced sulfur odors, were also investigated and are discussed. Acclimation is compared with re-acclimation following different periods of non-use. The influence of shock loads on the biofilter elimination efficiency was determined based on an abrupt increase in the contaminant feed as a

concentration pulse. Hydrogen sulfide, methyl mercaptan, and dimethyl disulfide (as a representative of methyl sulfides) the main odorous compounds that cause pulp mill odor problems were used as test contaminants individually in three separate experiments.

4.3. MATERIALS AND METHODS

4.3.1. Experimental Setup

Three identical bench-scale biofilter columns were used (Figure 4.1). The biofilter columns were constructed from transparent, rigid, Plexiglas (methyl methacrylate) tubing, with an inner diameter of 187 mm and a height of 910 mm. Each of these columns can be packed with the desired filter media up to a height of 660 mm. The filter bed in each column is divided into three equal sections, in series, leaving a 30 mm plenum in between the sections for representative gas sampling. The packed biofilter material in each section is supported by stainless steel sieve plates. There are three
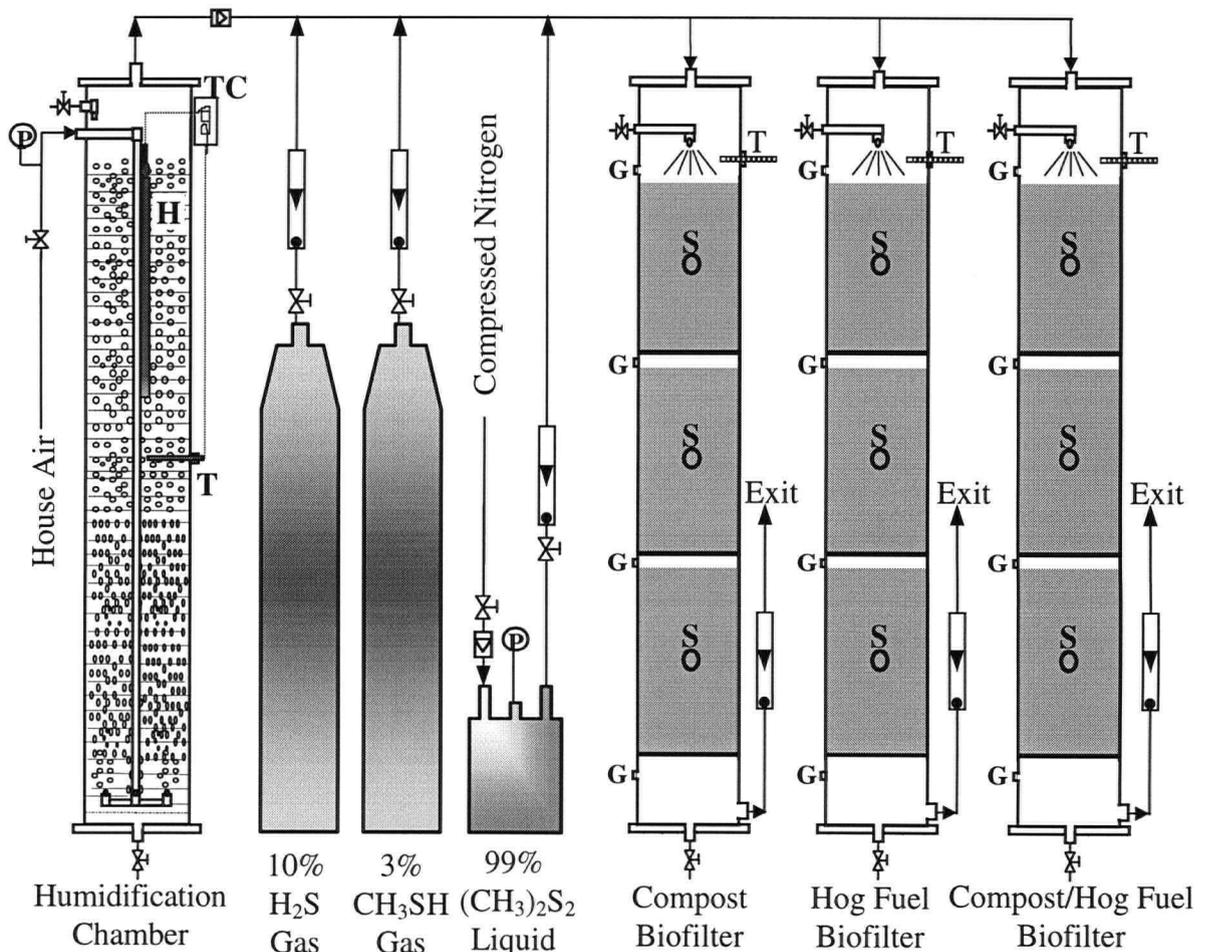
Figure 4.1. Schematics of the experimental setup: G, gas sampling ports; H, immersion heater;

P, pressure gauge; S, media sampling ports; T, thermocouples/thermometers;

TC, temperature controller.

ports in each segment allowing for sampling the air stream and biofilter media, and monitoring the temperature and pressure. The gas sampling ports, located along each column, are fitted with threaded PVC (polyvinyl chloride) stopcocks. The individual sampling ports were identified as inlet, upper, lower and outlet ports. The media sampling and temperature monitoring ports are fitted with threaded PVC stoppers and can be opened as desired. The biofilter columns were sealed at the top and bottom by clear Plexiglas covers provided with rubber o-rings. The top cover can be dismantled to replace the filter material and to clean the filter columns before and after use. The air used for creating the synthesized contaminated gas stream was taken from the laboratory compressed air distribution system. Before use the air was filtered to remove water and oil droplets. The airflow rate was controlled using pressure regulators located at the house air outlets. The inlet gas stream was conditioned by humidification to saturation. A transparent Plexiglas humidification column (187 mm in diameter and 910 mm in height) was used to add water vapor to saturate the air because the house air had less than 25% relative humidity at room temperature and pressure. Humidification was controlled by sparging the air through temperature controlled water. Maintaining the water at about 5 °C above room temperature, by using an immersion heater, provided the necessary driving force to ensure complete saturation of the air stream. The air was then passed through a trap to collect any condensates from the air supply lines before entering the biofilters. A wet/dry bulb apparatus was used to measure the relative humidity of air. The temperature of the inlet air stream was accordingly controlled by the humidifier's water temperature. The flow rates of the pollutant gas and the humidified air were controlled by needle valves and metered with high precision, stainless steel, Gilmont compact flow meters at the inlet and outlet lines of the biofilter columns, respectively. 3 mm PFA teflon tubing was used to carry the reduced sulfur gases to the distribution manifold, while all other gas lines were 12 mm diameter PVC pipes. A down flow direction in the biofilter was chosen because it allows for efficient moisture control in the filter bed.

4.3.2. Biofilter Media

The biofilter media materials used were: compost, because of its universal application as a biofilter media owing to its inherently diversified microbial communities; hog-fuel, because of its easy availability as on-site waste material from pulp and paper mills; and a mixture of compost and hog fuel as an attempt to combine the advantages of both materials. Compost was obtained from a local composting facility (Consolidated Enviro Waste, Aldergrove BC) and was mainly composed of

yard waste and some animal manure. Hog fuel (raw bark, wood waste and other extraneous materials that are pulverized and used as a fuel for power boilers in a pulp mill) was obtained from Western Pulp's Mill at Squamish, BC. Biofilter media materials were analyzed for their physical and chemical characteristics using standard methods for soil analysis (Appendix B), and the results are summarized in Table 3.1 (Chapter III). Media materials were stored at room temperature (25 °C) in sealed bags to prevent moisture loss.

New biofilter media, not previously exposed to TRS gases, were used for each TRS gas studied, except for dimethyl disulfide. When the dimethyl disulfide tests were done the media previously used for the methyl mercaptan study was retained in the columns.

4.3.3. Reactor Conditions and Operation

The filter medium for the three biofilters consisted of compost, hog fuel and the mixture of compost and hog fuel (1:1 w/w), respectively. Each medium was then amended with perlite, to provide structural strength and to increase the bed porosity, in a ratio of 4 parts media to 1 part perlite, by weight. Dolomitic lime was also added to the filter media at 25 kg m^{-3} of bed material, as a pH buffer. Waste activated sludge obtained from Western Pulp's Mill at Squamish, BC and Howe Sound Pulp & Paper's Mill at Port Melon, BC was used as the seeding for reduced sulfur-oxidizing microorganisms. The final moisture contents of the prepared media from compost, hog fuel and the mixture were 59.9, 53.4, and 56.7% respectively for the first test; and 58.6, 64.7, and 61.7% respectively for the second and third tests.

The prepared media were carefully introduced into the biofilter columns to avoid excessive initial compaction and fissuring of the bed. The total volume of filter bed in each biofilter column was 0.018 m^3 in three equal sections in series. The biofilter beds were replaced by new filtering materials after finishing each study in a series of three studies.

The three biofilter columns were subject to identical contaminant loading and operated in parallel. Downward airflow rates ranging from 1.7 to 3.2 m^3 h^{-1} (equivalent to empty bed residence times of 38 to 20 s) were used in these experiments, giving waste air surface loading rates of 60 to 112 m^3 m^{-2} h^{-1}. The synthetic waste air stream for each study was made using different reduced sulfur gases. For the first study (i.e., biofilter transient response to fluctuating hydrogen sulfide

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concentration) a synthetic waste air stream was made by injecting a known flow of compressed hydrogen sulfide (10 vol%, balance nitrogen) into the saturated air stream coming from the humidification column. Similarly for the second test (i.e., biofilter transient response to varying methyl mercaptan loading) compressed methyl mercaptan (3 vol%, balance nitrogen) was mixed with the humidified air stream. The artificial waste air stream for the third experiment (i.e., biofilter transient response to varying dimethyl disulfide concentration) was made by sparging a known flow of compressed nitrogen into a stainless steel tank (2 L) containing liquid dimethyl disulfide (CAS# 624-92-0; 99% purity; Aldrich Chemicals, Milwaukee USA) and finally injecting the dimethyl disulfide vapor laden nitrogen into the saturated air stream coming from the humidification column. Flow rates of the main humidified air stream and the contaminants or the nitrogen loaded with contaminants were controlled by high precision valves and monitored by previously calibrated rotameters in order to maintain the desired contaminant inlet concentrations and air residence times within the biofilter columns.

Table 4.1 summarizes the biofilter system design and operating parameters. The reduced sulfur gas concentrations in the inlet waste air stream ranged from 10 to 615 ppmv for hydrogen sulfide, 37 to 141 for methyl mercaptan, and 12 to 54 for dimethyl disulfide. The waste air had a relative humidity close to 100%, as a result there was no drying in the filter beds and the water spray nozzles designed for irrigating the filter beds were never used during the entire study. The pressure drop over the filter beds was always less than 10 mm water. The biofilter columns were maintained at room temperature (25 - 27 °C).

Table 4.1. Design and operating parameters

Parameters	Experiment I Hydrogen Sulfide	Experiment II Methyl Mercaptan	Experiment III Dimethyl Disulfide
Column inner diameter	0.187 m	0.187 m	0.187 m
Effective packing height[*]	0.66 m	0.66 m	0.66 m
Packed bed volume	0.018 m^3	0.018 m^3	0.018 m^3
Waste airflow rate	1.7 - 2.9 m^3 h^{-1}	1.7 - 2.9 m^3 h^{-1}	1.7 – 3.2 m^3 h^{-1}
Empty bed residence time	38 - 22 s	38 - 22 s	38 - 20 s
Contaminant inlet concentration	10 – 615 ppmv	37 – 141 ppmv	12 – 54 ppmv
Inlet waste air humidity	> 97 %	> 97 %	> 97 %
Temperature	25 – 27 °C	25 – 27 °C	25 – 27 °C
Pressure drop	< 10 mm H$_2$O	< 10 mm H$_2$O	< 10 mm H$_2$O

[*]in three equal sections

4.3.4. Analytical Techniques

The concentration of H_2S in the gas phase was determined by gas chromatographic analysis using a Hewlett-Packard (HP) 5890 II gas chromatograph (GC). A flame photometric detector (FPD) was utilized. The GC was equipped with a HP fused silica capillary column (30 m long, 0.32 mm diameter and 4 μm film thickness, cross-linked methyl silicone). The samples were injected into the GC via a 10-position switching valve (Valco Instruments Inc.) with a 1 mL sample loop. The samples were drawn via positive pressure through the valves and the sample loop to the column. The GC oven temperature was programmed from 50 to 230 °C in increments of 40 °C min^{-1} with a hold of 1 min at 50 °C and 2 min at 230 °C. The injection and the detector temperatures were set at 100 and 225 °C, respectively. Air, helium and hydrogen flow rates were 82, 4 and 85 mL min^{-1}, with a column head of 85 kPa. Increasing the injection sample volume, by regulating the valve opening time, allowed testing at very low concentrations, giving an effective detection limit of approximately 250 parts per billion by volume (ppbv). The GC was calibrated with a certified five component mixture (48.2 ppmv hydrogen sulfide, 50.2 ppmv methyl mercaptan, 50.1 ppmv dimethyl sulfide, 50.1 ppmv dimethyl disulfide, and balance nitrogen) using standard dilution methods. Hydrogen sulfide-, methyl mercaptan-, and dimethyl disulfide-air calibration standards were prepared at eight concentration levels by injecting small quantities (3-100 mL) of five component gas mixture into 500 mL pure nitrogen contained in tedlar bags. The volume of pure nitrogen in tedlar bags was measured by a high precision mass flow controller (MKS Instruments, Canada) with a measuring range of 5 - 1000 mL min^{-1}. The samples were analyzed in triplicate.

The gas samples taken from the inlet and outlet streams as well as axially along the biofilter columns were passed through a concentrated phosphoric acid impinger to remove moisture prior to collection into 1 L tedlar bags[37]. All the gas samples were analyzed within 4-5 hours. The tedlar bags were flushed with activated carbon filtered, house air overnight for reuse.

4.3.5. Surface and Mass Loading, and Biofilter Elimination Capacity

The surface loading rate is a measure of the volumetric gas loading to a biofilter. Mass loading rate, a combination of the waste airflow rate and the contaminant concentration in the waste gas stream, is defined as the mass of pollutant introduced into a biofilter per unit volume of filter material per unit time. Elimination capacity, a measure of the contaminant destruction capacity of a biofilter bed, is defined as the mass of contaminant degraded per unit volume of filter material per unit time;

while removal efficiency is the operating parameter used to judge the success of a biofilter in terms of bio-conversion of a contaminant. Waste air empty bed residence time and surface loading rate, contaminant mass loading rate, and biofilter elimination capacity and removal efficiency were determined using the relationships between the influent and effluent gas phase concentrations, waste airflow rate, and the volume of the biofilter material as follows:

$$\tau = (V/Q)*3600 \tag{1}$$

$$L_s = (Q/A) \tag{2}$$

$$L_m = (Q/V)*C_{in}* \ \beta \tag{3}$$

$$EC = (Q/V)*(C_{in} - C_{out})*\beta \tag{4}$$

$$RE = [(C_{in} - C_{out})/C_{in}]*100 \tag{5}$$

where, τ is the empty bed residence time (s), V is the volume of filter material (m^3), Q is the waste airflow rate ($m^3 \ h^{-1}$), L_s is the waste air surface loading rate ($m \ h^{-1}$), A is the area of cross-section of biofilter column (m^2), L_m is the contaminant mass loading rate ($g \ m^{-3} \ h^{-1}$), EC is the biofilter elimination capacity ($g \ m^{-3} \ h^{-1}$), RE is the biofilter removal efficiency (%), C_{in} and C_{out} are the contaminant concentrations in the influent and effluent waste gas streams (ppmv), $\beta = [(M*10^{-3})/\{22.4*(273+T)/273\}]$ is the conversion factor, M is the contaminant molecular weight (34 for hydrogen sulfide, 48 for methyl mercaptan, and 94 for dimethyl disulfide), and T is the operating temperature (^{o}C).

4.4. RESULTS AND DISCUSSION

This section deals with some typical responses that might be encountered in real systems like initial startups, step-changes in pollutant concentration and/or in the waste airflow rate, concentration spikes in the case of a process malfunction, and periods of non-use. Re-acclimation tests were conducted to examine the response of previously acclimated biofilters to starvation periods, to evaluate whether the biofiltration process can withstand such situations and to determine the time needed to recover full efficiency. Influence of humidification, during the downtime period, on the re-acclimation time course was evaluated by comparing the re-acclimation periods following the idle phase and the no-contaminant-loading phase, respectively. Starvation included both the "idle phase" when there was no airflow through the biofilter bed and the "no-contaminant-loading phase" when only water saturated air was flowing through the biofilter. Two periods of idle phase (2-3 and 7 days) and a period of no-contaminant-loading phase (2-3 days) were selected. These periods were

chosen to closely mimic the real world periods of non-operation, such as 2 to 3 day weekends, and a 7 day period that could occur during mill shutdowns, retooling and/or process upsets.

4.4.1. Experiment I. Transient Behavior of Biofilters Degrading Hydrogen Sulfide

4.4.1.1. Biofilter Acclimation to Hydrogen Sulfide

The biofilters were acclimated by increasing the hydrogen sulfide concentration gradually from 10 to 500 ppmv to establish steady state conditions as indicated by hydrogen sulfide removals remaining constant with time. Waste airflow rate ($1.7 \text{ m}^3 \text{ h}^{-1}$) was kept constant and the hydrogen sulfide concentration was increased by varying the compressed hydrogen sulfide feed rate into the saturated air stream. Relatively high hydrogen sulfide loading conditions were used during the acclimation period to ensure that there was enough chemical to stimulate the growth of the biofilm microorganisms after saturating the adsorption capacity of the filter material. Due to a break down of the gas chromatograph, the outlet concentration could not be regularly monitored; rather the effluent concentration was occasionally measured by GASTEC detector tubes (GASTEC Corporation, Japan), thus no information on chemical-specific acclimation rates could be obtained.

4.4.1.2. Biofilter Transient Response to Step-Changes in Hydrogen Sulfide Loading

Following the biofilter acclimation, three tests (a) with stepwise changes in inlet hydrogen sulfide concentration maintaining constant residence time, (b) with varying waste airflow rate maintaining fixed hydrogen sulfide concentration, and (c) with an introduction of a hydrogen sulfide concentration spike were performed to examine the transient response of the biofilters.

(a) Step-Changes in Hydrogen Sulfide Concentration: Keeping the residence time ($\tau = 38$ sec) fixed, the effect of abrupt changes in hydrogen sulfide inlet concentration from 73.6 to 202.4 ppmv, specified in terms of mass loading, on the biofilter dynamics was investigated. The hydrogen sulfide feed rate was increased stepwise maintaining the airflow constant so that the hydrogen sulfide mass loading changed proportionally. After adjusting the hydrogen sulfide concentrations the system was allowed to stabilize for 40-48 hours before changing to another mass loading. A series of five tests (L_m, $2.75*L_m$, $0.0*L_m$, $1.92*L_m$, $1.35*L_m$) starting with the base case condition of $L_m = 9.7 \text{ g m}^{-3} \text{ h}^{-1}$ was carried out. The transient response of the biofilters to these abrupt changes in inlet hydrogen sulfide concentrations is presented in Figure 4.2.
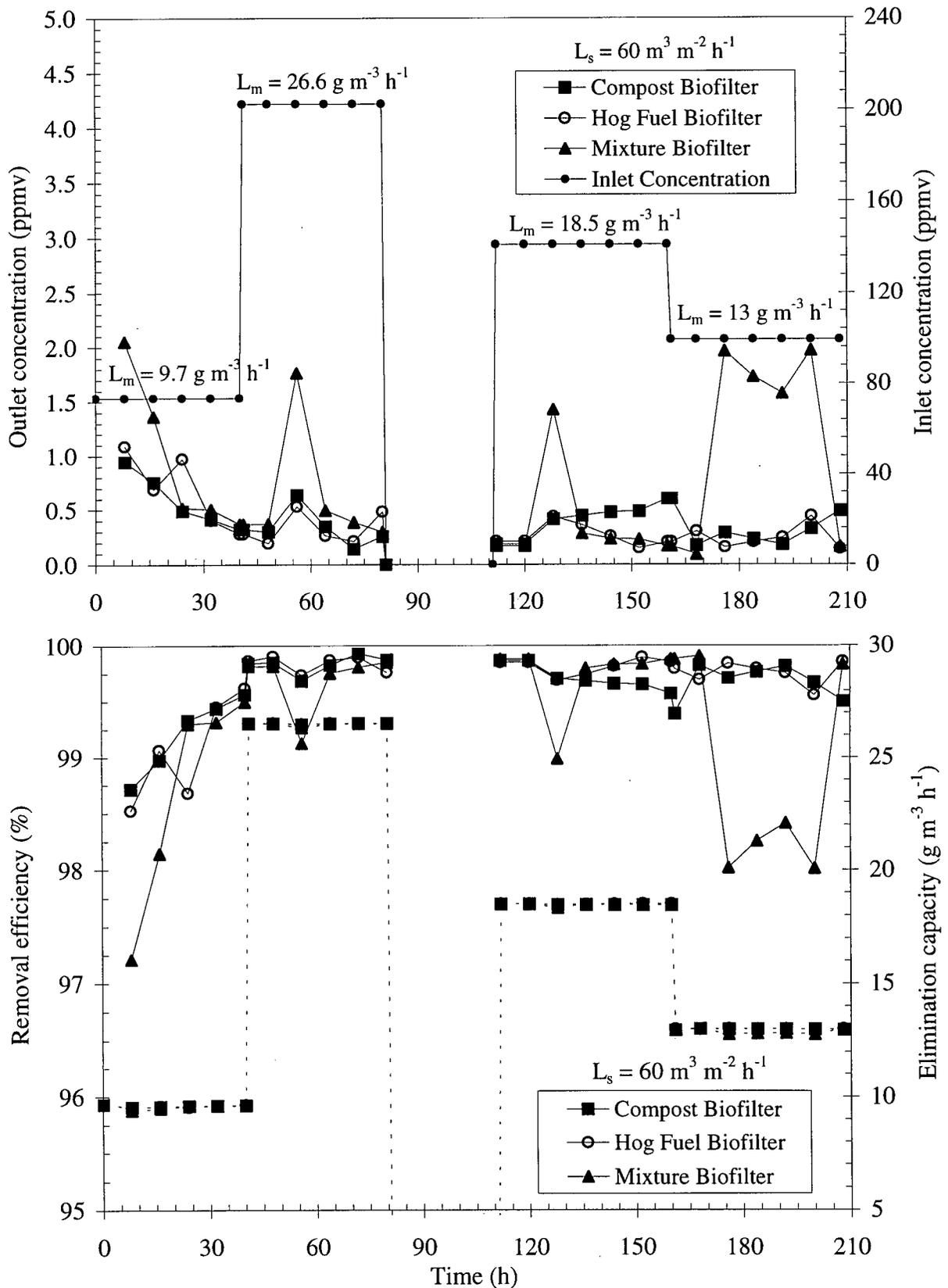
Figure 4.2. Transient behavior of biofilters to step-changes in contaminant concentration for hydrogen sulfide degradation. Solid lines represent the removal efficiency and dashed lines the elimination capacity.

(Elimination capacities were the same for all three media)

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The compost and the hog fuel biofilters showed similar responses without any breakthroughs. The bio-elimination efficiency for hydrogen sulfide remained > 99% for all the five step-changes in inlet concentration. The mixture biofilter exhibited two minor "breakthroughs" (only a few ppmv) in the second and the third steps and recovered to its original removal rates within 12 hours. The third breakthrough in the mixture biofilter for the last step was longer and took 30 hours to recover to its initial state. Even in these breakthrough situations the outlet hydrogen sulfide concentration never rose above 2 ppmv.

(b) Step-Changes in Waste Airflow Rate: Maintaining the hydrogen sulfide inlet concentration (C_{in} = 99 ppmv) constant, the effect of short time changes in airflow rate from 1.7 to 2.9 m^{-3} h^{-1}, characterized in terms of residence time, on the transient behavior of biofilters was investigated. Airflow rate was changed stepwise keeping the hydrogen sulfide inlet concentration constant, so that the mass loading of hydrogen sulfide changed proportionally. After adjusting the airflow rate/hydrogen sulfide concentrations the system was allowed to stabilize for 40-48 hours before another step change. A sequence of four test periods (τ, 0.85*τ, 0.6*τ, 0.7*τ) starting with the base case condition of τ = 38 sec were carried out. The transient response of the biofilters to fluctuating airflow rates (Figure 4.3), was similar to that of step-changes in the hydrogen sulfide concentration, with the compost and the hog fuel biofilters showing no *breakthrough*. The mixture biofilter showed short-lived peaks in outlet gas hydrogen sulfide concentration, which never exceeded 2.5 ppmv, that lasted for 10-20 hours, with each increment in the waste airflow rate that eventually increased the contaminant mass loading.

The reason why the mixture biofilter exhibited short-lived peaks after every step change in hydrogen sulfide mass loading, in both the tests, is not clear. One possible explanation may be the reduced adsorptive capacity of the mixture filter bed. This was evident in the first test as the mixture biofilter started with lowest removal efficiency. In the case of the compost and hog fuel biofilters hydrogen sulfide was essentially removed by sorption after the step increases during the time the inactive microorganisms located in the unexposed parts of biofilter became active to turn on their pollutant degrading mechanisms. Additionally, the reduction in the removal efficiency may be because of short gas-liquid contact time as a result of low gas retention time in the second test (changes in waste airflow rate) as reported by Chung et al.[19], rather than reaction limitation because Sublette and Sylvester[38] reported that microorganisms could metabolize H_2S
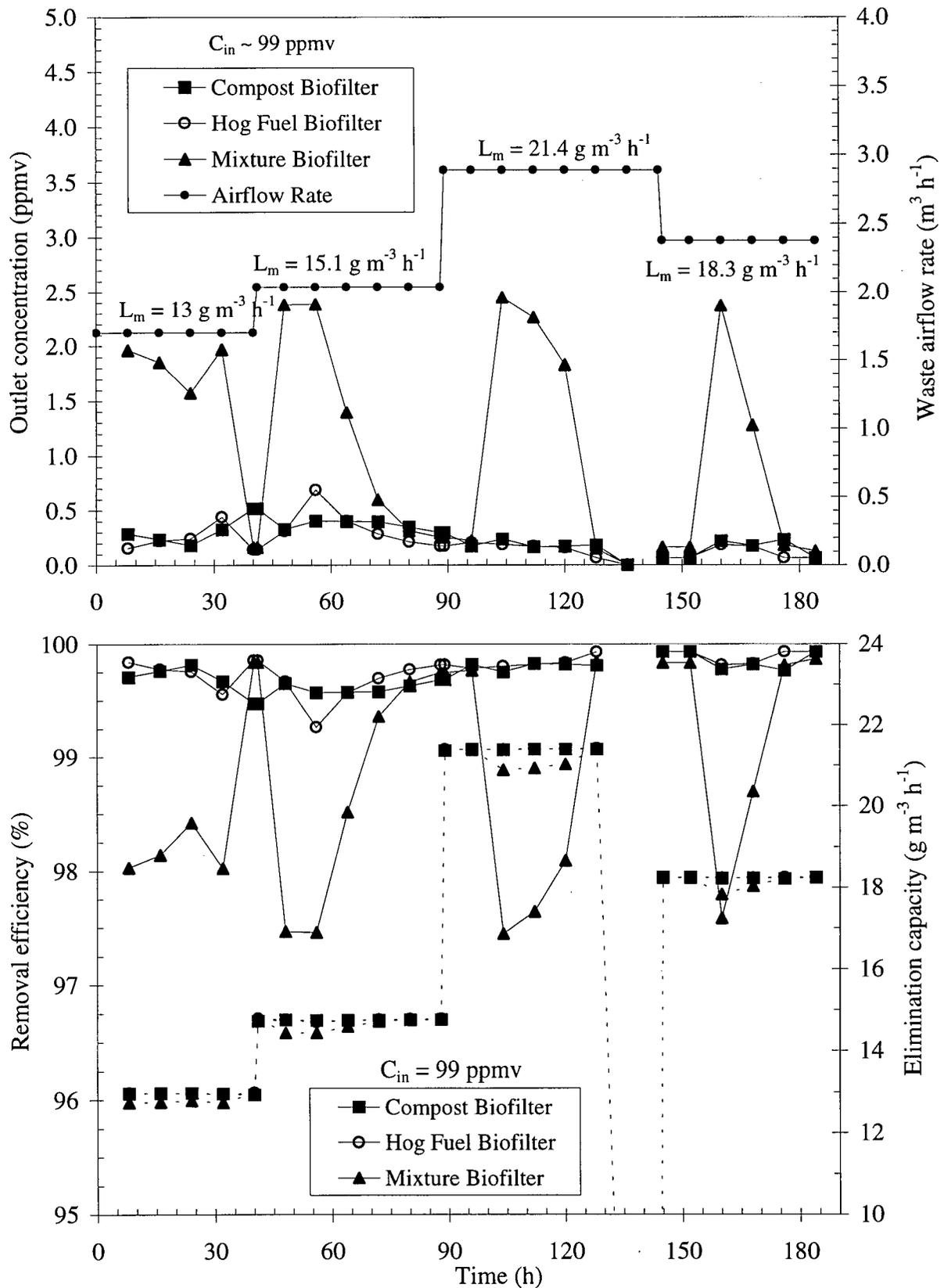
Figure 4.3. Transient behavior of biofilters to step-changes in waste airflow rate for hydrogen sulfide degradation. Solid lines represent the removal efficiency and dashed lines the elimination capacity. (Elimination capacities were the same for all three media)

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within 1-2 seconds. Nonetheless, no significant changes in the elimination capacity of any of the biofilters were observed as a result of the imposed step-changes, which indicates that the biofilters were operated below their critical hydrogen sulfide mass loading and operating in the zero order kinetic regime.

(c) Hydrogen Sulfide Concentration Spike: An hydrogen sulfide spike of 615 ppmv was applied for half an hour after a steady inlet concentration of 370 ppmv had been applied for about 6 hours (corresponding to an increase in the mass loading from 48.7 to 80.9 g m^{-3} h^{-1}) (Figure 4.4). The concentration spike caused an immediate increase in the outlet concentration in all the three biofilters, resulting in decreased removal efficiency. The removal efficiency, monitored immediately after the pulse was stopped, dropped from >99.8% to 97% for the compost and the mixture biofilter, while in hog fuel biofilter it dropped to 96% from an initial value of about 98%. The biofilters then performed at relatively low removal rates for a few hours before the microorganisms started to re-acclimate and gradually the removal efficiency improved. The elimination efficiency rapidly recovered to its original value for the hog fuel and the mixture biofilter within 1.5 hour while it took about 2.5 hours to reach its initial value in the case of the compost biofilter. Surprisingly in this test the hog fuel biofilter could not reach a removal efficiency of greater than 98%, for some unknown reasons. One possible reason might be a toxic effect of higher concentrations of hydrogen sulfide on the resident microbial communities by altering the media buffering capacity, as reported in an earlier study[18], because the hog fuel biofilter had the lowest bed pH (6.85) in comparison to the compost (7.40) and mixture (7.15) biofilters. Nutrient (nitrogen) limitation also may be a contributing factor for the lowest removal efficiency because hog fuel has a very low content of total nitrogen (Table 3.1). Nevertheless, the recovery time was relatively short suggesting that the microorganisms present in the biofilter media only require a short re-acclimation period to adopt to moderate disturbances/spikes in hydrogen sulfide concentration.

4.4.1.3. Biofilter Dynamic Response to Hydrogen Sulfide Elimination after Starvation

Three re-acclimation tests after (a) a one week and (b) a three month idle phase, and (c) a three day no-contaminant loading phase were performed to examine the re-acclimation time course of the three biofilter media materials degrading hydrogen sulfide. Like the initial start-up, re-acclimation was considered to have been achieved when 99% removal was attained.
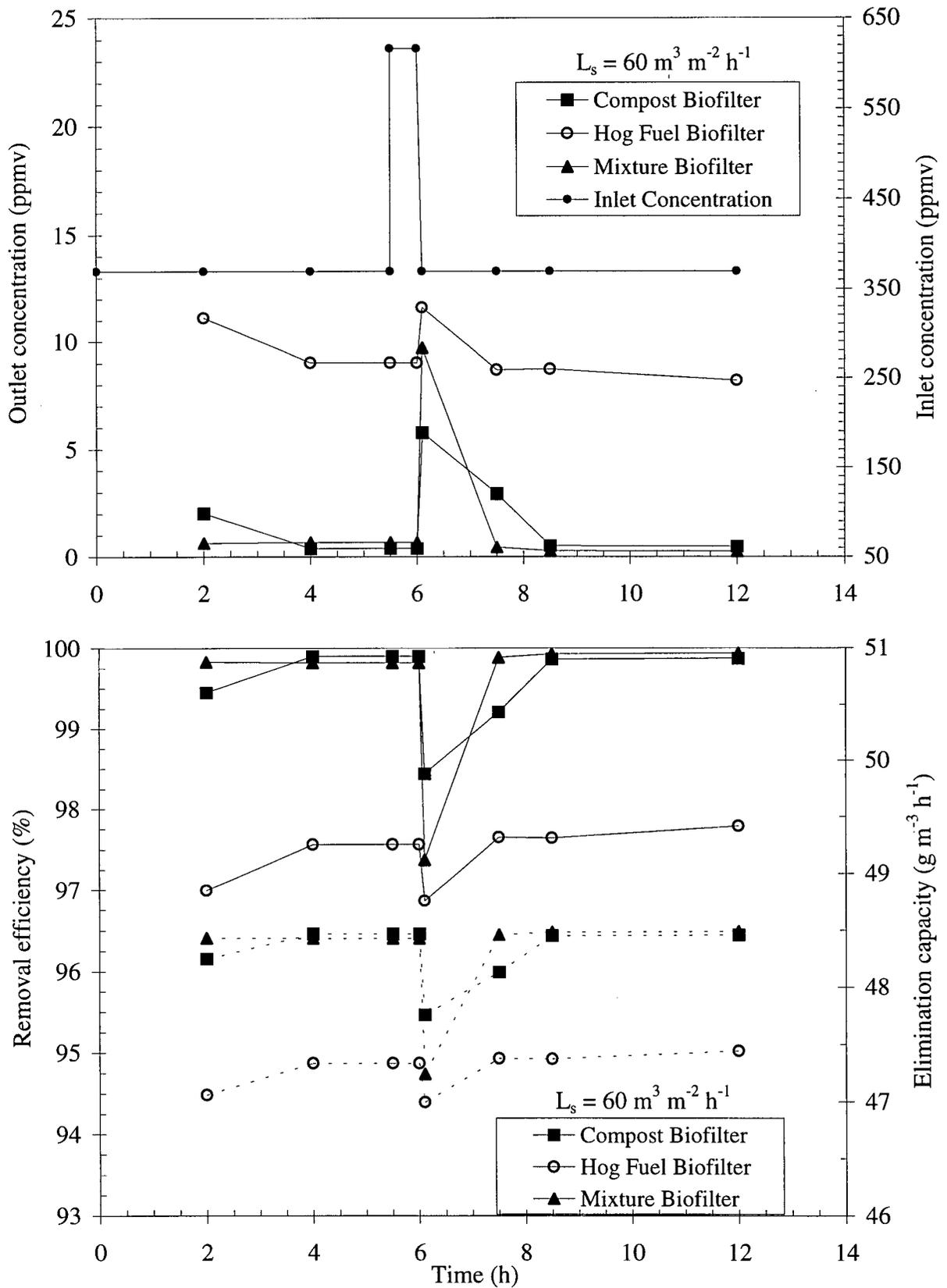
Figure 4.4. Transient behavior of biofilters to concentration spike for
hydrogen sulfide degradation. Solid lines represent the removal efficiency
and dashed lines the elimination capacity.

(a) Re-acclimation after a One Week Idle Phase: In this test the biofilters were left idle (no airflow) for a week, after which the system was restarted under the same conditions pertaining prior to the interruption. At the end of this period, the hydrogen sulfide mass loading was re-started at about 45 g m^{-3} h^{-1} (corresponding to a C_{in} of 340 ppmv and an L_s of 60 m^3 m^{-2} h^{-1}). Figure 4.5 shows the restart-up time course for the three biofilters after a seven day starvation period. All the three biofilters rapidly recovered their initial removal efficiency of 99% within 25-30 hours. The recovery pattern was almost same in all the three biofilters; however, the mixture biofilter showed the lowest removal efficiency after restart-up. Although hydrogen sulfide removal efficiencies were low in the initial hours after the restart, some biodegradation took place immediately after the process was restarted, indicating that the hydrogen sulfide degrading microorganisms already existed in the biofilters, but they may not have been quite active because of seven days of starvation. This eventually led to a much shorter re-acclimation time as compared to the initial acclimation periods of 10-12 days for biofilters treating hydrogen sulfide reported in the literature[20,21].

(b) Re-acclimation after a Three Month Idle Phase: The biofilters were restarted after a period of three months during which there was no airflow through the biofilters at all. The operating conditions after the restart were same as before the break. The re-acclimation was started with the addition of hydrogen sulfide mass loading at about 50 g m^{-3} h^{-1} (corresponding to a C_{in} of 379 ppmv and an L_s of 60 m h^{-1}). The biofilter re-acclimation is presented in Figure 4.6. Here the biofilters showed a mixed pattern of recovery. Initially after the re-start the removal efficiency increased for first 24 hours, except in the mixture biofilter, probably due to adsorption on the filter media, and then started declining for up to 47 hours in case of the hog fuel and the mixture biofilters while even further up to 71 hours for the compost biofilter. After 71 hours the performance of the compost and the mixture biofilters increased steadily reaching an elimination efficiency of 99% by 122 hours. The elimination efficiency of the hog fuel biofilter decreased further after 71 hours reaching approximately 97% by 122 hours. After 122 hours the removal efficiency for the compost and the mixture biofilter remained stable at around 99% while the hog fuel biofilter performance improved and reached 98% by 142 hours. This re-confirmed the hypothesis of toxicity of higher hydrogen sulfide concentrations on the microbial populations resident in the hog fuel biofilter as observed in the earlier test with the biofilter response to hydrogen sulfide concentration spike. The test could not be continued further because a hydrogen
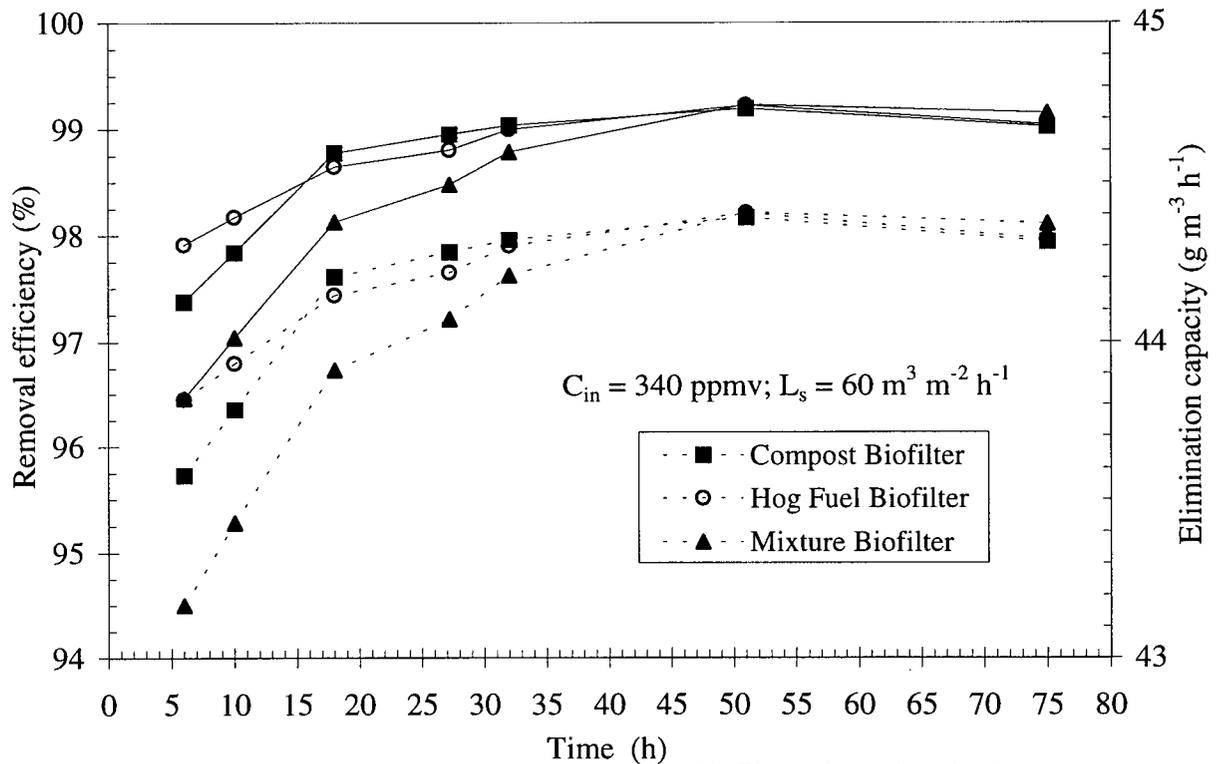
Figure 4.5. Reacclimation time course for biofilters degrading hydrogen sulfide after one week idle phase. Solid lines represent the removal efficiency and dashed lines the elimination capacity.
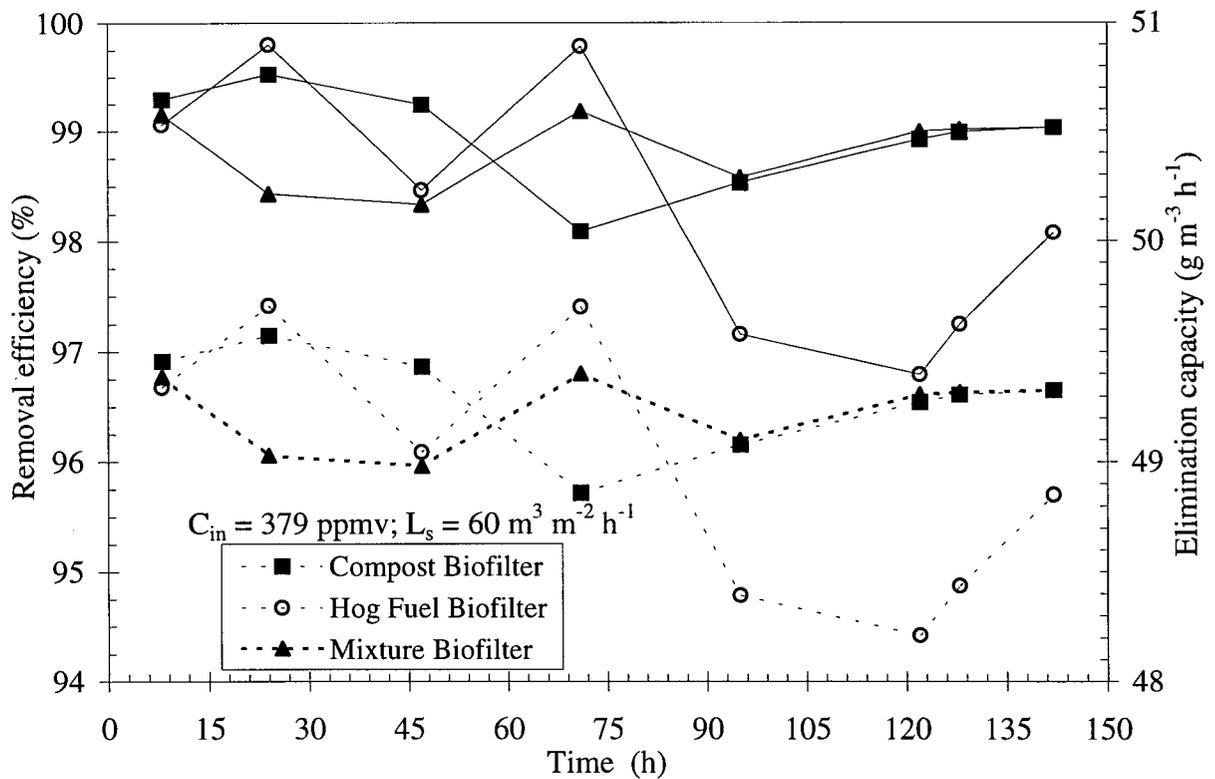
Figure 4.6. Reacclimation time course for biofilters degrading hydrogen sulfide after three month idle phase. Solid lines represent the removal efficiency and dashed lines the elimination capacity.

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sulfide gas cylinder was not available at the time. Nevertheless, the re-acclimation, although taking longer than for the seven days starvation period, confirmed the earlier results of Martin and Loehr[30]. It was significantly short (5 days) as compared to the initial acclimation times of 10 to 12 days reported by Degorce-Dumas et al[20] and Furusawa et al[21] mainly because biodegradation had already occurred during the sorption phase with immediate and efficient biodegradation restoration.

(c) Re-acclimation after a Three Day No-Contaminant-Loading Phase: The biofilters were restarted under the same conditions as before, after a no-contaminant-loading phase of three days. The re-acclimation was started with the addition of a hydrogen sulfide mass loading at about 49 g $m^{-3} h^{-1}$ (corresponding to a C_{in} of 370 ppmv and an L_s of 60 m h^{-1}). The results are summarized in Figure 4.7. The re-acclimation pattern was similar to one after the idle phase, however the biofilters started with a removal efficiency of around 98 %. The elimination efficiency increased in the case of the compost and the mixture biofilter reaching > 99% within 17 hours. However, in case of the hog fuel biofilter the removal efficiency further dropped to about 96%. 25 hours after restart-up the hydrogen sulfide destruction efficiency was almost constant and > 99% for the compost and the mixture biofilter, while it reached about 97.5% in case of the hog fuel biofilter by 42 hours. Once again the hog fuel biofilter could not achieve a removal efficiency of greater than 98% even after 42 hours of restart-up time, possibly indicating the acidification of filter bed as a result of bio-oxidation of hydrogen sulfide. It may be noted that these tests were conducted after 6 months of continuous operation of the biofilters treating hydrogen sulfide. Nevertheless, the re-acclimation time was much shorter, about half of the restart-up time after the seven day idle phase, justifying the results of a previous study[30] that re-acclimation measured by achieving a desirable removal efficiency is achieved significantly faster if humidified air containing no contaminant is passed through the biofilter rather than letting the biofilter stagnate with no air flow.

4.4.2. Experiment II. Transient Behavior of Biofilters Degrading Methyl Mercaptan
4.4.2.1. Biofilter Acclimation to Methyl Mercaptan
The biofilters were acclimated to methyl mercaptan by gradually increasing the contaminant mass loading in order to establish steady state conditions as indicated by contaminant removals remaining constant with time. While keeping the waste airflow rate (1.7 $m^3 h^{-1}$) constant, the
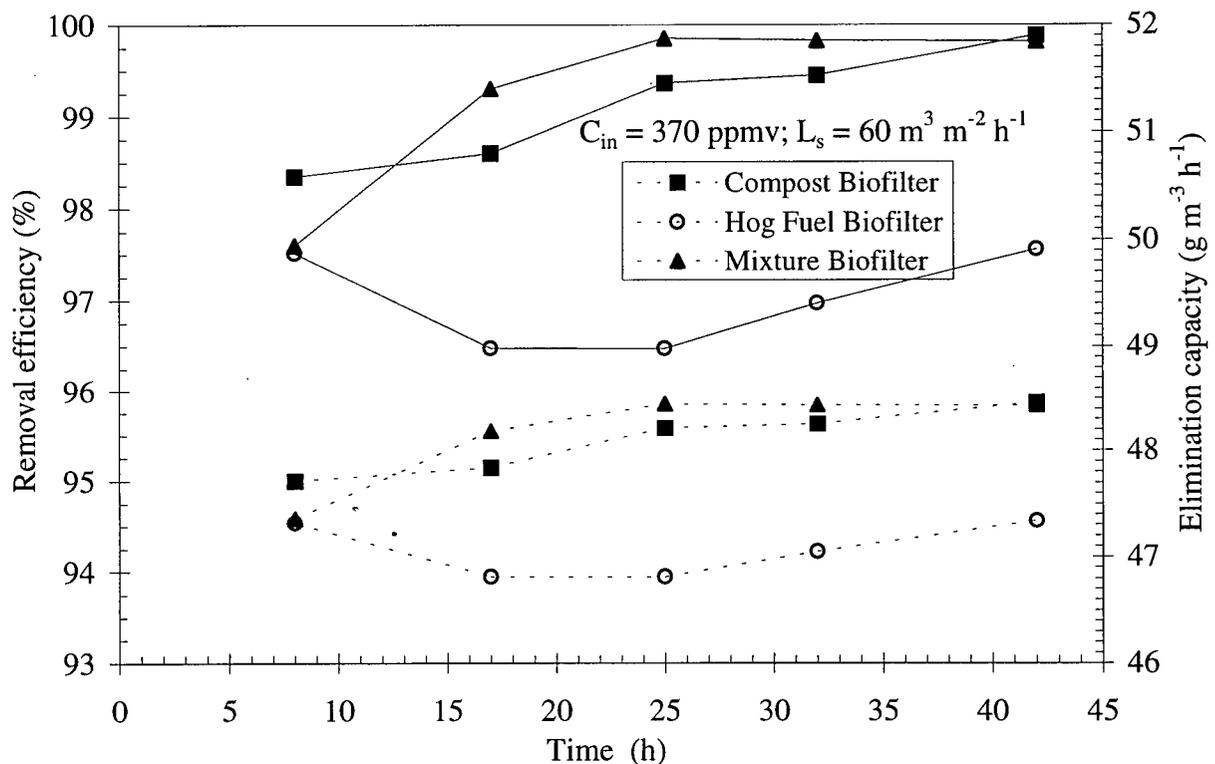
Figure 4.7. Reacclimation time course for biofilters degrading hydrogen
sulfide after three day no-contaminant-loading phase. Solid lines represent
the removal efficiency and dashed lines the elimination capacity.

contaminant mass loading was increased stepwise by gradually increasing the methyl mercaptan feed rate into the saturated air stream. Previous research[39] had suggested that it is beneficial to initially expose the biofilters to dilute pollutant gas streams and only when conditioning has been achieved should the loading be increased in steps. Relatively high contaminant loading conditions were used during the acclimation period to ensure that there was enough chemical to stimulate the growth of the biofilm microorganisms after saturating the adsorption capacity of the filter material. The inlet concentration was kept constant at about 35 ppmv for first 56 hours and then increased to around 104 ppmv.

Figure 4.8 shows the initial acclimation period for the biofilters when exposed to a methyl mercaptan concentration of 35 ppmv. The hog fuel biofilter exhibited little variation over the first part of the experiment. It started at about 93% removal, oscillated up and down a bit during the first 18 hours, but gradually rose to reach 97% removal after 40 hours. The outlet concentration started at about 2 ppmv and gradually went down to 1 ppmv after about 40 hours.
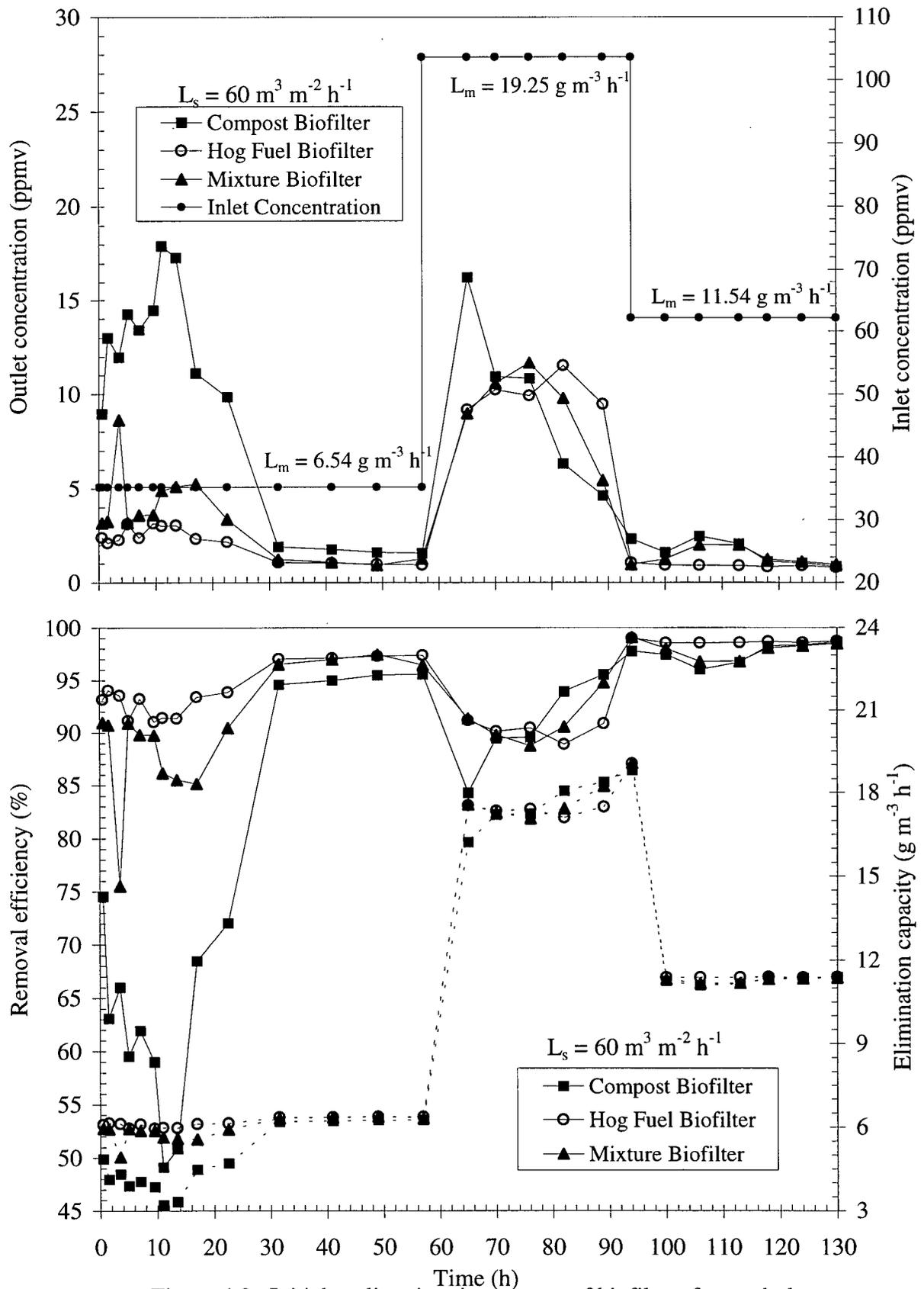
Figure 4.8. Initial acclimation time course of biofilters for methyl mercaptan degradation. Solid lines represent the removal efficiency and dashed lines the elimination capacity.

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The elimination capacity was essentially constant at 6 g m^{-3} h^{-1} over the initial acclimation period of 56 hours. The behavior of the compost biofilter was more erratic. Its % removal started at 75%, dropped to 48% after 12 hours, then rose to achieve 97% removal 50 hours after start-up. The outlet concentrations reflect the % removal results. The elimination capacity started at about 4.5 g m^{-3} h^{-1}, dropped to 3 g m^{-3} h^{-1}, then rose to 6 g m^{-3} h^{-1} after 30 hours and stayed there for the rest of the acclimation period. The mixture biofilter tended to behave in a way that was intermediate between the compost biofilter and the hog fuel biofilter, but closer to the latter. Thus the hog fuel biofilter acclimatized faster than the mixture biofilter which acclimatized faster than the compost biofilter. In experiment I (Section 4.4.1) the mixture biofilter took longest to acclimatize for hydrogen sulfide, while the hog fuel and compost biofilters took the same length of time to acclimatize. However, in experiment III (Section 4.4.3) the hog fuel biofilter again achieved higher % removals of dimethyl disulfide somewhat more quickly than the compost biofilter, which in turn acclimatized a little more quickly than the mixture biofilter. We therefore conclude that there appears to be no superiority of one biofilter medium over the others in terms of reaching an initial steady state defined, rather arbitrarily, by achieving and maintaining a % removal > 97.

This initial acclimation (5-6 days) was fairly rapid, however, in comparison to the startup times that have been reported previously. Hirai et al[22] reported that 17 days elapsed before complete removal of 46 ppmv methyl mercaptan was achieved, while Allen and Phatak[35] reported that very little activity was observed in compost biofilters treating methyl mercaptan (28 ppmv) over a period of 10 days. In this study, inoculation of the filter material with pulp mill waste activated sludge was probably a major reason for the brevity of the startup.

One might speculate that the differences we observed in acclimation time behavior were attributable to differences in adsorptive capacity between hog fuel and compost. If that were the case then there should have been similar acclimation pattern for hydrogen sulfide, methyl mercaptan and dimethyl disulfide, but they behaved differently. Table 3.1 (Chapter III) indicates that the particle size distributions for the three biofilter materials are similar. So it would appear that there would not be very significant differences in the external specific surfaces of these three media. We have no data on the internal pore structure of these biofilter bed particles, but since

they were wet when our measurements were made, we expect the internal pores would have been full of water and so their surfaces would not have been very accessible for adsorption.

To explain these variations in initial acclimation time we suggest that they are attributable to variations in the time it takes to establish a microbial population on the biofilters that is compatible with the biofilter material and the TRS gas being used.

After 57 hours the methyl mercaptan inlet concentration was raised from 35 ppmv to 104 ppmv. All three biofilters responded with a drop from around 95% removal to about 88% over approximately 20 hours. The compost biofilter point at 82% removal and 67 hours appears to be a sampling aberration, we can think of no other explanation for it. The % removal of the biofilters then rose to 97% or more over a period of another 20 hours and remained at that level after the inlet methyl mercaptan concentration was reduced to 62 ppmv. The behavior of the outlet concentration as a function of time is compatible with the % removals since the % removal, see Equation 4, depends on the outlet concentration. Thus it took about 40 hours for the biofilters to recover from a step increase in methyl mercaptan concentration from 35 to 104 ppmv. In response to a decrease in methyl mercaptan concentration, from 104 ppmv to 62 ppmv, there was no change in the % removal performance for the hog fuel biofilter, while % removal for the compost and mixture biofilters dropped from 99% to 96% over a 13 hour period then rose back to 99% removal in 17 hours. Thus there was a minor decrease in % removal performance for the compost and mixture biofilters over a 30 hour period in response to a step change down in methyl mercaptan concentration.

When the methyl mercaptan concentration rose from 35 ppmv to 104 ppmv the elimination capacities rose quickly over a period of 8 hours from 6 g m^{-3} h^{-1} to 16 g m^{-3} h^{-1} for the compost biofilter and 17 g m^{-3} h^{-1} for the other two biofilters. If Monod type kinetics suitably represents the macro-kinetic behavior of these biofilters when removing methyl mercaptan, this rise in elimination capacity implies that the biofilters in this experiment were not operating in the zero order kinetics regime, since if they had been there should have been no change in the elimination capacity. Because of the lack of sufficient experimental data for methyl mercaptan removal macro-kinetic analysis (using a Monod kinetic model) could not be performed, however, for

hydrogen sulfide, dimethyl sulfide and dimethyl disulfide removal Monod kinetics model did fit the data well under steady state conditions (see Chapter V).

4.4.2.2. Biofilter Transient Response to Step-Changes in Methyl Mercaptan Loading

Following the initial acclimation experiment on media previously unexposed to methyl mercaptan (outlined in Figure 4.8), three tests were conducted. These investigated (a) step changes in methyl mercaptan inlet concentration at constant residence time, (b) step-changes in waste airflow rate at fixed methyl mercaptan mass loading (hence at varying inlet concentration) and (c) introduction of a pulse change in methyl mercaptan concentration. The goal of these studies was to examine the transient response of the biofilters to conditions typical of those that might be encountered in real systems.

(a) Step-changes in Methyl Mercaptan Concentration: Maintaining the empty bed contact time ($\tau = 38$ s) constant, the effects of short-term changes in methyl mercaptan inlet concentration from 37 to 141 ppmv on the transient behavior of the biofilters were investigated. The methyl mercaptan concentration was increased stepwise at a fixed waste airflow rate so that the mass loading changed proportionally. After adjusting the methyl mercaptan concentration the system was allowed to stabilize for 36 hours before changing to another mass loading. A series of five tests with different mass loadings (L_m, 2.95*L_m, 1.75*L_m, 0.0*L_m and 3.81*L_m), starting with the base case condition of $L_m = 6.87$ g m^{-3} h^{-1}, were performed. Figure 4.9 summarizes the biofilters' dynamic responses to fluctuating methyl mercaptan inlet concentrations. In fact, not much change occurred over this period of exposure to 37 ppmv. The elimination capacities were constant. It took the three biofilters previously acclimatized to methyl mercaptan, about 40 hours to stabilize at 97% removal after exposure to a methyl mercaptan concentration of 37 ppmv giving an outlet mercaptan concentration of 1 - 2 ppmv.

After the inlet methyl mercaptan concentration was changed from 37 ppmv to 109 ppmv, % removal in the compost biofilter dropped from 97% to 82% over a 6 hour period. A similar drop occurred in the initial acclimatization of this biofilter (see Figure 4.8) when it was exposed to a step change increase in methyl mercaptan concentration. The reasons for this are inexplicable to us. Such a phenomenon was not observed in the hog fuel and the mixture biofilters. All three biofilters were able to recover to 97% removal in 36 hours. The outlet concentrations over this
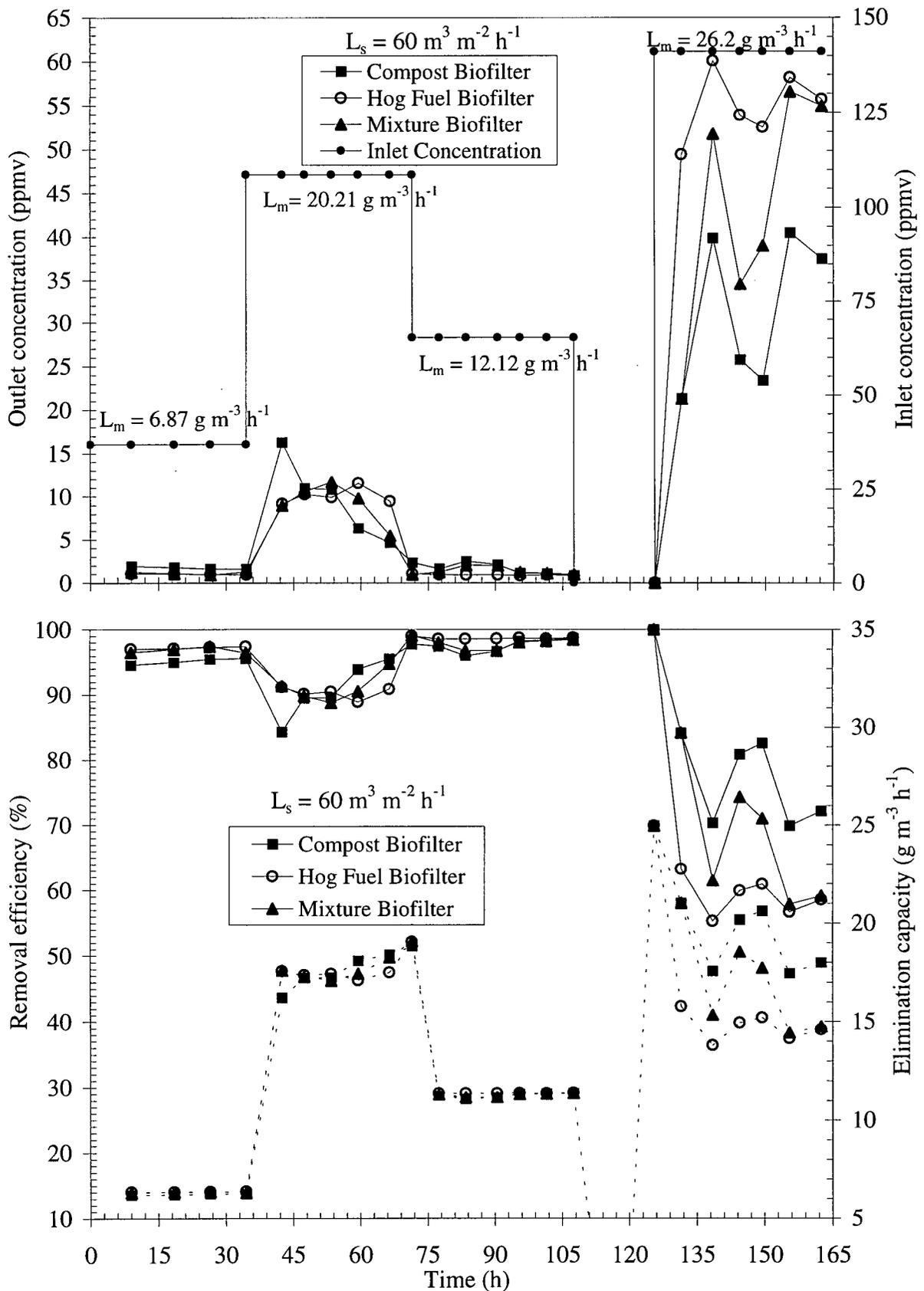
Figure 4.9. Transient behavior of biofilters to step-changes in contaminant concentration for methyl mercaptan degradation. Solid lines represent the removal efficiency and dashed lines the elimination capacity

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period are what would be expected based on the % removal observations. The elimination capacities quickly rose to higher levels, over an 8 hour time period, to 16 - 17 g m^{-3} h^{-1}, then more slowly to 19 g m^{-3} h^{-1} over the next 36 hours. Next the inlet methyl mercaptan concentration was reduced to 65 ppmv. This had no effect on the hog fuel biofilter but resulted in a minor decrease in % removal for the other two biofilters. This behavior is consistent with the behavior shown in Figure 4.8 during the initial acclimatization when there was a step change down in methyl mercaptan concentration. Recovery to > 97% removal took about 24 hours. The elimination capacities of the three biofilters dropped to 11 g m^{-3} h^{-1} over 5 hours, then held constant at 11 g m^{-3} h^{-1} until the methyl mercaptan concentration was set = 0. Subsequently the inlet methyl mercaptan concentration was lowered to 0 and held there for about 18 hours. No gas analyses were done during this period.

Then the inlet methyl mercaptan concentration was raised to 141 ppmv. This caused a major decline in performance with the hog fuel biofilter's % removal dropping most rapidly followed by the mixture biofilter and the compost biofilter. After this last increase in methyl mercaptan concentration none of the biofilters was able to regain its original level of % removal in 40 hours. During the initial drop in % removal the compost and mixture biofilters had the same rate of decline but the rate of decline in the compost biofilter slowed before that of the mixture biofilter did. This initial decline in the removal efficiency was followed by an increase in % removal (not much increase for the hog fuel biofilter) then by a further decline and after that a small increase. The outlet concentrations were high after this increase in inlet concentration and remained high. Elimination capacities rapidly rose to 25 g m^{-3} h^{-1}, but then declined and fluctuated in the range 14 - 21 g m^{-3} h^{-1}, with the hog fuel and the mixture biofilters having lower values than the compost biofilter.

The failure of the biofilters to recover from this increase in methyl mercaptan feed concentration suggests an overload condition in which the capacity of the biofilm for removal of methyl mercaptan was exceeded. Possibly this occurred because of inhibition of the microorganisms in the biofilm by too high a methyl mercaptan concentration or because the microorganisms, working at full capacity (i.e. in the zero order reaction rate regime of Monod kinetics), were unable to cope with this high rate of methyl mercaptan mass loading. This decrease in

performance was not permanent since in the next set of experiments on the effects of airflow rate changes at constant inlet concentration (see below) the biofilters again performed effectively.

At lower mercaptan mass loadings (lower inlet concentrations) the biofilters were able to recover removal capacity within about 40 hours and to achieve new levels of elimination capacity in about 8 hours or less. This is contrary to the findings reported by Allen and Phatak[35] that biofilter efficiency was very sensitive to small changes in methyl mercaptan inlet concentration, which they attributed to instability in their biofilters.

(b) Step-Changes in Waste Airflow Rate: Holding the methyl mercaptan mass loading ($L_m \approx$ 16.85 g m^{-3} h^{-1}) constant, the effect of short term changes in waste airflow rate from 1.7 to 2.9 m^{-3} h^{-1} on the transient behavior of the biofilters was investigated. Airflow rate was changed stepwise thereby varying the methyl mercaptan inlet concentration proportionally. As a result the mass loading remained unchanged. After adjusting the airflow rate (gas residence time) the system was allowed to stabilize for 36 hours before another step change. A sequence of four tests with various gas residence times (τ, 0.6*τ, 0.7*τ and τ), starting with the base case condition of τ = 38 sec was carried out.

The transient response of the biofilters to fluctuating airflow rates is shown in Figure 4.10. As the airflow rate rose from 1. 7 to 2.9 m^3 h^{-1} the % removals of all three biofilters went down, the hog fuel and mixture biofilters more so than the compost biofilter. As a result of this change in airflow rate at constant mass loading, the inlet methyl mercaptan concentration went from 91.2 ppmv to 52.5 ppmv. The results illustrated in Figure 4.9 also showed a drop in % removal as mercaptan concentration decreased. After 36 hours at this airflow rate the compost biofilter had recovered to 97% removal and the hog fuel and mixture biofilters had recovered to 96% removal. An airflow rate reduction to 2.4 m^3 h^{-1} resulted in no significant changes in % removal for the compost biofilter and the mixture biofilter. The hog fuel biofilter's % removal fluctuated a little. A further decrease in airflow rate to 1.7 m^3 h^{-1} caused no change in % removal for any of the biofilters even though these decreases in airflow rate were accompanied by increases in methyl mercaptan concentration to 91.2 ppmv.
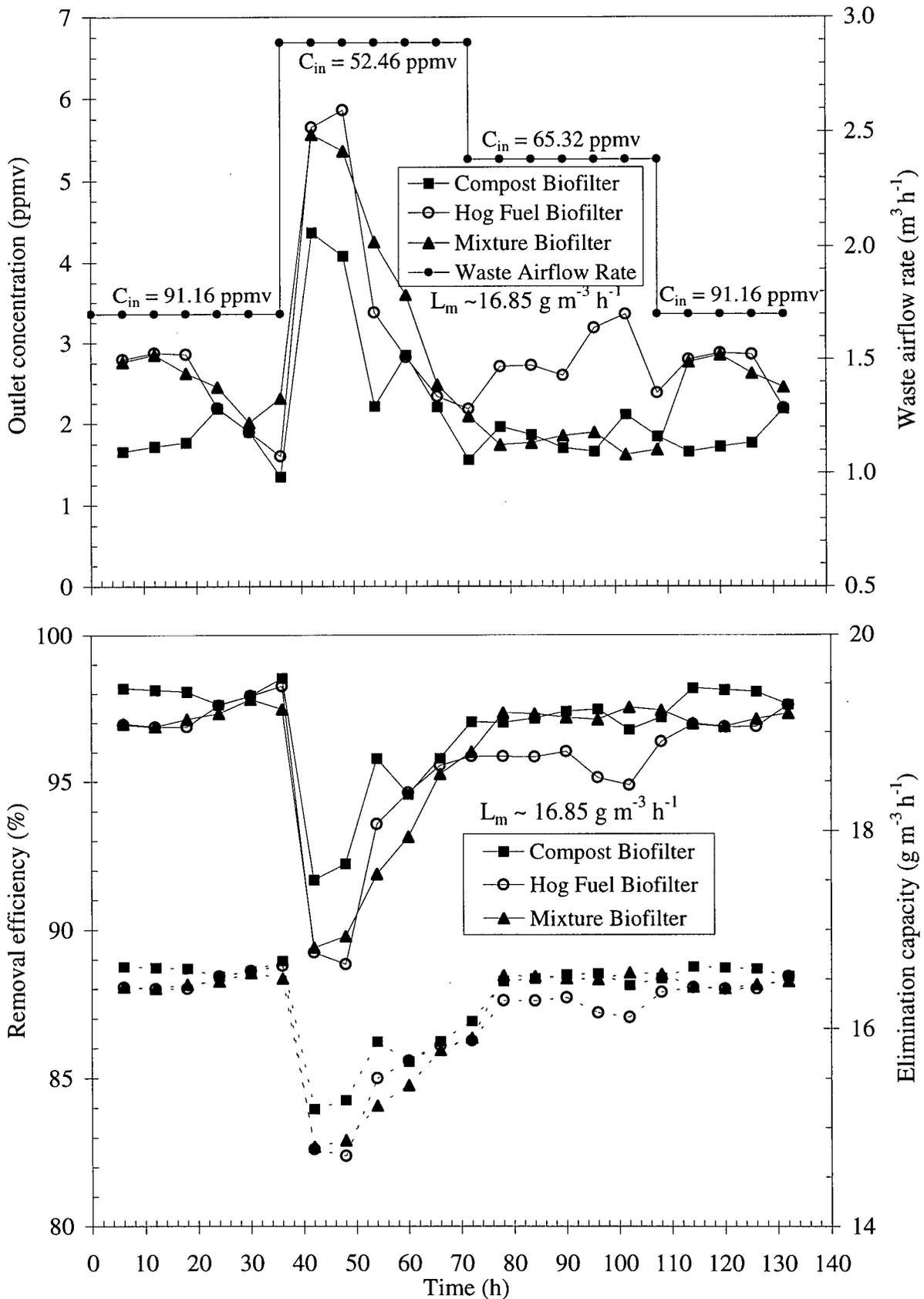
Figure 4.10. Transient behavior of biofilters to step-changes in waste airflow rate for methyl mercaptan degradation. Solid lines represent the removal efficiency and dashed lines the elimination capacity.

The outlet concentrations went from 1.3 ppmv (compost), 1.4 ppmv (hog fuel) and 2.2 ppmv (mixture) to 4.3, 5.4 and 5.4 ppmv respectively over a period of 7 hours. They then dropped back down to more or less their original levels after 36 hours. This is in contrast to the results shown in Figure 4.9 where a decrease in concentration in the inlet led to a decrease in the outlet concentration.

After the airflow rate was reduced from 2.9 to 2.4 m^3h^{-1} the outlet concentrations for the compost and mixture biofilters were unaffected. The outlet concentration for the hog fuel biofilter went up and came back down again. A further reduction in airflow rate to 1.7 m^3h^{-1} resulted in the compost biofilter's outlet concentration rising from 1.7 to 2 ppmv. The mixture biofilter's outlet concentration went from 1.6 to 2.7 then to 2.3 ppmv. The hog fuel biofilter's outlet concentration went from 2.5 to 3.0, then to 2.3 ppmv.

At an airflow rate of 1.7 m^3 h^{-1} the elimination capacities of the three biofilters were more or less the same and constant at 16.5 g m^{-3} h^{-1}. When the airflow rate was raised to 2.9 m^3 h^{-1} the elimination capacities of the three biofilters were lowered to 15.5 g m^{-3} h^{-1} for the compost biofilter and 14.7 g m^{-3} h^{-1} for the other two over 7 hours. These elimination capacities then gradually increased over 36 hours, regaining their original values of 16.5 g m^{-3} h^{-1} (a little less for the hog fuel biofilter) and staying at that level as the airflow rate was reduced to 2.4 and later to 1.7 m^3 h^{-1}.

As airflow rate increases the residence time of the gas in the biofilter decreases; so there is less time for compounds to be removed from the air and be taken into the biofilm. Thus methyl mercaptan could have been swept through the biofilter without being transferred when the airflow rate was increased. This could explain the increase in methyl mercaptan concentration shown in Figure 4.10 to occur right after the increase in the airflow rate. However this increased outlet mercaptan concentration did not persist as the airflow rate continued at the high level. In fact, the outlet concentrations decreased more or less back to their pre-increase values. It would then seem that this rise in outlet concentration accompanying an increased airflow rate and decreased inlet concentration was not primarily a residence time effect. Another possible explanation is that mercaptan was adsorbed at the higher concentration of the first stage of this experiment. When the airflow rate increased the inlet concentration decreased in order to

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maintain the constant, controlled mass loading rate. There would be less adsorbed mercaptan in equilibrium with the lower gas concentration in the air under these conditions. The transient rise in outlet mercaptan concentration could then be a result of desorption from the biofilm/biofilter media into the air stream. A similar effect can be discerned in the data shown in Figure 4.11 below for a spike (pulse) increase in inlet mercaptan concentration. In Figures 4.8 and 4.9 when the mercaptan concentration went from a high level to a lower value for both the compost and mixture biofilters there was a slight transient increase in outlet mercaptan concentration, which lends support to this argument about desorption effects.

(c) Methyl Mercaptan Concentration Spike: Pulse experiments were performed to study the dynamic response of these biofilters to short term pulse increases in contaminant concentration similar to what might occur in the case of a process malfunction. A concentration spike of 158 ppmv was applied for half an hour after a steady inlet concentration of 88 ppmv had been applied for about 12 hours (corresponding to a two-fold increase in the mass loading from 16.4 to 29.3 g m^{-3} h^{-1}). This concentration (158 ppmv) was greater than the 141 ppmv used in the experiments, summarized in Figure 4.9, that caused a major decline in biofilter performance. The results of this test are presented in Figure 4.11. The concentration spike caused an immediate increase in the outlet concentration in all of the three biofilters, resulting in decreased % removal. The compost biofilter was less affected by this (99% removal to 83%) than the hog fuel and mixture biofilters, which suffered similar declines in % removal (99% to 63%). The % removal efficiency of the compost biofilter rapidly recovered to its original value within an hour while it took about 5 - 6 hours for the hog fuel and the mixture biofilters to reach their initial performance levels. The outlet concentrations returned to their original levels after the same time intervals as the % removal recoveries noted in the previous sentence.

The elimination capacities rose in response to the spike increase in methyl mercaptan concentration, then dropped below their original, pre-spike values and regained their original values 6 hours after start of the pulse. In fact the compost biofilter was almost back to its original level 1 hour after the beginning of the pulse. Conceivably this drop below the original elimination capacity could have been the result of desorption, as the concentration dropped after the pulse, of some of the methyl mercaptan that might have been adsorbed at the higher concentration that prevailed during the pulse.
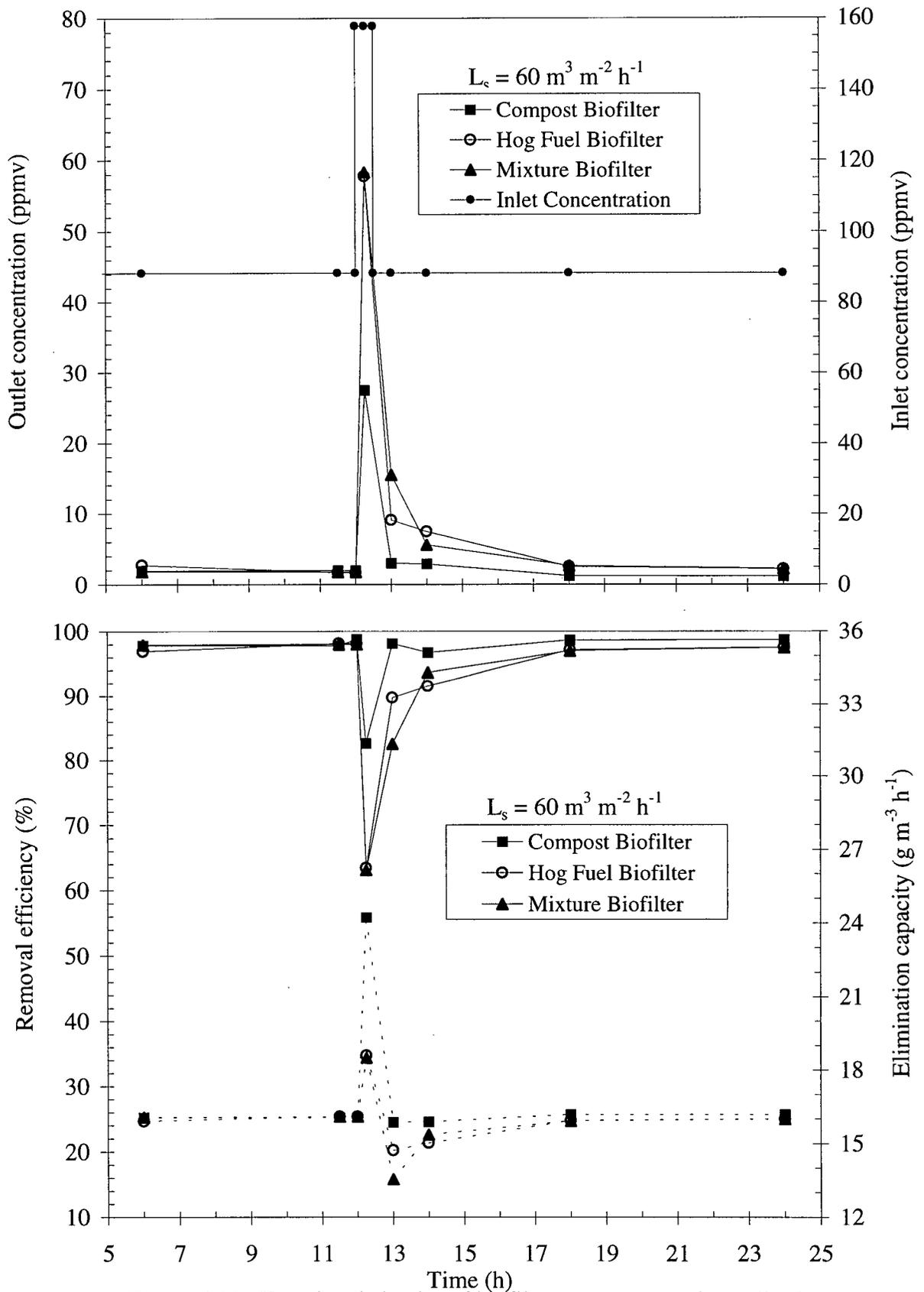
Figure 4.11. Transient behavior of biofilters to concentration spike for methyl mercaptan degradation. Solid lines represent the removal efficiency and dashed lines the elimination capacity.

A significant decrease in the removal capacity of all three biofilters was observed during the concentration pulse experiment. This is in accord with the findings noted above with step-changes in concentration in that it seems that the biofilters were overloaded at this concentration peak. However, the recovery time was relatively short suggesting that the microorganisms present in the biofilter media did not suffer any permanent impairment in their abilities to remove methyl mercaptan since they did recover fairly quickly from this shock load pulse.

4.4.2.3. Biofilter Dynamic Response to Methyl Mercaptan Elimination after Starvation

Re-acclimation tests were performed after two different idle phases (2 and 7 days) and a no-contaminant-loading phase (2 days). As with initial acclimation, biofilter re-acclimation was considered to have been achieved when 98% removal was attained.

(a) Re-acclimation after a Two Day Idle Phase: The biofilters were left idle for two days, after which the system was restarted under the same conditions prevailing prior to the interruption. At the end of the idle phase methyl mercaptan mass loading was re-started at 16.9 g m^{-3} h^{-1} (corresponding to an inlet concentration of 91.1 ppmv and an L_s of 60 m^3 m^{-2} h^{-1}). Figure 4.12 shows the restart-up time course for the three biofilters after an idle period of two days. All three biofilters rapidly recovered their previous removal efficiency of 98% and elimination capacity of 16.5 g m^{-3} h^{-1} within 10-15 hours.

(b) Re-acclimation after a One Week Idle Phase: In this test the biofilters were restarted after an idle period of one week. The operating conditions after the restart were the same as before the break i.e., as at the end of the two day idle phase test. The re-acclimation time course for the biofilters is presented in Figure 4.13. Here the biofilters showed a similar pattern of rapid recovery, and reached the original elimination efficiency of 97% within 25-30 hours. The recovery pattern was almost same in all the three biofilters in this test.

For some unknown reason, in the first test the compost biofilter showed the lowest removal efficiency after the restart-up while in the second test the hog fuel biofilter exhibited the most sluggish restart. Although the methyl mercaptan removal efficiencies were low in the initial hours of restart after a week's starvation, some biodegradation took place immediately after the
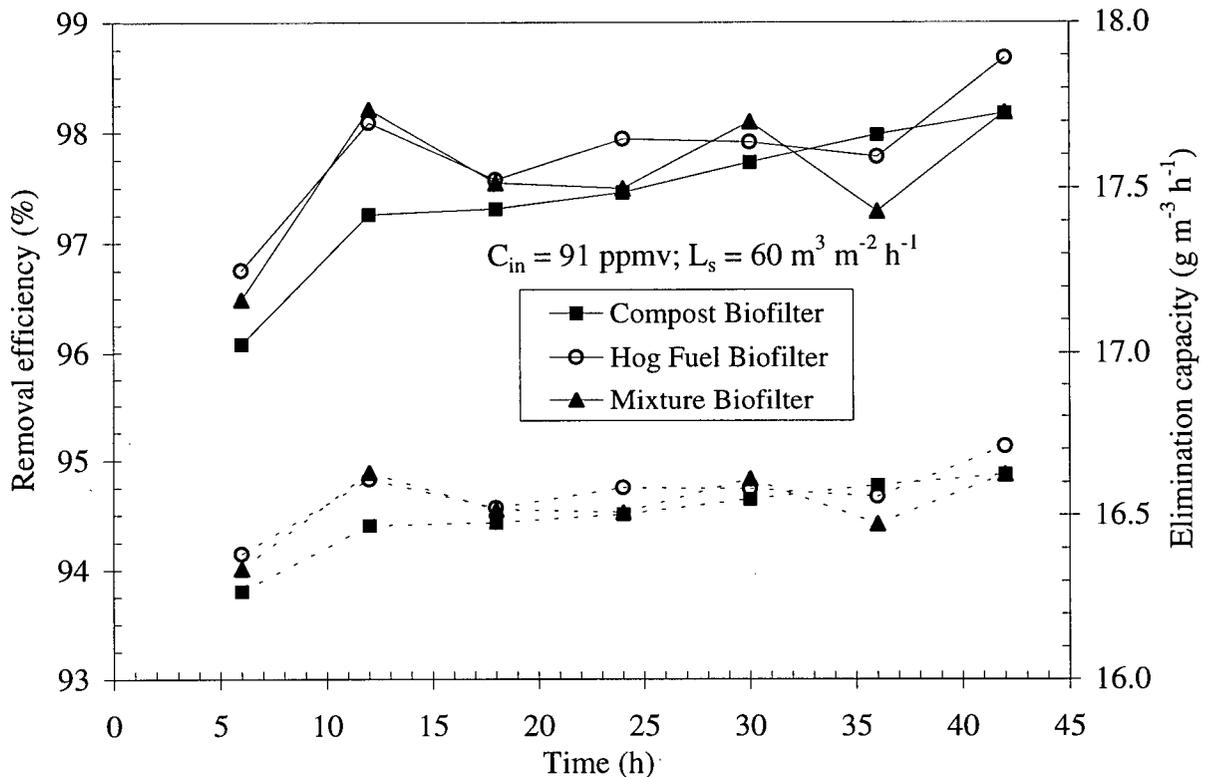
Figure 4.12. Reacclimation time course for biofilters degrading methyl mercaptan after two day idle phase. Solid lines represent the removal efficiency and dashed lines the elimination capacity.
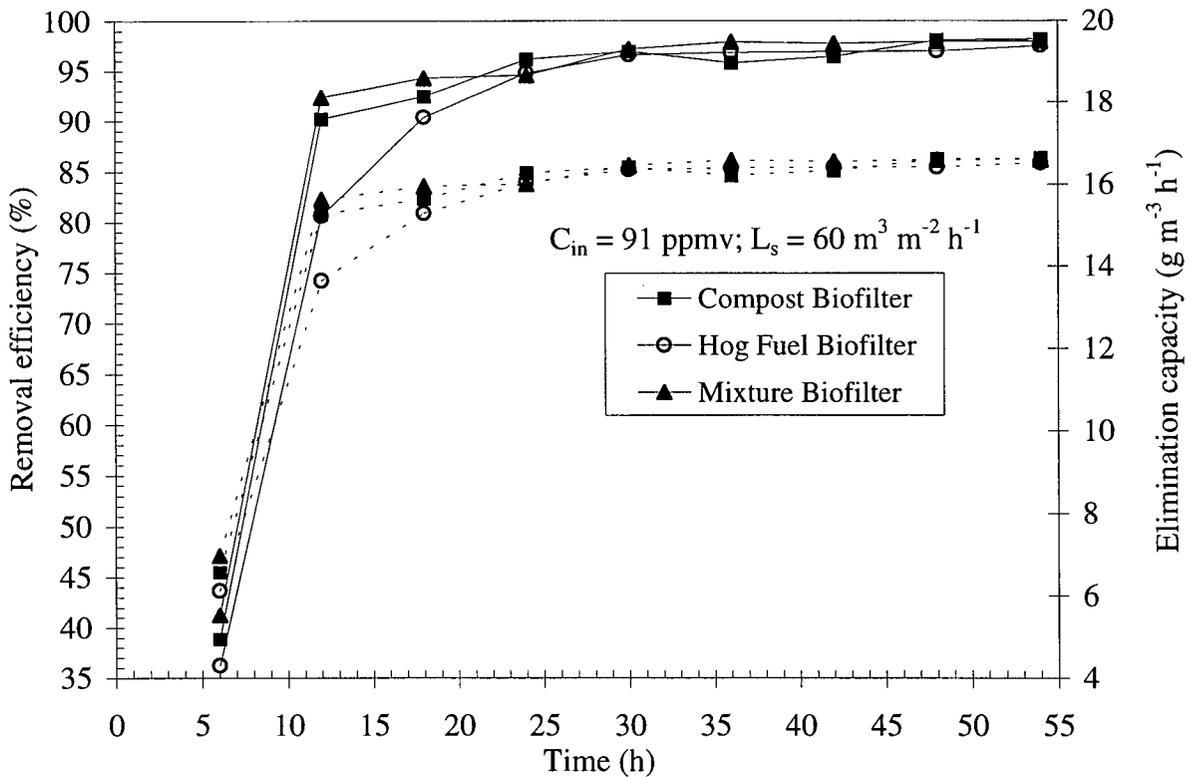
Figure 4.13. Reacclinmation time course for biofilters degrading methyl mercaptan after one week idle phase. Solid lines represent the removal efficiency and dashed lines the elimination capacity.

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restart, indicating that the methyl mercaptan degrading microorganisms were still active in the biofilters, but they were not quite as active because of 7 days of starvation.

Re-acclimation times (less than 1 day) after these idle phases were much shorter than the initial acclimation time of 5-6 days noted above. These results confirm those of Martin and Loehr[30].

(c) Re-acclimation after a Two Day No-Contaminant-Loading Phase: The biofilters were restarted under the same conditions as before, after a no-contaminant-loading phase of two days. The re-acclimation was started with the addition of methyl mercaptan at a mass loading at about 16.9 g m^{-3} h^{-1} (corresponding to an initial methyl mercaptan concentration of 91.1 ppmv and L_s of 60 m^3 m^{-2} h^{-1}). The results are summarized in Figure 4.14. The re-acclimation pattern was similar to the one observed after the idle phase (Figure 4.12). However the biofilters started with a higher elimination capacity reaching removal efficiency of around 98% and removal capacity of
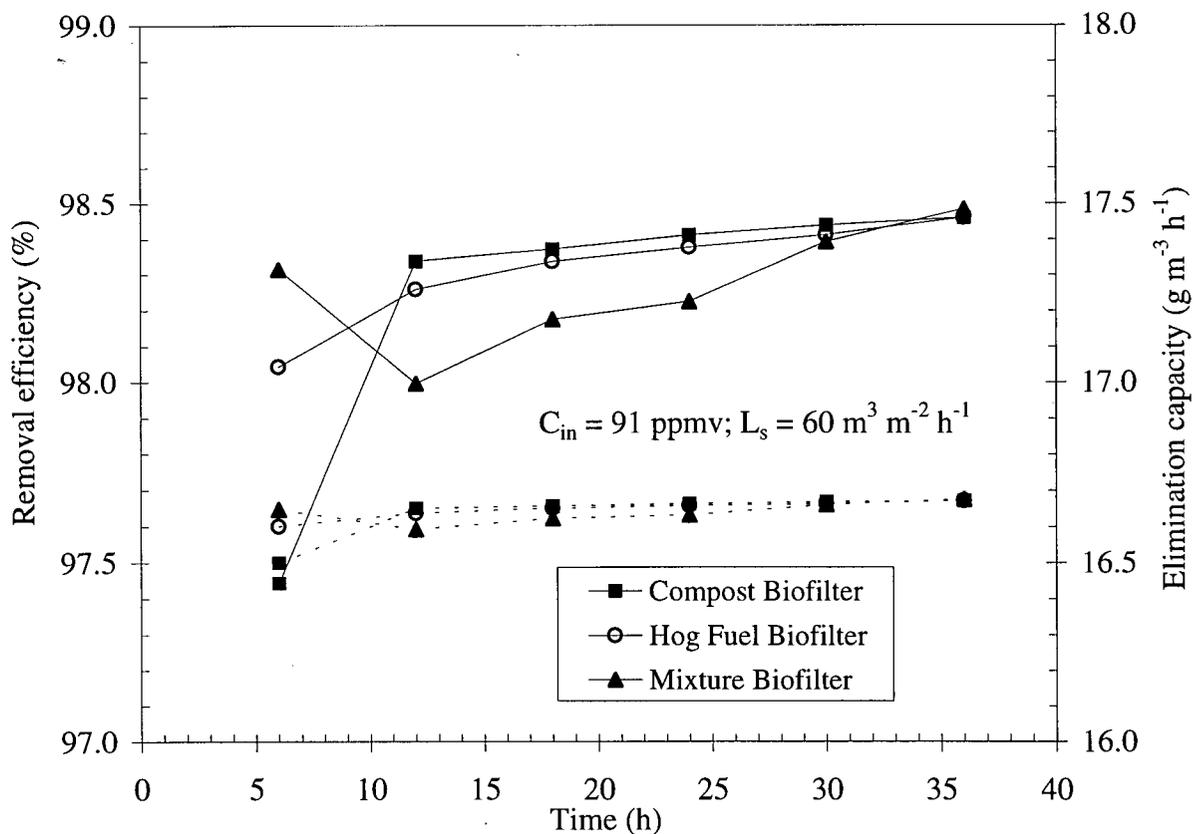

Figure 4.14. Reacclimation time course for biofilters degrading methyl mercaptan after two day no-contaminant loading phase. Solid lines represent the removal efficiency and dashed lines the elimination capacity

91

16.5 g m^{-3} h^{-1} within 6 hours of restart-up. However, once again the compost biofilter started with a lower removal efficiency as compared to other two biofilters. The re-acclimation time in this test was much shorter, about half that of the restart-up time after an idle phase of the same duration. Thus justifying earlier results[30] that re-acclimation time, as measured by the time it takes to achieve a certain % removal efficiency is achieved significantly faster if humidified air containing no contaminant is passed through the biofilter rather than letting the biofilter stagnate with no airflow.

4.4.3. Experiment III. Transient Behavior of Biofilters Degrading Dimethyl Disulfide
4.4.3.1. Biofilter Acclimation to Dimethyl Disulfide

There are many ways to describe the biofilter acclimation. For the experiment presented in this paper the biofilters were considered to be acclimated when 98% removal efficiency was achieved. This was chosen to allow consistent comparisons among many different experimental runs. Figure 4.15 shows the performances of the compost, hog fuel and mixture biofilters during the start-up period. The experiment was started with a loading of about 4.23 g m^{-3} h^{-1} corresponding to an inlet concentration of 11.6 ppmv and 38 sec empty bed residence time. The removal of dimethyl disulfide was instantaneous starting at around 85% and all three biofilters progressively gained efficacy reaching 90% removal and outlet concentrations of < 1 ppmv after 20 h. The effect of adsorption on the time required for acclimation was small because the sorption capacity of the biofilters was probably already saturated as a result of prior experiments on methyl mercaptan removal (Section 4.4.3.1). Moreover, the biofilter bed already supported a microbial population acclimated to TRS gases. However, it has been reported that the adsorption rate of dimethyl disulfide on soil is considerably less than the adsorption rate of hydrogen sulfide and methyl mercaptan[40]. In further tests the waste airflow rate (1.7 m^3 h^{-1}) was kept constant and the contaminant mass loading was increased gradually. It has been shown that it is beneficial to initially expose the biofilters to dilute waste air streams and then to increase the contaminant loading in steps once conditioning has been achieved[39]. After 20 h the dimethyl disulfide inlet concentration was approximately doubled, and further increased three-fold to 34 ppm after 110 hours. The percent removals continued to increase as a result of these concentration changes. The outlet concentrations dropped initially, rose after the first increase in inlet concentration. They then gradually decreased as the inlet concentration increased. The elimination efficiencies of the three biofilters reached close to 98% after 6 days, and with further increase in inlet concentration
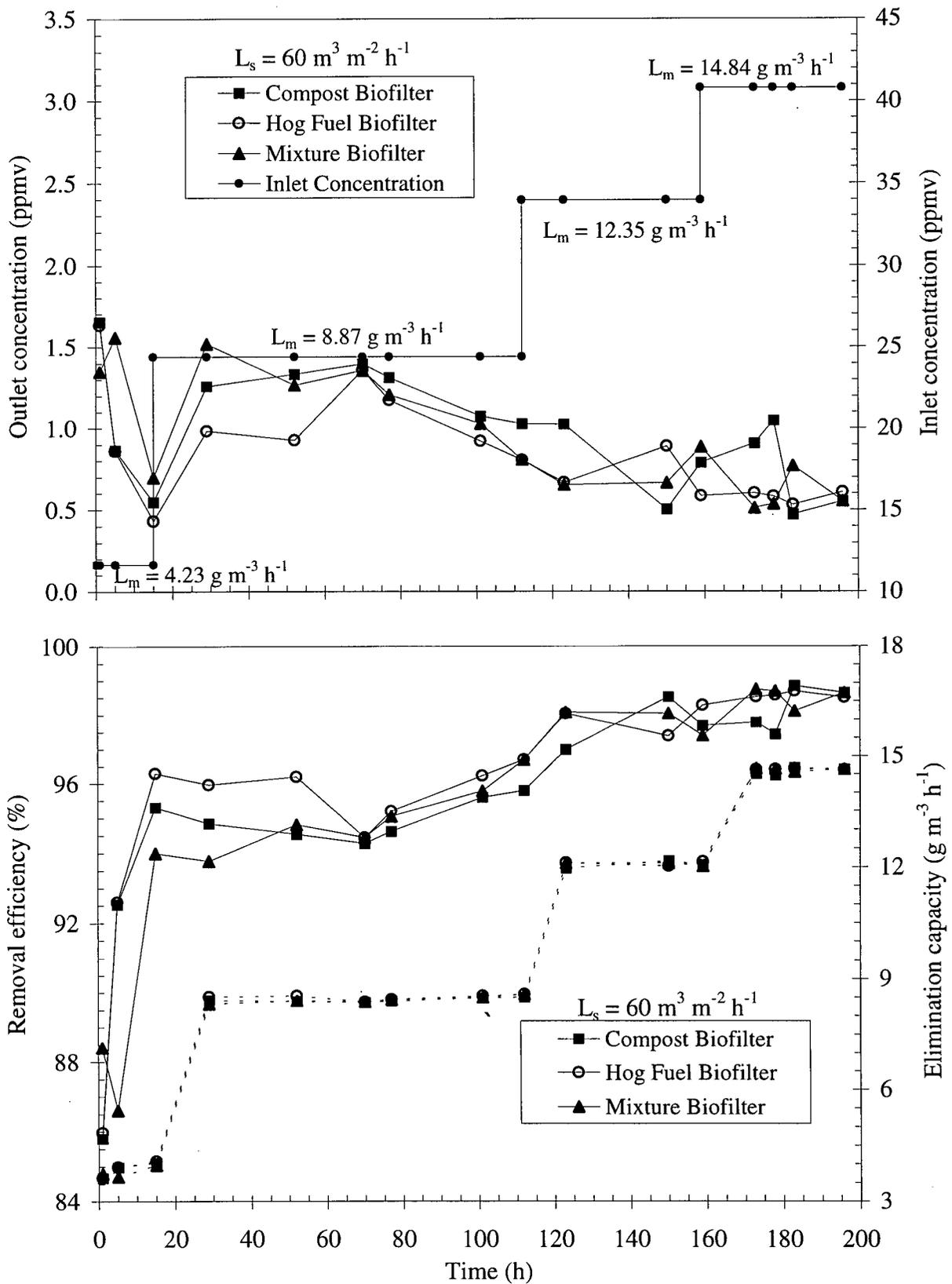
Figure 4.15. Initial acclimation time course of biofilters for dimethyl disulfide degradation. Solid lines represent the removal efficiency and dashed lines the elimination capacity.

to 41 ppmv the removal capacity remained unchanged confirming the biofilter acclimation. This initial acclimation time is close to that reported by Cho et al.[16] However, their reported acclimation period of 6 to 7 days was obtained for an inlet concentration of 5 ppmv. The brevity in the biofilter start-up time in our experiments was probably because of the prior application of the filter materials for methyl mercaptan removal, after seeding with pulp mill activated sludge.

4.4.3.2. Biofilter Transient Response to Step-Changes in Dimethyl Disulfide Loading

Two experimental runs (a) with step-changes in dimethyl disulfide inlet concentration at constant gas residence time, and (b) with fluctuating waste airflow rates at fixed dimethyl disulfide mass loading were conducted to investigate the influence of these typical conditions on the biofilters' performance.

(a) Step-Changes in Dimethyl Disulfide Concentration: Maintaining the empty bed contact time ($\tau = 38$ s) constant, the effect of short-term changes in contaminant concentration on the transient behavior of the biofilters was investigated by varying the dimethyl disulfide concentration from 34 to 54 ppmv. The dimethyl disulfide feed rate was increased stepwise at a fixed waste airflow rate so that the mass loading changed proportionally. After adjusting the dimethyl disulfide concentration the system was allowed to stabilize for 36 h before changing to another mass loading. A series of four tests with different mass loadings (L_m, $1.2*L_m$, $1.45*L_m$, and $1.6*L_m$), starting with the base case condition of $L_m = 12.35$ g m^{-3} h^{-1}, was performed. Figure 4.16 summarizes the biofilter dynamic responses to fluctuating dimethyl disulfide inlet concentrations. There was no measurable variation in the biofilter removal efficiencies until the step increment in concentration from 40 to 49 ppmv occurred. Below this the removal efficiency remained at 98+% for all three biofilters. With a further increase in concentration (≈ 54.4 ppmv), the dimethyl disulfide bioelimination efficiency dropped to close to 90% in all three biofilters and the reduction was much higher in the case of the compost biofilter. This could indicate that up to 49 ppmv, dimethyl disulfide removal was under a zero order kinetic regime and a further increase in concentration resulted in substrate inhibition. The elimination efficiency could not recover to its original value suggesting an overloading of the biofilters. However, after 24 hours the removal efficiency rose to close to 96%. Nevertheless, the observed critical concentration is much higher than the one reported by Arpacioglu and Allen[2]. They have reported that the % removals were reduced to 70% when dimethyl disulfide concentration was raised to about 50 ppmv.
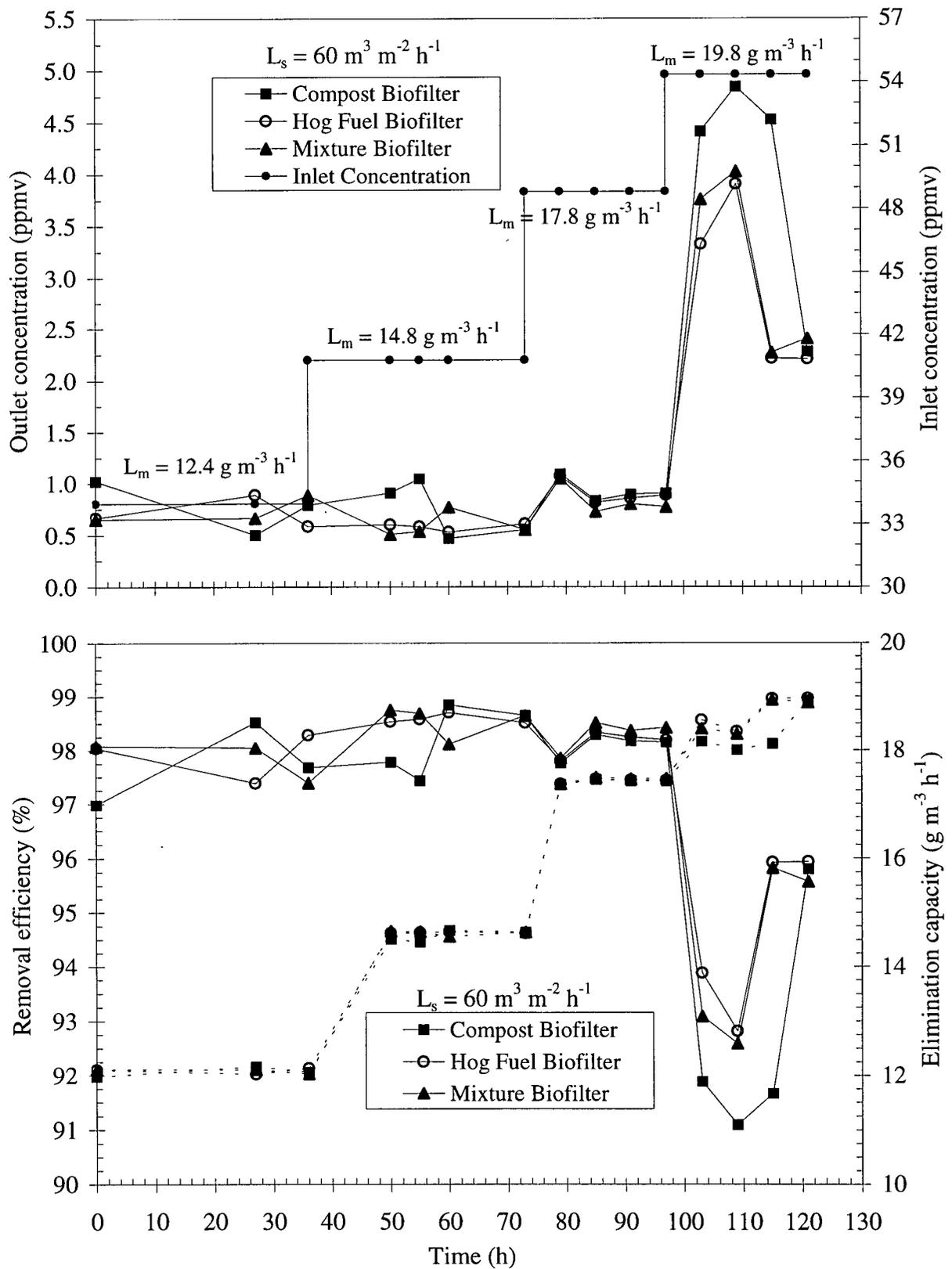
Figure 4.16. Transient behavior of biofilters to step-changes in contaminant concentration for dimethyl disulfide degradation. Solid lines represent the removal efficiency and dashed lines the elimination capacity.

(b) Step-Changes in Waste Airflow Rate: Holding the dimethyl disulfide mass loading ($L_m \approx 20$ g m^{-3} h^{-1}) constant, the effect of short term changes in waste airflow rate from 1.7 to 3.2 m^{-3} h^{-1} on the transient behavior of biofilters was investigated. The airflow rate was changed stepwise thereby varying the dimethyl disulfide inlet concentration proportionally and as a result the mass loading remained unchanged. After adjusting the airflow rate (gas residence time) the system was allowed to stabilize for 36 hours before another step change. A sequence of three tests with different gas residence times (τ, 0.7*τ, and 0.45*τ), starting with the base case condition of $\tau = 38$ sec, was carried out. The transient response of the biofilters to fluctuating airflow rates (Figure 4.17), was similar to that of step-changes in the inlet concentration. Even though the waste gas residence time got down to about 20 sec, increases in the waste airflow rate improved the % removals and lowered the outlet concentration. This was mainly because of the reduction in the pollutant concentration as a result of waste air dilution. These observations are contrary to the findings of Arpacioglu and Allen[2] that a minimum residence time of 30 seconds is necessary for achieving dimethyl disulfide removal efficiencies greater than 90%. Nonetheless, no significant changes in the elimination capacity of any of the biofilters were observed as a result of the imposed step-changes, which indicates that the biofilters were operating above the critical gas residence time.

4.4.3.3. Biofilter Dynamic Response to Dimethyl Disulfide Elimination after Starvation

Three re-acclimation tests were conducted to examine the influence of periods of non-use on biofilter dynamics and to determine the time needed to recover full efficiency. Re-acclimation was considered to have been achieved when 98% removal was attained.

(a) Re-acclimation after a Two Day Idle Phase: In this test the biofilters were left idle for two days, after which the system was restarted under the same conditions prevailing prior to the interruption. At the end of the idle phase the dimethyl disulfide mass loading was re-started at 9 g m^{-3} h^{-1} (corresponding to a C_{in} of 24.7 ppmv and an L_s of 60 m^3 m^{-2} h^{-1}). Figure 4.18 shows the restart-up time course for the three biofilters after a starvation period of two days. All three biofilters rapidly recovered their initial removal efficiency of 98 % within 10 - 15 hours.

(b) Re-acclimation after a One Week Idle Phase: Biofilters were restarted after a period of one week during which there was no airflow through the biofilters at all. The operating conditions after the restart were the same as before the break i.e., during the first test after 1 week idle phase.
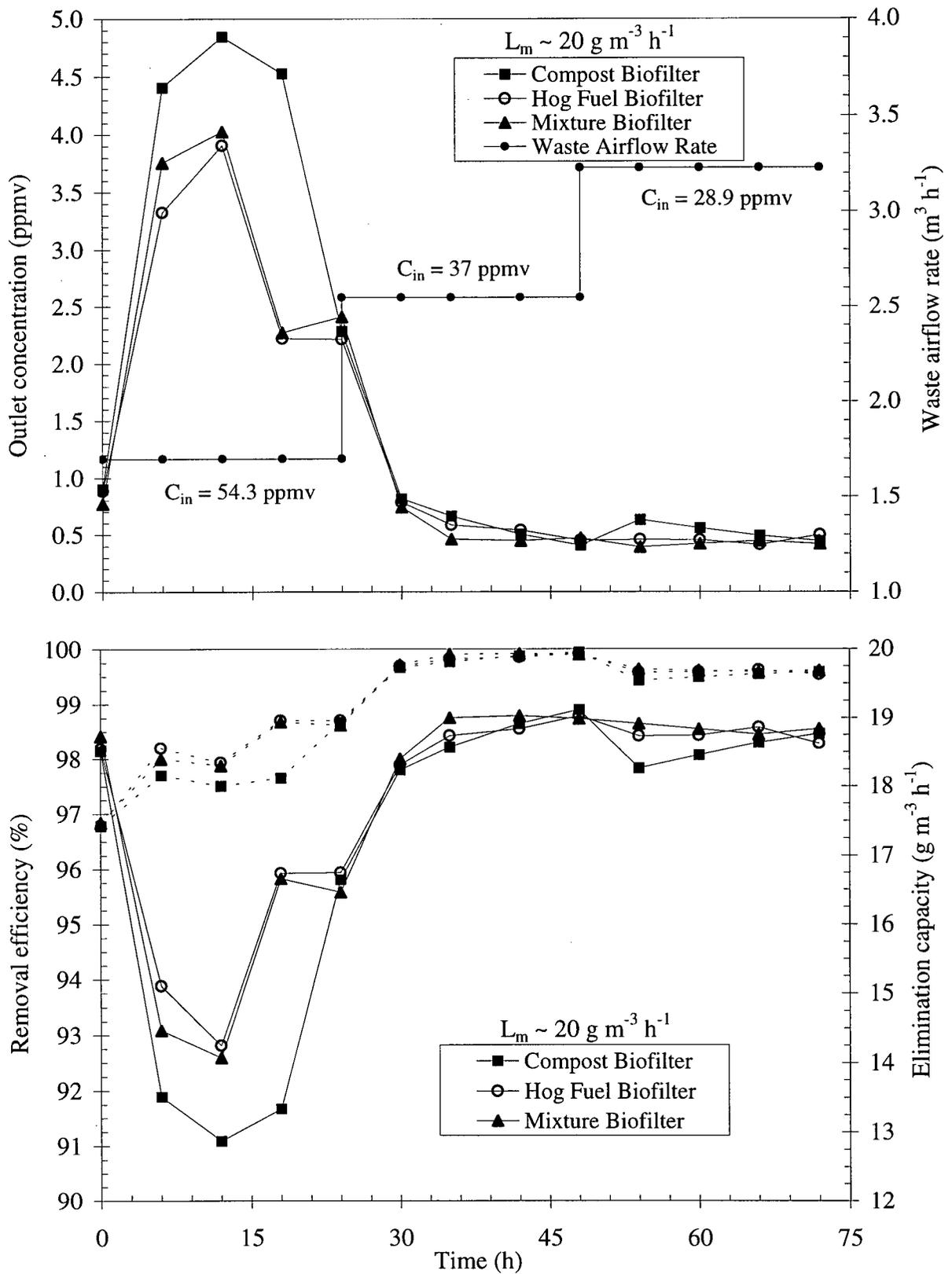
Figure 4.17. Transient behavior of biofilters to step-changes in waste airflow rate for dimethyl disulfide degradation. Solid lines represent the removal efficiency and dashed lines the elimination capacity.
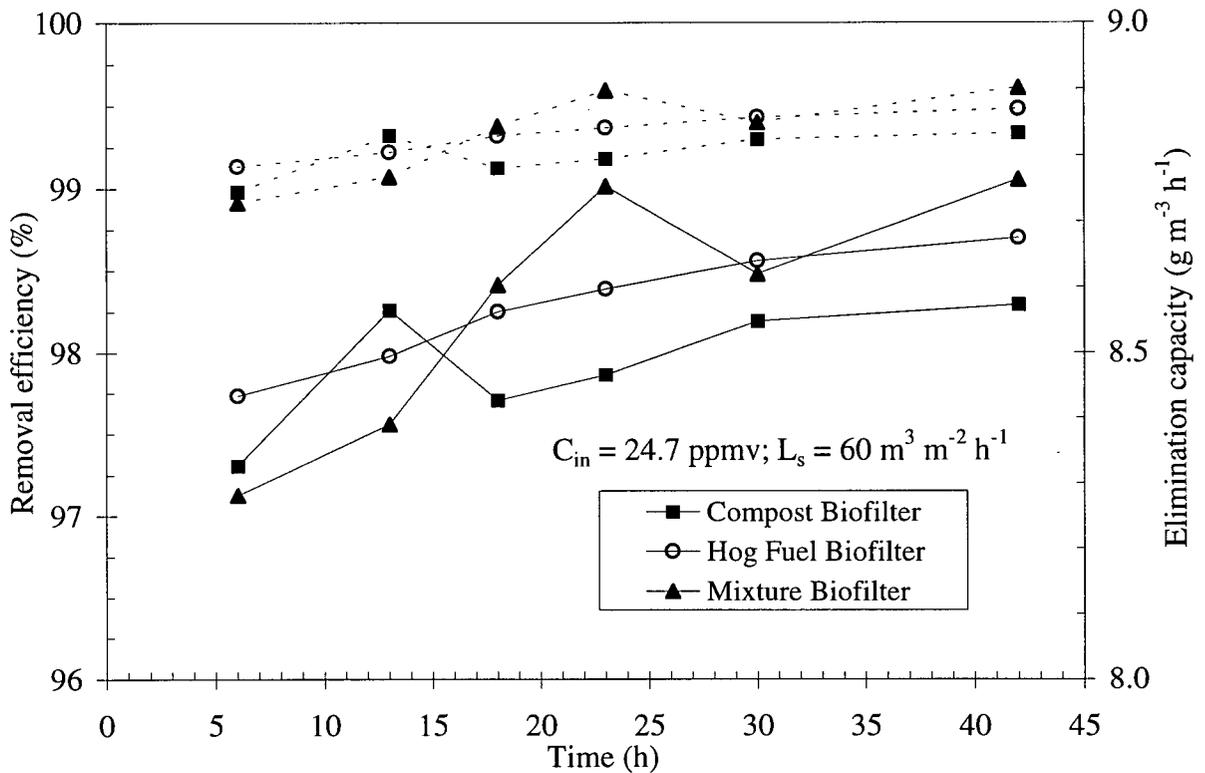
Figure 4.18. Reacclimation time course for biofilters degrading dimethyl disulfide after two days idle phase. Solid lines represent the removal efficiency and dashed lines the elimination capacity.
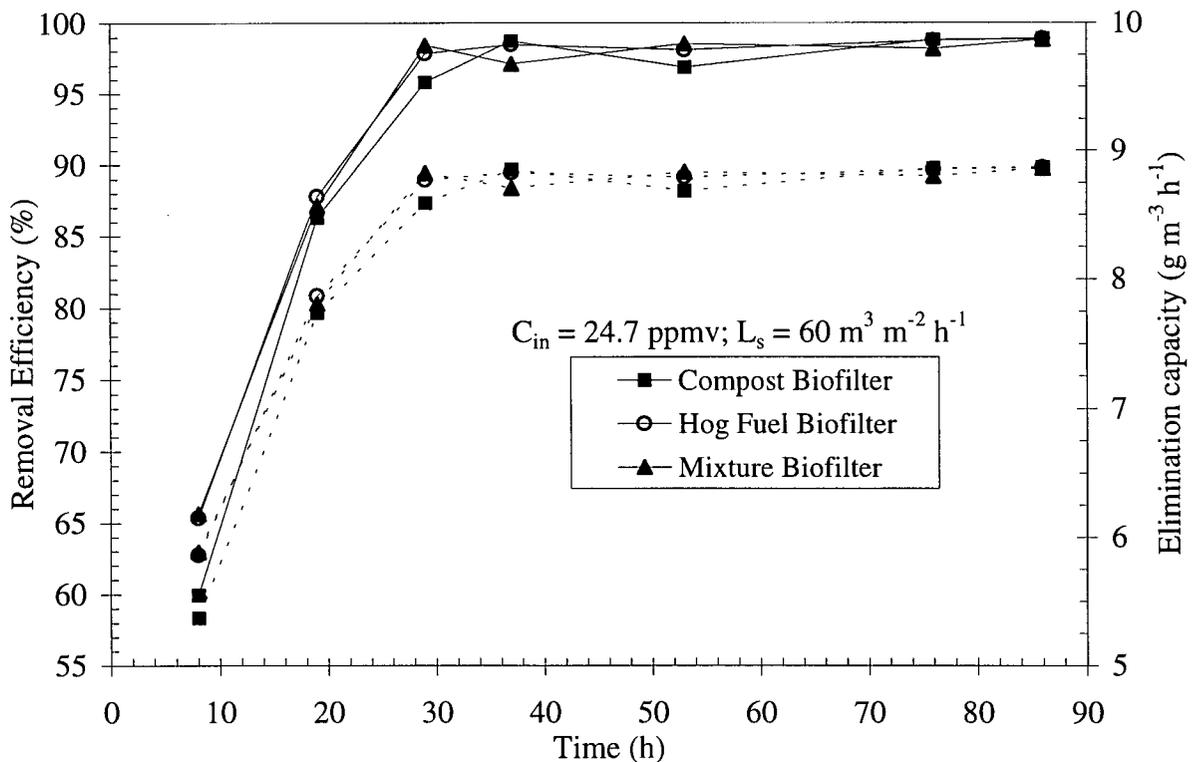
Figure 4.19. Reacclimation time course for biofilters degrading dimethyl disulfide after one week idle phase. Solid lines represent the removal efficiency and dashed lines the elimination capacity.

The re-acclimation time course for the biofilters is presented in Figure 4.19. Here the biofilters showed a similar pattern of rapid recovery, and reached the original elimination efficiency of 98 % within 25-30 hours. The recovery pattern was almost the same in all the three biofilters for both of the tests. Although the dimethyl disulfide removal efficiencies were low (60-65%) in the initial hours of restart after a week's starvation, some biodegradation took place immediately after the restart, indicating that the dimethyl disulfide degrading microorganisms already existed in the biofilters, but they may not have been quite active because of seven days of starvation. This eventually led to a much shorter re-acclimation time of about a day as compared to the initial acclimation time of 6 days, confirming the earlier results of Martin and Loehr[30].

(c) Re-acclimation after a Two Day No-Contaminant-Loading Phase: The biofilters were restarted under the same conditions as before, after a no-contaminant-loading phase of two days. The re-acclimation was started with the addition of dimethyl disulfide at a mass loading at about 9 g m^{-3} h^{-1} (corresponding to a C_{in} of 24.7 ppmv and an L_s of 60 m^3 m^{-2} h^{-1}). The results are summarized in Figure 4.20. The re-acclimation pattern was similar to the one observed after the idle phase, however the biofilters started with a higher elimination capacity reaching removal efficiency of around 98% within 6 hours of restart-up. However, the mixture biofilter started with lower removal efficiency as compared to other two biofilters. The re-acclimation time in this test was much shorter, about half of the restart-up time after the same duration of an idle phase, justifying the earlier results[30] that re-acclimation measured by achieving desirable removal efficiency is achieved significantly faster if humidified air containing no contaminant is passed through the biofilter rather than letting the biofilter stagnate with no air flow.

4.5. CONCLUSIONS

Transient experiments on the biofilters provided valuable information to assist in understanding the complex phenomena occurring in such biological reactors under actual operating conditions and in developing the operational protocols for mitigating the breakthrough of contaminants resulting from such transient loading.

The initial acclimation times of the biofilters for methyl mercaptan and dimethyl disulfide degradation were quite short, with less than a week being required before very high % removal was achieved. The lag phase (5-6 days) for methyl mercaptan removal was significantly shorter than the
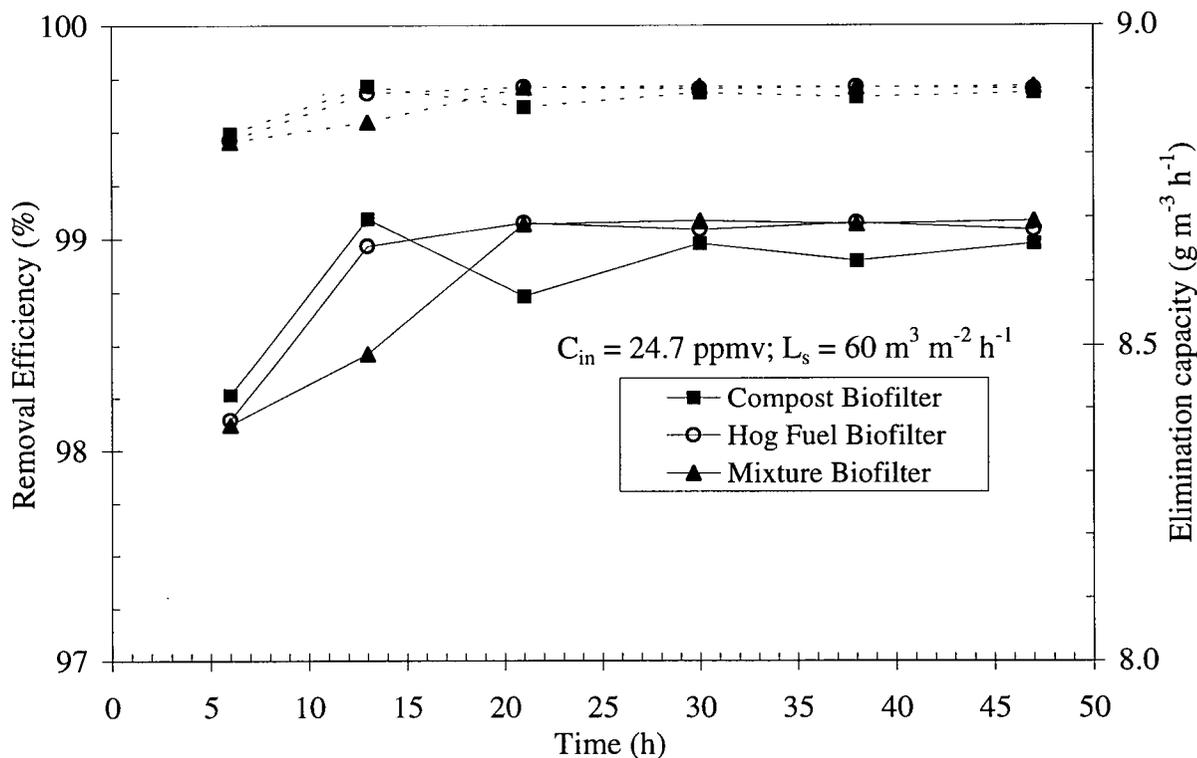
100 ──────────────────────────────────── 9.0

$C_{in} = 24.7$ ppmv; $L_s = 60$ m³ m⁻² h⁻¹

Removal Efficiency (%)

Elimination capacity (g m⁻³ h⁻¹)

──■── Compost Biofilter
──O── Hog Fuel Biofilter
──▲── Mixture Biofilter

99

98

97 ──────────────────────────────────── 8.0

0   5   10   15   20   25   30   35   40   45   50

Time (h)

8.5

Figure 4.20. Reacclimation time course for biofilters degrading dimethyl disulfide after two days of no-contaminant-loading phase .Solid lines represent the removal efficiency and dashed lines the elimination capacity.

previously reported[15,22,35] initial startup time of 10-17 days. Effective inoculation of the packing material appears to favorably influence the startup. In this study the brevity of the biofilter startup was probably because of the seeding of the biofilter media materials with pulp mill wastewater sludge that contains reduced sulfur degrading microorganisms.

Step changes both in contaminant concentration and/or in waste airflow rate demonstrated that the biofilters adapted rapidly to new operating conditions. In case of hydrogen sulfide removal all three biofilters required about 2-8 hours after the step changes to recover to initial removal efficiency within the maximum inlet concentration (202 ppmv) and the shortest empty bed residence time (23 s) tested, except for the mixture biofilter that exhibited a short term breakthroughs at each increment in hydrogen sulfide mass loading. The recovery times of about 8-12 hours needed after the step-changes were almost same for methyl mercaptan and dimethyl disulfide. However, an inlet concentration of about 108 ppmv methyl mercaptan caused a measurable decrease in the removal efficiency of biofilters, so did a waste airflow rate of 2.9 m³

h^{-1}, and the biofilters took about 36 hours to reach their original removal levels. A massive reduction in the removal capacity of all three biofilters for methyl mercaptan was observed at an inlet concentration of about 141 ppmv, and the biofilters could not recover to their initial removal levels because of the substrate inhibition. In case of dimethyl disulfide an inlet concentration of about 54 ppmv caused a significant decrease in the removal efficiency of all three biofilters and the biofilters could not recover to their initial removal levels, indicating microbial toxicity due to substrate inhibition. However, with an increase in waste airflow rate, irrespective of the reduction in the gas residence time within the range of 20-38 s, the removal efficiency improved. These findings are similar to those reported by Deshusses et al[7,29] for ketones in compost based biofilters.

Contaminant pulses to the biofilters showed that when hydrogen sulfide or methyl mercaptan were pulsed the degradation rates were reduced initially in all the three biofilters for few hours until the microorganisms started to adapt to the new environment. The removal efficiency gradually increased as the microorganisms got adapted to the new conditions and reached the initial level prevalent before the concentration spike. The biofilters took about 1.5-2.5 hours to reach the original removal capacity after the hydrogen sulfide or methyl mercaptan pulse was stopped. This demonstrated that under the extremely high concentrations, hydrogen sulfide as well as methyl mercaptan degradation was self-inhibitory as reported by Chung et al[18], and Allen and Phatak[35].

The biofilters degrading hydrogen sulfide, methyl mercaptan, or dimethyl disulfide were found to be capable of withstanding different periods of starvation with rapid recovery to full performance when starvation ceased. Longer periods of downtime required longer re-acclimation times to reactivate the microbial population. However, after the no-contaminant-loading phase the re-acclimation time was shorter as compared to idle periods of same duration indicating humidification of the filter bed has a positive impact on the resident microbial community, that eventually results in a higher initial removal efficiency after the no-contaminant-loading phase than the idle phase. The re-acclimation time of about five days for the biological activity after the longest starvation period of three months was much shorter than the literature reported[20,21], initial start-up period of 10-12 days for hydrogen sulfide degradation. In case of methyl mercaptan or dimethyl disulfide the re-acclimation time after the longest starvation period of one week was about a day, much shorter than the initial start-up times of 5-6 days.

From these results it can be concluded that on a short-term basis there was not any significant difference between the three biofilter media materials treating hydrogen sulfide, methyl mercaptan, or dimethyl disulfide in responding to these imposed operational changes.

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CHAPTER V

BIOELIMINATION MACROKINETICS AND BIOFILTER MEDIA EFFECTIVENESS FOR REDUCED SULFUR GAS DEGRADATION

5.1. ABSTRACT

The research work reported here has been directed towards the treatment of reduced sulfur gas emissions in biofilters. Bioelimination rates of reduced sulfur gases in three different filter media materials evaluated under pseudo-steady state conditions with different contaminant mixes and inlet concentrations are reported. Biofiltration tests were performed in three bench-scale biofilter columns using compost, hog fuel, and the mixture of compost and hog fuel as the filtering media. The biofilter columns were operated continuously, in parallel, in three different phases. In the first experiment hydrogen sulfide was used as a main substrate with other organo-sulfur compounds as co-substrates. Dimethyl sulfide removal characteristics both singly and with co-supply of other reduced sulfur gases were evaluated in the second experiment, and the third experiment was devoted to the estimation of bioelimination rates of dimethyl disulfide independently and in co-existence with other reduced sulfur gases. The main purpose of these experiments was to evaluate the media effectiveness for the bioremoval of reduced sulfur gases and to illustrate the inhibition effects, if any, of co-substrates on the removal rate of the main contaminant in each experiment.

A Michaelis-Menten type kinetic equation, modified for plug flow behavior with the assumption of steady state, minimal back mixing, and rapid contaminant transfer between the phases was used to describe the bioremoval rates and to estimate the apparent macrokinetic[*] parameters, V_{max} (maximum elimination rate) and K_m (half saturation concentration). No significant differences in the hydrogen sulfide elimination capacity among the three biofilters were observed. The V_{max} ranged between 136.1 and 138.3 g m^{-3} h^{-1} with K_m values of 43.9 to 53.1 ppmv when hydrogen sulfide was degraded singly. Hydrogen sulfide elimination capacity was

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[*] The use of the word macrokinetics implies that no attempt was made to separate mass transfer rate effects from reaction rate effects.

not affected by the presence of any of the organo-sulfur species in all of the three biofilters, confirming earlier results that hydrogen sulfide removal in biofilters is independent of the presence of organo-sulfur compounds mainly because of its easy biodegradability.

The dimethyl sulfide elimination rate, when treated singly, varied from 3.8 to 5 g m^{-3} h^{-1} with the corresponding K_m range of 6.5 to 7.3 ppmv in the three biofilters investigated. The compost biofilter achieved the highest elimination capacity (5 g m^{-3} h^{-1}) as compared to hog fuel (3.8 g m^{-3} h^{-1}) and the mixture (4.6 g m^{-3} h^{-1}) biofilters. Dimethyl sulfide biodegradation was significantly inhibited, by a factor of 1.5 to 2, in the presence of methyl mercaptan and dimethyl disulfide, however the co-existence of hydrogen sulfide slightly improved the dimethyl sulfide elimination capacity in all the three biofilters.

In the case of dimethyl disulfide, the maximum bioelimination capacity of the three filtering media studied ranged between 12.3 and 16.9 g m^{-3} h^{-1} with K_m values between 5 and 7.7 ppmv. Once again the biofilter column using compost as the filtering media demonstrated the maximum removal rate (16.9 g m^{-3} h^{-1}) compared to the other two biofilters with hog fuel (12.3 g m^{-3} h^{-1}) and the mixture (13.6 g m^{-3} h^{-1}) as filtering material, confirming the results of previous studies that compost is a better carrier material than wood waste for the biofiltration control of methylated sulfur. The co-supply of hydrogen sulfide and dimethyl sulfide caused a significant reduction, down to 50%, in the biodegradation rates of dimethyl disulfide in all of the three biofilter columns.

5.2. INTRODUCTION

The kraft pulping process is associated with the emission of noxious and unpleasant smelling compounds. The offending gases that are typically found in kraft pulp mill emissions include a wide range of volatile organic compounds (VOCs); and low molecular weight mercaptans, methyl sulfides and hydrogen sulfide, collectively known as "total reduced sulfur (TRS)" gases. Sulfurous gases and vapors such as hydrogen sulfide (H_2S), methyl mercaptan (MM), dimethyl sulfide (DMS), and dimethyl disulfide (DMDS) are of strong malodorous nature. They exceed odor thresholds even at low concentrations and therefore are highly objectionable from an environmental point of view. Hydrogen sulfide is a corrosive and extremely toxic air pollutant. Excess amounts of hydrogen sulfide can irritate human eyes or injure the developing central

nervous system[1]. Organo-sulfur compounds (methyl mercaptan, dimethyl sulfide, and dimethyl disulfide) although not necessarily posing a health hazard at regulated levels, are considered to be a nuisance and an irritation. Because of their low odor threshold level, TRS gases are recognized nuisances even at much lower concentration than those considered being safe. In light of increasingly stringent regulations of air emissions, the technologies that control VOCs and odorous gas emissions have received much attention in recent years. The literature identifies a number of technologies that involve chemical and/or physical principles for the treatment of waste air streams. Biological processes are one of the newest options that can also be used for the treatment of odorous air streams. The low concentration of these odorous gases to be cleaned makes the use of conventional control technologies such as catalytic oxidation, incineration, absorption and adsorption difficult and expensive, and these traditional technologies are associated with their own pollution problems (e.g., emission of large amounts of carbon dioxide, oxides of nitrogen or disposal of spent adsorbents). Biofiltration is a preferable alternative to other conventional physico-chemical methods for the purification of waste air of large volume and low pollutant concentration[2-7]. When compared to traditional control technologies, biofiltration processes are much more economical[4-7]. Moreover in contrast with the more recent biological processes, some of the conventional methods do not lead to the destruction of pollutants and cause secondary water, air or soil pollution that needs further treatment; and consume more energy[4,7,8].

Biofiltration utilizes the ability of a mesophilic mixed culture of microorganisms to biodegrade the pollutants without cross-media transfer of the contaminants. Biofiltration, an air treatment technology, is based on the aerobic metabolic breakdown of contaminants by microorganisms attached to the surfaces of stationary carrier matrices such as soil, peat, compost, wood bark or synthetic materials. The process is catalyzed enzymatically and takes place at ambient conditions, thus requiring little energy for operation and maintenance. These systems have the potential to run for periods of years without replacement of the biofilter matrix and under optimum conditions, the pollutants are fully biodegraded without the formation of aqueous effluents. Generally the natural organic filtering materials can provide sufficient inorganic nutrients for the resident microorganisms and therefore the addition of nutrients is not required[2].

Biofilters present a tremendous potential for air treatment. Historically biofiltration has been used primarily for the removal of odorous compounds from air streams. However, in recent years biofiltration has been increasingly used for the removal of VOCs from air streams, and more recent research and development has aimed at applying it to higher concentrations and to contaminants that are less easily degraded. Biofiltration is now treating industrial discharges, soil vapor extraction effluents, and wastewater treatment plant off-gases[7].

Biofilters excel in two main domains; in the removal of odoriferous compounds[8-21] and in the elimination of VOCs[2-5,32-37] from waste air. Studies on biofiltration for odor control have focused on VOCs and odorous sulfur compounds such as hydrogen sulfide, methyl mercaptan, dimethyl sulfide, and dimethyl disulfide for the last two decades in both lab-scale[8-19] and pilot systems[20-21]. In pilot tests high elimination rates, with hydrogen sulfide removal to an undetectable level, and 88-90% and 50-60% removal for methyl mercaptan and methyl sulfides respectively, have been achieved[21].These studies indicated that good results could be obtained with mixtures of hydrogen sulfide, methyl mercaptan, dimethyl sulfide and dimethyl disulfide, and that biofiltration was a viable treatment process. However, the results also indicated that although hydrogen sulfide was removed with extremely high efficiency (>99%), it was removed preferentially and that the other TRS compounds could be more persistent. Exceptionally high bioelimination rates of 120-327 g m^{-3} packing h^{-1} have been reported[9] for hydrogen sulfide using peat biofilters seeded with anaerobically digested night soil sludge. Peat biofilters have also been used to remove hydrogen sulfide, methyl mercaptan, dimethyl sulfide, and dimethyl disulfide singly as well as in mixtures[9-11,30,31]. These biofilters showed an efficient removal of hydrogen sulfide, methyl mercaptan, dimethyl sulfide, and dimethyl disulfide achieving maximum elimination rates (V_{max}) of 23.2-25.2 g H_2S, 3.7-7.3 g MM, of 3.2-4.1 g DMS, and 4.7-6.3 g DMDS m^{-3} packing h^{-1} with corresponding saturation concentrations (K_m) of 55-85, 10-32, 4.8-10, and 1-7 ppmv, respectively depending upon the seeding materials used for inoculating the filter bed[11,30,31].

The microbial metabolism of organo sulfur species has been the subject of several scientific publications. An in vitro study carried out by Suylen et al.[22] has shown that methyl mercaptan can only be degraded under aerobic conditions and the degradation is catalyzed by methyl mercaptan oxidase. The enzyme plays a key role in the oxidation of methylated sulfur by cleaving of the C-S bond. The researchers reported that *Hyphomicrobium* species apparently utilize the methyl group

as the carbon and energy source with the sulfur group serving as an additional energy source. The stoichiometry of oxidation is given by the following reaction:

$$CH_3SH + O_2 + H_2O \longrightarrow HCHO + H_2S + H_2O_2$$
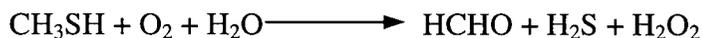
Products of this primary reaction are easily biodegradable and are ultimately degraded to carbon dioxide, water and elemental sulfur, which gets converted to sulfate/sulfuric acid.

Disappearance of the sulfide moiety suggests that either methyl mercaptan oxidase has a sulfide oxidizing capacity or the *Hyphomicrobium* may contain another sulfide-oxidizing enzyme of a similar nature[22]. Figure 5.1 shows the metabolic pathways for the microbial breakdown of dimethyl sulfide[23,24] and dimethyl disulfide[25] to sulfate and carbon dioxide with methyl mercaptan, hydrogen sulfide, formaldehyde and formic acid as intermediate products. However, dimethyl sulfide is not produced as a metabolic byproduct during the microbial breakdown of dimethyl disulfide because of its reductive cleavage to methyl mercaptan[25].
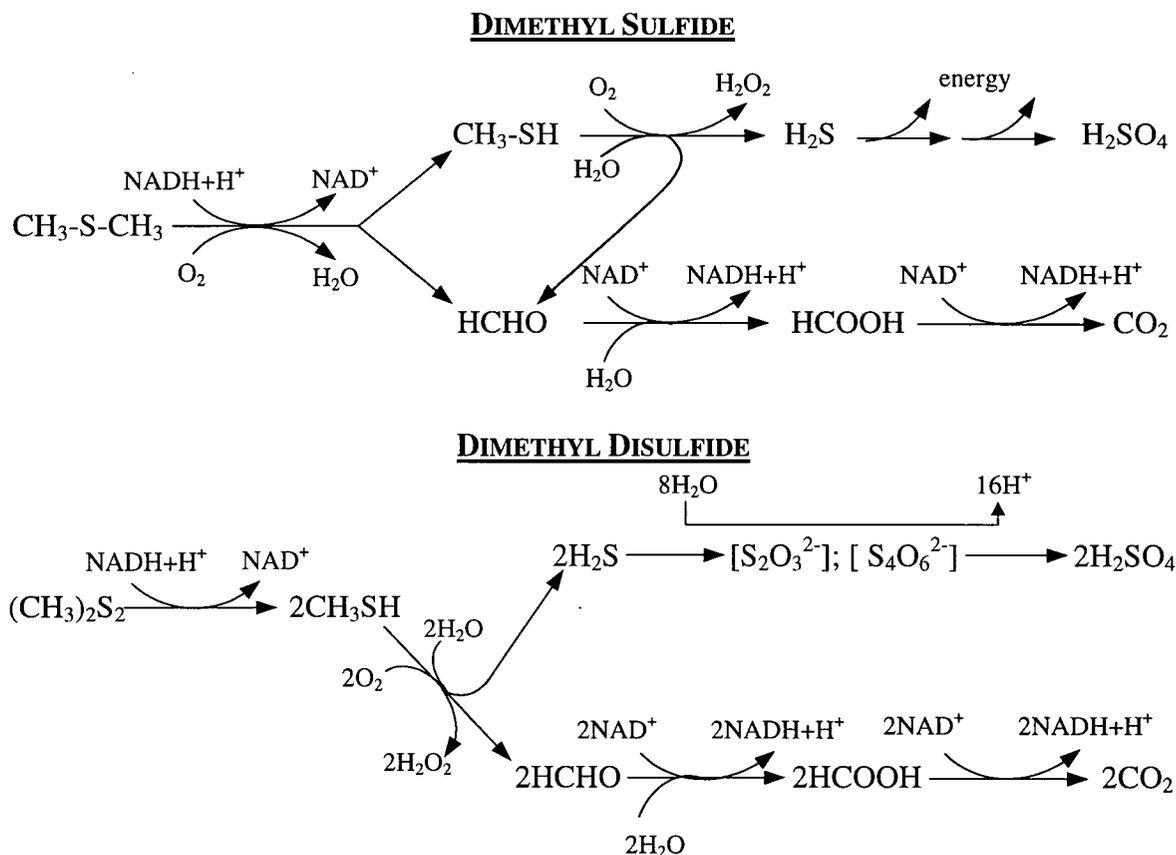
Figure 5.1. Metabolic pathways for microbial breakdown of dimethyl sulfide and dimethyl disulfide

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It has also been reported that sulfate is produced stoichiometrically during the microbial breakdown of these reduced sulfur species[26,27].

Biofilters have the potential to treat chemical mixtures, however, the competitive effects between the chemicals play an important role in both the mass transfer and biodegradation steps of the biofiltration process[28]. Biodegradation rates are known to be significantly affected by compound concentration, compound structure, and the presence of other compounds[28,29]. This is especially true for biodegradation where inhibition can occur due to preferential uptake (diauxy) of one substrate over another or by toxic interactions[29]. Such coexistence effects have been reported in peat biofilters treating mixtures of reduced sulfur gases, where degradation of organo-sulfur compounds was noticeably inhibited or stimulated by the co-supply of hydrogen sulfide or in the presence of other organo-sulfur species[30,31]. However, the researchers did not explain the inhibitory effects of one or more gases on the removal rates of another. Obviously it is desirable to quantify the removal rate relationships amongst these TRS compounds in order to gain a better understanding of their removal mechanisms.

Most of the previous studies related to the biofiltration of reduced sulfur gases have focused on the effects of operating parameters on biofilter performance, and studies addressing the interactions between reduced sulfur gases, when treated in a mixture, and their effects on the removal capacity of different filtering materials are scarce. To address these issues a series of four studies was performed to examine the removal characteristics of reduced sulfur compounds using compost and wood-waste based bench-scale biofiltration. Specific objectives included the evaluation of biofilter media effectiveness for reduced sulfur gas biodegradation. Aspects of reduced sulfur gas bioelimination macrokinetics (with lumped mass transfer and reaction rate effects) when used alone and in presence of other sulfur gases have been evaluated and are reported. Hydrogen sulfide, dimethyl sulfide, and dimethyl disulfide were used as test contaminants in three different experiments, with one as a main substrate and the rest as secondary, possibly competing or inhibitory, substrates. These three reduced sulfur gases were selected because of their different breakdown pathways that might influence their biodegradation. Methyl mercaptan was not used in this study because it is the primary metabolic byproduct produced in dimethyl disulfide degradation as a result of the reductive cleavage of dimethyl

disulfide molecule, and it was assumed that its biodegradation might not differ significantly from dimethyl disulfide.

5.3. MATERIALS AND METHODS

5.3.1. Experimental Setup

The main components of the experimental setup used in the experiments reported here are shown in Figure 5.2. A detailed description of the design and construction of the bench-scale biofiltration system has been previously reported in Chapter IV (4.3.1).
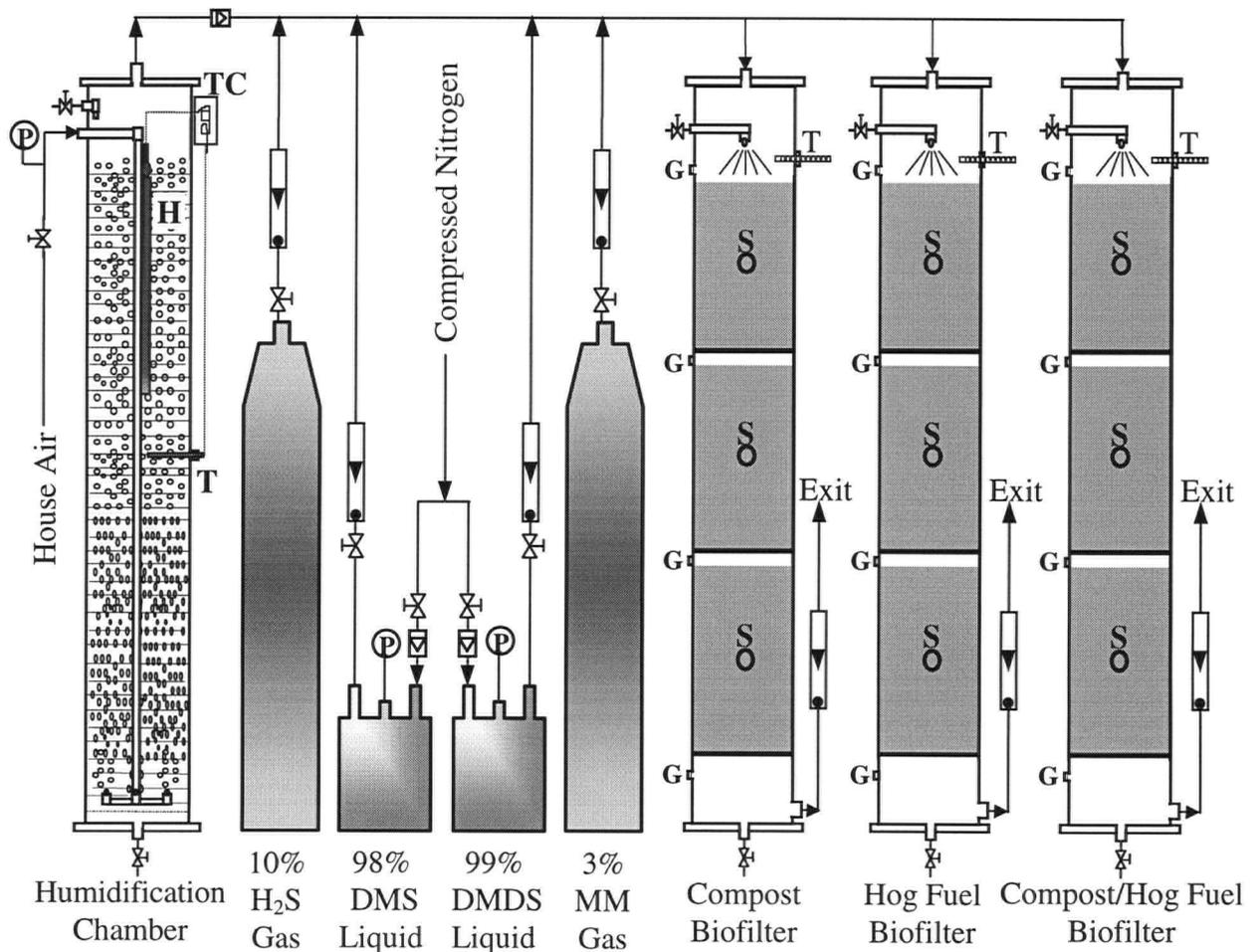

Figure 5.2. Experimental setup schematics: G, gas sampling ports; H, immersion heater;
P, pressure gauge; S, media sampling ports; T, thermocouples/thermometers;
TC, temperature controller.

5.3.2. Biofilter Media

The filtering media materials used in these experiments were the same as described in Chapter IV (4.3.2). After finishing the transient-state behavior studies the same packed columns were used

for these tests, unless otherwise mentioned. The three Plexiglas (methyl methacrylate) biofilter columns were packed with filter media prepared from compost, hog-fuel (pulverized raw bark, wood waste and other extraneous wood materials), and a mixture of compost and hog fuel (1:1 w/w). Characterization of these biofilter packing materials was performed using standard methods for soil analysis (Appendix B). Values for the density, percent moisture, wet porosity, percent ash, total nitrogen, total carbon, pH, and particle size distribution are summarized in Table 3.1 (Chapter III). Each medium was amended with perlite in a ratio of 4 parts media to 1 part perlite, by weight, to provide structural strength and to increase the bed porosity. At 25-30 kg m^{-3} of bed material, dolomitic lime was manually mixed with the media mixtures as a pH buffer. Filter media materials were microbially seeded with waste activated sludge obtained from Western Pulp's mill at Squamish, BC and Howe Sound Pulp and Paper's mill at Port Mellon, BC. The prepared media were then packed into the biofilter columns to a total effective filter bed height of 660 mm, in each column, in three equal sections giving a filter volume of 0.006 m^3 in each section.

5.3.3. Reactor Conditions and Operation

The three biofilter columns were subjected to identical loading conditions of waste gas flow rate and contaminant inlet concentrations. A downward gas flow rate of 1.7 m^3 h^{-1}, unless otherwise mentioned, giving a surface loading of about 60 m^3 m^{-2} h^{-1} (empty bed residence time of 38 s) was used in these experiments. A series of three tests were done and for each test the biofilters were previously acclimated for the particular reduced sulfur gas under investigation.

The inlet concentration of the reduced sulfur compounds was varied according to their use (whether main contaminant or a co-substrate) in each study and the details are summarized in Table 5.1. The synthetic waste air stream was made by injecting small flows of compressed hydrogen sulfide (10 vol%, balance nitrogen), and methyl mercaptan (3 vol%, balance nitrogen) into the humid air stream coming from the humidification column; and by sparging known flows of compressed nitrogen separately into two 2 L stainless steel tanks containing liquid dimethyl sulfide (CAS# 75-18-3, 98% purity) and dimethyl disulfide (CAS# 624-92-0, 99% purity), respectively and finally mixing the dimethyl sulfide and dimethyl disulfide vapor laden nitrogen streams with the water-saturated air stream coming from the humidification column. Flow rates of the water-saturated air stream, the compressed contaminants, and the contaminant vapor laden nitrogen were controlled by high precision valves and monitored by previously calibrated rotameters in order to maintain the

desired contaminant inlet concentrations and waste air residence times within the columns. The concentration profiles of reduced sulfur gases in the biofilters were obtained by withdrawing samples from the inlet, outlet and side ports along the height of the biofilters. Solid samples were taken from the media for measuring media pH. The waste air had a relative humidity of greater than 97%. Throughout the study there was no drying in the filter beds, as a result the water spray nozzles designed for irrigating the filter beds were never used. The pressure drop over the filter beds was always less than 10 mm water. The biofilters were maintained at room temperature (25 - 27 °C).

Table 5.1. Design and operating parameters

Parameters	Experiment I Hydrogen Sulfide	Experiment II Dimethyl Sulfide	Experiment III Dimethyl Disulfide
Column inner diameter	0.187 m	0.187 m	0.187 m
Effective packing height[a]	0.66 m	0.66 m	0.66 m
Packed bed volume	0.018 m^3	0.018 m^3	0.018 m^3
Waste airflow rate	1.7 m^3 h^{-1}	1.51 m^3 h^{-1}	1.7 m^3 h^{-1}
Empty bed residence time	38 s	43 s	38 s
Contaminant inlet concentration[b]			
▪ Hydrogen sulfide	**10 - 450 ppmv**	23.6 ppmv	15.9 ppmv
▪ Methyl mercaptan	not used	15.4 ppmv	not used
▪ Dimethyl sulfide	10.8 ppmv	**3 – 25 ppmv**	9.1 ppmv
▪ Dimethyl disulfide	6.6 ppmv	7.2 ppmv	**5 - 45 ppmv**
Inlet waste air humidity	> 97 %	> 97 %	> 97 %
Temperature	25 - 27 °C	25 – 27 °C	25 – 27 °C
Pressure drop	< 10 mm H_2O	< 10 mm H_2O	< 10 mm H_2O

[a]in three equal sections.

[b]pollutant with concentration range in bold face served as the main substrate, and the pollutants with fixed concentration were used as co-substrates with the main pollutant in each individual study.

5.3.5. Surface and Mass Loading, and Biofilter Elimination Capacity

Waste air empty bed residence time, τ (s); space velocity, SV (h^{-1}), surface loading rate, L_s (m^3 m^{-2} h^{-1}), biofilter elimination capacity, EC (g m^{-3} h^{-1}) and removal efficiency, RE (%) were determined using the relationships between the inlet (C_{in}) and outlet (C_{out}) gas phase concentrations (ppmv); waste airflow rate, Q (m^3 h^{-1}); and the effective filter bed volume, V (m^3) as follows:

$$\tau = (V/Q)*3600 \qquad (1)$$

$$SV = (Q/V) \qquad (2)$$

$$L_s = (Q/A) \qquad (3)$$

$$EC = SV*(C_{in} - C_{out})*\beta \qquad (4)$$

$$RE = [(C_{in} - C_{out})/C_{in}]*100 \qquad (5)$$

where, A is the cross-section area of biofilter column (m^2) and $\beta = [(M*10^{-3})/\{22.4*(273+T)/273\}]$, is the conversion factor, in terms of pollutant molecular weight (M) and operating temperature (T).

5.3.6. Biodegradation Macrokinetics

Two processes, mass transport and the microbial utilization of contaminants simultaneously occur in biofiltration. The particles in the filter bed are surrounded by a wet, biologically active layer, called a biofilm. Between the air phase and the surface of the particles are a liquid film and a biofilm. Convection and dispersion of TRS gases take place in the air phase, while the biodegradation occurs within the liquid layer/biofilm. In general, by assuming that the oxygen concentration required for the aerobic respiration of the microorganisms in the biofilm is not limiting, under selected conditions, the substrate utilization rate of a compound by the microbial flora as well as enzymatic reaction can be expressed by a Michaelis-Menten type relationship[32-34]. At steady state the growth rate of the microorganisms due to biodegradation is balanced by its own decay, resulting in no net growth and eventually biological equilibrium is achieved[35-36], so that kinetic constants remain constant over the time period considered[34]. Under such conditions i.e., when the microbial population does not change, the half saturation constant (K_m) and the substrate concentration (C) may have comparable values. Simple reduction to zero or first order kinetics then is not possible.

Gas flow through the biofilter can be characterized as pseudo plug flow with minimal back mixing[37]. For instance Deshusses[37] has shown that his compost biofilter could be represented by 26 stirred tanks in series. At the mass loading rates of air commonly applied to biofilters, the air flow is in the turbulent regime and mass transport rates in the air phase are correspondingly rapid[38]. Such an ideal plug flow reactor without dispersion at steady state can be modeled by the following equation[39]

$$\frac{\partial C}{\partial t} = -\frac{Q}{A}\frac{\partial C}{\partial H} + R_r \qquad (6)$$

At steady state $\partial C/\partial t = 0$, and if the reaction rate is defined as $R_r = [(V_{max}.C)/(K_m+C)]$, where C is the pollutant concentration (ppmv), H is the height of the filter bed (m), V_{max} is the maximum bio-

elimination rate (ppmv $\cdot$ m^3 air $\cdot$ m^{-3} packed bed $\cdot$ h^{-1}), K$_m$ is the saturation (Michaelis-Menten) constant (ppmv), integrating equation 6 under conditions C = C$_{in}$ at H = 0 and C = C$_{out}$ at H = H, we get

$$\frac{\left(V\!\!\Big/\!Q\right)}{C_{in} - C_{out}} = \frac{K_m}{V_{max}}\frac{1}{C_{ln}} + \frac{1}{V_{max}} \tag{7}$$

where, V = (A*H) and C$_{ln}$ = [(C$_{in}$-C$_{out}$)/ln(C$_{in}$/C$_{out}$)] is the logarithmic mean concentration of the contaminant at biofilter inlet and outlet. Rearranging and substituting the bio-elimination capacity, EC from equation 4, the above equation results in a modified Michaelis-Menten equation, i.e.:

$$EC = \frac{V_{max} \cdot C_{ln}}{K_m + C_{ln}} \tag{8}$$

The reaction rate parameters V$_{max}$ and K$_m$ were estimated from the modified Michaelis-Menten model (Equation 8) fitting of the independent single and mixed pollutant degradation experiments, assuming that mass transfer rates of the TRS gases from air to the biofilm were not rate limiting.

Considering a non-growing biofilm, the bio-elimination rate, with noncompetitive inhibition, when two substrates are biodegraded simultaneously, can be estimated as follows[40]:

$$EC = \frac{V_{max} \cdot C_{ln}}{\left(1 + I\!\!\Big/\!K_i\right) \cdot (K_m + C_{ln})} \tag{9}$$

where, I is the concentration of co-substrate (inhibitor) (ppmv) and K$_i$ is the inhibition constant of co-substrate on the main contaminant (ppmv).

The noncompetitive type of kinetic inhibition was assumed because the V$_{max}$ (see next section) was reduced when the main contaminant was biodegraded in coexistence with a co-substrate, except for hydrogen sulfide whose biodegradation was not influenced by the presence of co-substrates. However, at the same time the K$_m$ was also increased, so the noncompetitive model given by equation 9 could not be used, because it is based on the main assumption that under such a kinetic inhibition K$_m$ remains unchanged. The noncompetitive model fitting of the mixed pollutant degradation using SYSTAT software gave vague results because K$_m$ is not constant. Thus simple enzymatic kinetics do not describe the inhibition kinetics in biofilters when a mixture of contaminants is treated simultaneously. Deshusses[37] has reported similar observations while treating a mixture of ketones.

Rearranging equation 8 after inserting the value of EC from equation 4 results in a design relationship, between waste air space velocity and the inlet contaminant concentration, for the biofilter scale-up[41,42] as follows:

$$SV = \frac{1}{\beta.(C_{in} - C_{out})} * V_{max} * \frac{C_{In}}{(K_m + C_{In})} \qquad (10)$$

Knowing the effluent concentration to be met at the outlet of the biofilter column, equation 10 can be used to estimate the maximum inlet concentrations of the contaminant that can be treated, while meeting the desired outlet concentration, at various space velocities.

5.4. RESULTS AND DISCUSSION

In this section experimental observations on the performance of three biofilter materials in degrading reduced sulfur gases singly as well as in mixtures are presented.

5.4.1. Experiment I. Biodegradation Macrokinetics of Hydrogen Sulfide

The biofilters were acclimated to H₂S over a period of two weeks by increasing the hydrogen sulfide concentration gradually from 10 to 500 ppmv to establish steady state conditions as indicated by hydrogen sulfide removals remaining constant with time. Following the acclimation, the transient behavior of biofilters to fluctuating hydrogen sulfide concentrations, varying waste airflow rates, and different periods of downtime were evaluated (results described in Chapter IV), before starting the evaluation of removal rates of hydrogen sulfide independently, as well as in association with organo-sulfur compounds.

The initial hydrogen sulfide concentration, ranging from 10 to 450 ppmv, in the inlet gas stream was varied from low to high values in order to determine hydrogen sulfide biodegradation macrokinetics under different situations. Three sets of experiments were performed by altering the contaminant composition and concentration in the waste air stream. Dimethyl sulfide and dimethyl disulfide were fed at constant concentration levels of 10.8 and 6.6 ppmv, respectively. The biofiltration system was allowed to stabilize for 24 hours prior to analyzing the outlet concentration and changing to new inlet concentration. Concentration profiles over the top section of the filter bed (packed bed volume of 0.006 m³) were used in estimating the apparent macrokinetic parameters because (as shown in Figure 5.3) hydrogen sulfide concentrations up to 250 ppmv
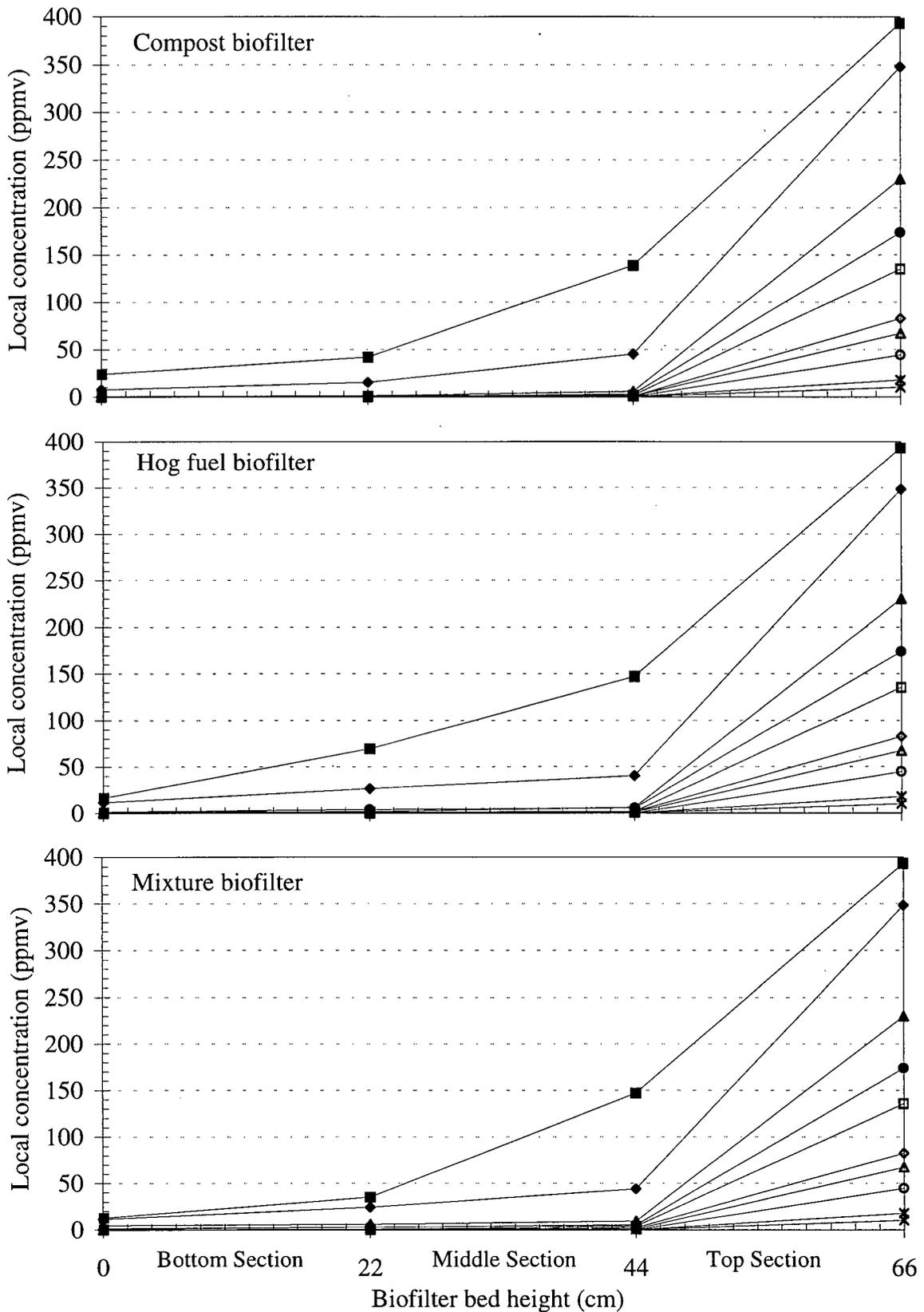
Figure 5.3. Axial concentration profile of hydrogen sulfide in biofilters. Different line markers represent different inlet concentration levels for each stage.

were completely removed in this section and the destruction efficiency for the inlet concentrations higher than 250 ppmv was more than 90%.

Biofilter media pH showed a considerable decrease (Figure 5.4), over an operating period of more than six months (including the period for the analysis of biofilter transient behavior), as a result of the formation of acidic metabolites as by-products from the biodegradation of reduced sulfur compounds. Since the hydrogen sulfide inlet concentrations in the waste air stream were almost completely removed in the upper sections of the biofilter, as a result the pH drop was more significant in first two sections of the biofilter. The pH drop in the second section might be because of the trickling of the condensates from the upper to lower sections as a downward gas flow direction was used in the biofilter columns. The pH was higher in the third (lower) section compared to the second section probably because of the lower microbial activity in this section as compared to upper sections. Thus the third section had less of a change from its original pH. However, the pH drop in the lower section was more pronounced in hog fuel biofilter as compared to other two biofilters.

5.4.1.1. Hydrogen Sulfide Biodegradation in the Compost Biofilter

The bioelimination capacities of the compost biofilter degrading hydrogen sulfide, under three different operating conditions (a) hydrogen sulfide as a sole substrate, (b) hydrogen sulfide with a co-supply of dimethyl sulfide, and (c) hydrogen sulfide in the presence of dimethyl disulfide, plotted versus the logarithmic mean concentration of hydrogen sulfide are shown in Figure 5.5. The apparent macrokinetic parameters, V_{max} and K_m, for the biodegradation of hydrogen sulfide were calculated by performing non-linear regression between EC (g m^{-3} h^{-1}) and C_{ln} (ppmv) according to equation 8. Non-linear regression was done by using SYSTAT statistical software[43]. The NONLIN Model of the software estimates the parameters for a variety of nonlinear models using a Gauss-Newton algorithm by simultaneous optimization of the parameters while minimizing the loss function. In Figure 5.6, the contour plot of the objective function for the simultaneous optimization of V_{max} and K_m for hydrogen sulfide degradation in compost biofilter is reported. The ellipse-shaped area near the center of the plot represents the region where the loss function is minimized. Any parameter value combination i.e., any point inside this elliptical area produces approximately the same loss function. The best combination of maximum elimination rate and the saturation constant for hydrogen sulfide biodegradation, when treated singly, was obtained when

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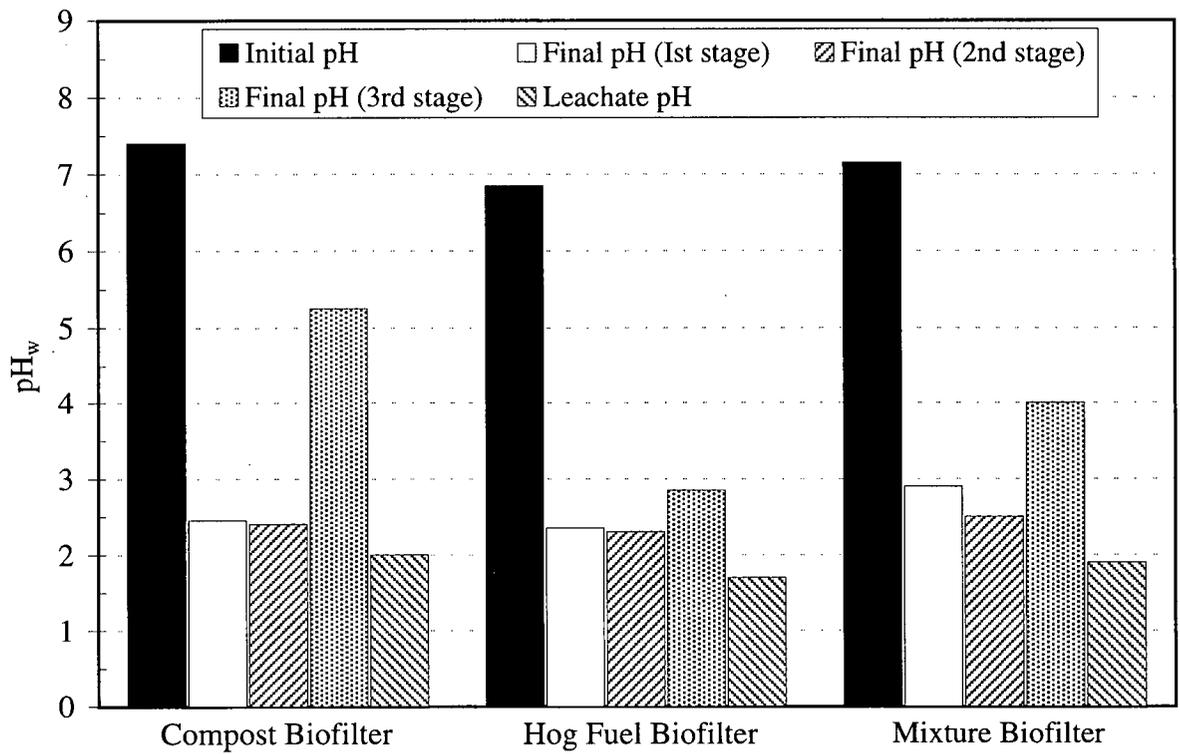
Figure 5.4. Biofilter media and leachate pH after degrading hydrogen sulfide
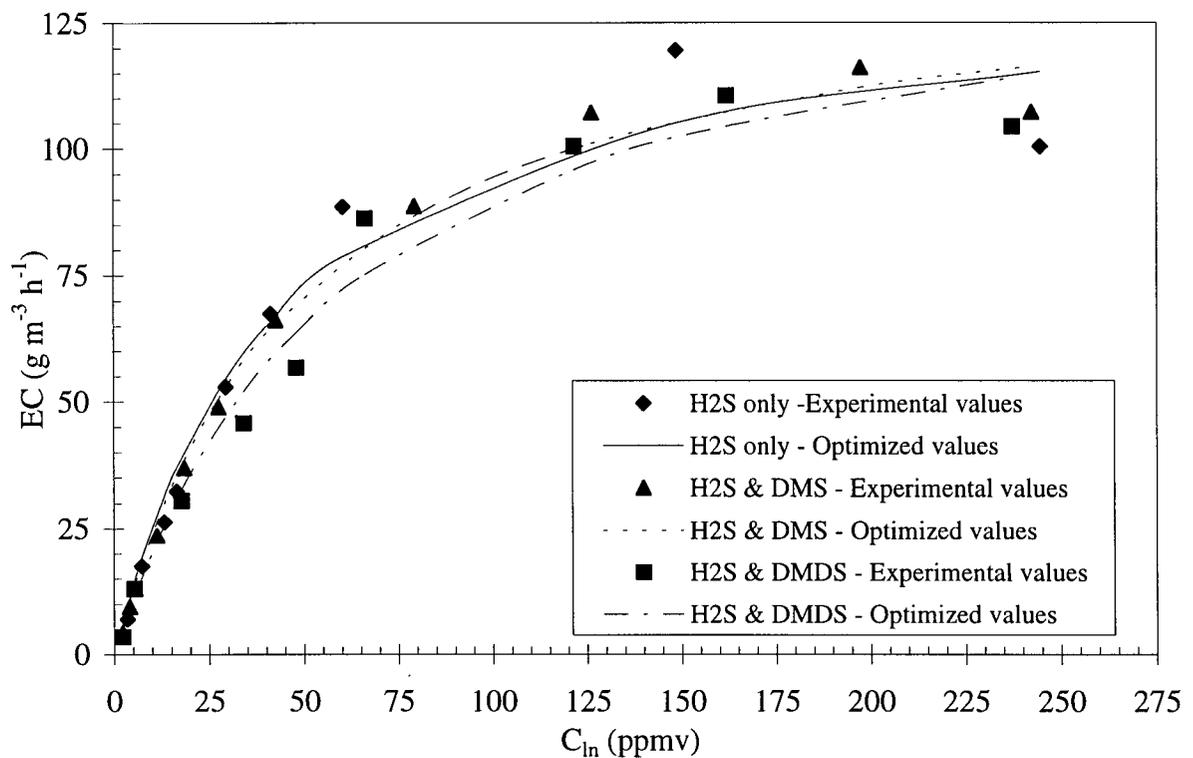

Figure 5.5. Hydrogen sulfide elimination capacity of compost biofilter

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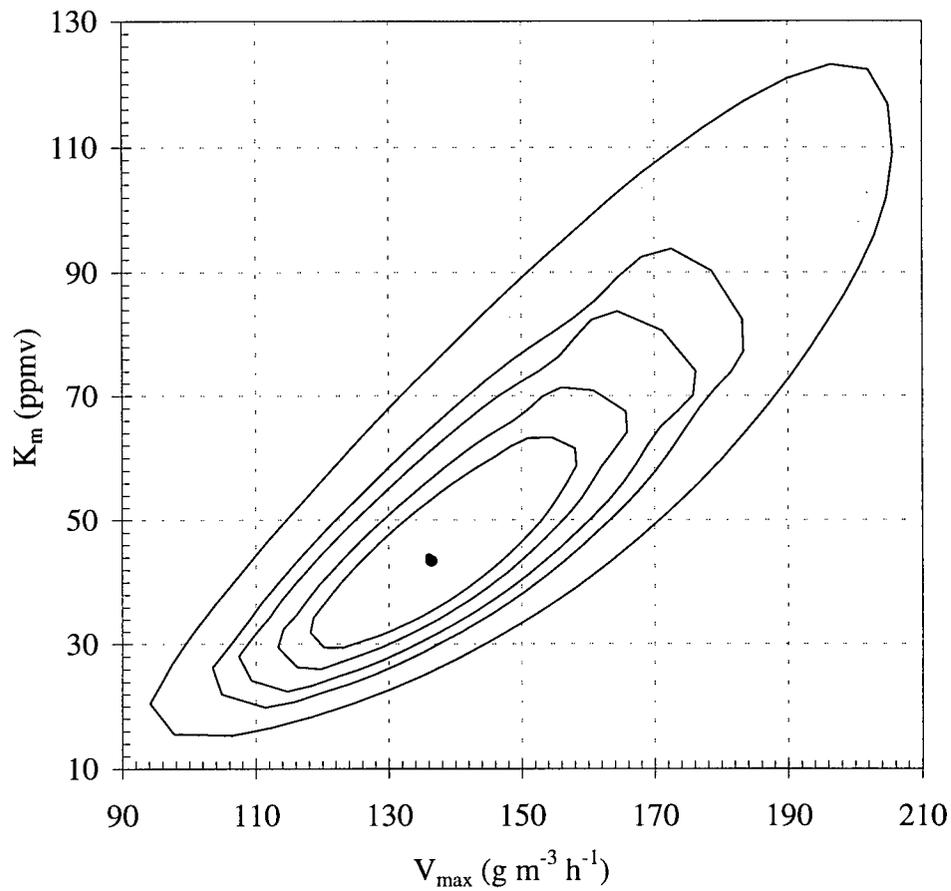
Figure 5.6. Simultaneous optimization of V_{max} and K_m for hydrogen sulfide biodegradation in compost biofilter. The best combination obtained is V_{max} = 136.07 g m^{-3} h^{-1} and K_m = 43.98 ppmv

V_{max} = 136.1 g m^{-3} h^{-1} and K_m = 43.9 ppmv. Similarly, the simultaneous optimization of V_{max} and K_m for hydrogen sulfide biodegradation with co-existence of dimethyl sulfide, and dimethyl disulfide respectively, was performed and the best combination values for V_{max} and K_m are summarized in Table 5.2.

No significant differences in the values of K_m and V_{max} were observed under the three operating regimes. At low concentrations hydrogen sulfide was removed completely. In this region the kinetic behavior was like first-order kinetics. With an increase in the inlet concentration the reaction changed to fractional-order (saturation) kinetics and ultimately leveled off indicating the commencement of substrate inhibition.

Table 5.2. Apparent kinetic parameters for hydrogen sulfide bioremoval in biofilters

Filtering Media	Kinetic Parameter	Contaminant Feed Conditions			Mean ± SD
		H_2S only	H_2S + DMS	H_2S + DMDS	
Compost	V_{max}	136.1	139.5	142.6	139.4 ± 3.3
	K_m	43.9	48.3	59.3	50.5 ± 7.9
Hog Fuel	V_{max}	136.8	140.7	137.1	138.2 ± 2.16
	K_m	47.9	47.8	54.8	50.2 ± 3.9
Mixture	V_{max}	138.3	146.8	139.7	141.6 ± 4.6
	K_m	53.1	46.5	54.6	51.4 ± 4.3

Units: V_{max} in g $m^{-3} h^{-1}$, and K_m in ppmv. SD = Standard deviation

The removal efficiencies of the co-substrates - dimethyl sulfide and dimethyl disulfide - were very low (Figure 5.7). Dimethyl sulfide elimination efficiency (30-35%) was slightly better than dimethyl disulfide removal efficiency (< 25%) because it has been reported[31] that the presence of hydrogen sulfide had a positive impact on the bioelimination of dimethyl sulfide.

5.4.1.2. Hydrogen Sulfide Biodegradation in the Hog Fuel Biofilter

Hydrogen sulfide elimination capacities of the hog fuel biofilter, for the three operating conditions described above for the compost biofilter, as a function of the logarithmic mean concentration of hydrogen sulfide at biofilter inlet and outlet are graphed in Figure 5.8. For all the three experimental runs, the experimental results and the predicted values are in good agreement with R^2 values greater than 0.95. The maximum elimination rate for hydrogen sulfide, when fed singly, in the hog fuel biofilter was estimated to be 136.8 g $m^{-3} h^{-1}$ with a biodegradation half-saturation constant of 47.9 ppmv. These values were obtained by performing the simultaneous optimization of V_{max} and K_m using the experimental data of EC and C_{ln}.

Maximum bioelimination capacities of the hog fuel biofilter for hydrogen sulfide in the presence of dimethyl sulfide, and dimethyl disulfide respectively, were estimated using the same optimization technique as described for the compost biofilter, and the best combination values obtained for V_{max} and K_m in presence of these methyl sulfides are given in Table 5.2. As in the compost biofilter, hydrogen sulfide bioelimination capacity was not affected by the co-supply of either dimethyl sulfide or the dimethyl disulfide; instead the presence of these methyl sulfides caused a small increase in V_{max}. However, in presence of dimethyl disulfide there was also a slight increase in
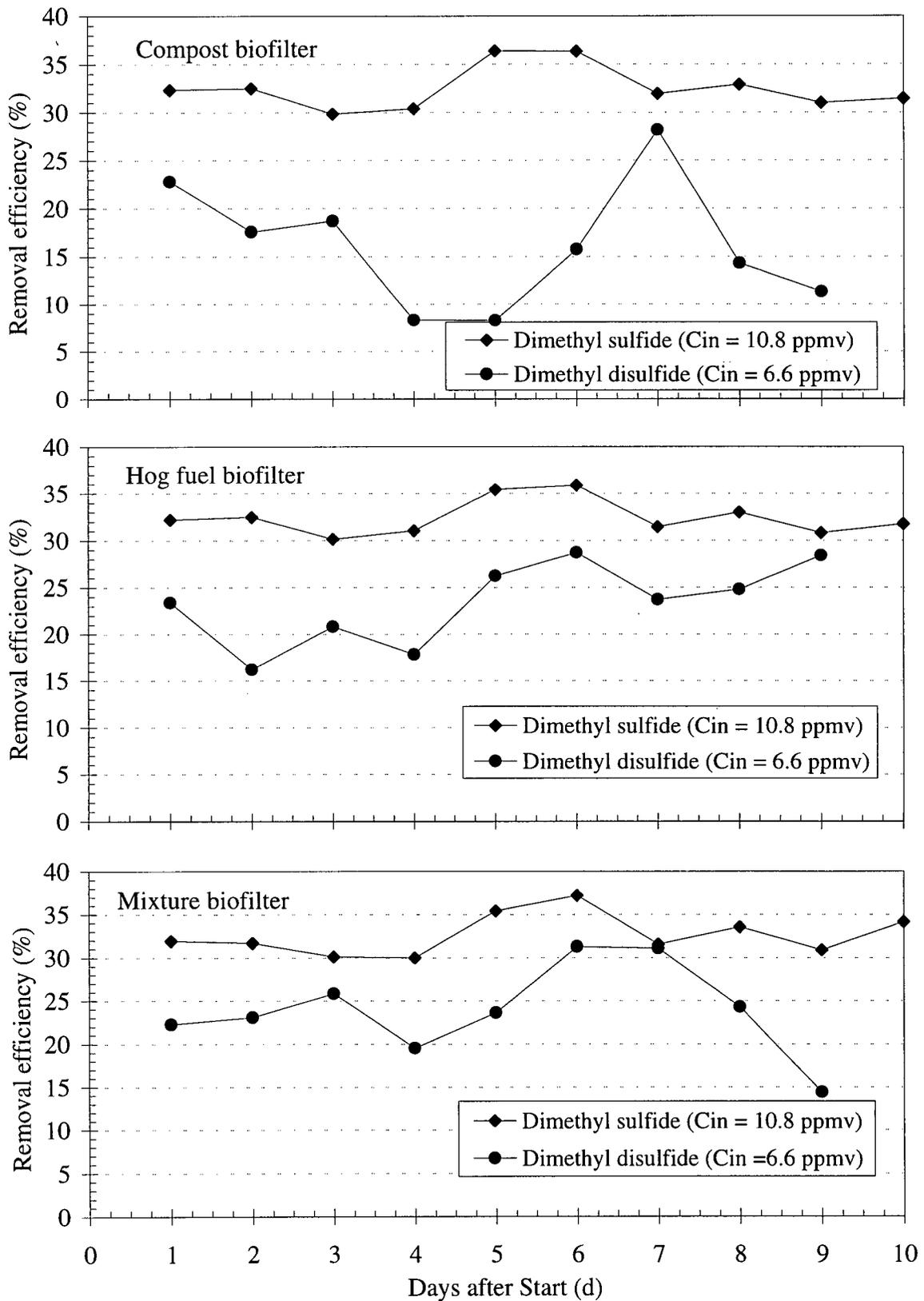
Figure 5.7. Bioelimination efficiency of dimethyl sulfide and dimethyl disulfide as co-substrates with hydrogen sulfide in biofilters

the K_m value perhaps as a result of decreased microbial affinity for hydrogen sulfide, if the physical meaning of K_m is assumed to be analogous to what it means in enzymatic kinetics.

The removal ratios of dimethyl sulfide, and dimethyl disulfide, used as co-substrates with hydrogen sulfide, in the hog fuel biofilter were less than 35%, and the removal patterns were similar to those observed in the compost biofilter (Figure 5.7).

5.4.1.3. Hydrogen Sulfide Biodegradation in the Mixture Biofilter

In Figure 5.9, hydrogen sulfide elimination capacities of the mixture biofilter for the same three operational conditions as used for the compost biofilter are plotted against the logarithmic mean concentration of hydrogen sulfide at the inlet and outlet of biofilter. The experimental data and the predicted values are in close agreement ($R^2 > 0.95$). The maximum elimination rate for hydrogen sulfide alone in the mixture biofilter was estimated to be 138.3 g m^{-3} h^{-1} with a K_m value of 53.1 ppmv. The maximum elimination capacities of the mixture biofilter for hydrogen sulfide biodegradation in coexistence with two co-substrates were estimated by performing the simultaneous optimization of V_{max} and K_m using the experimental data of EC and C_{In} obtained for these experimental runs, and the best combination values for V_{max} and K_m are given in Table 5.2. There were no significant variations in the hydrogen sulfide bioelimination capacity of the mixture biofilter in the presence of either dimethyl sulfide or dimethyl disulfide. However, in the presence of dimethyl sulfide there was a decrease in the K_m value perhaps as a result of an increased microbial affinity for hydrogen sulfide that consequently increased the bioelimination rate of hydrogen sulfide.

The mixture biofilter performed the same way, as the compost and hog fuel biofilters in removing the co-substrates (dimethyl sulfide, and dimethyl disulfide) and the removal ratios were similar to those of the compost and the hog fuel biofilters (Figure 5.7).

The maximum hydrogen sulfide elimination capacities for the compost, hog fuel and mixture biofilter were 136.1, 136.8 and 138.3 g m^{-3} h^{-1}, respectively. There are no significant differences among the three biofilter media. These results compare favorably to those obtained in previous studies in which V_{max} varied from about 120 to 327 g m^{-3} h^{-1}, using lab-scale peat biofilters[9]. These comparative studies, however, were conducted using lab-scale peat biofilters with different
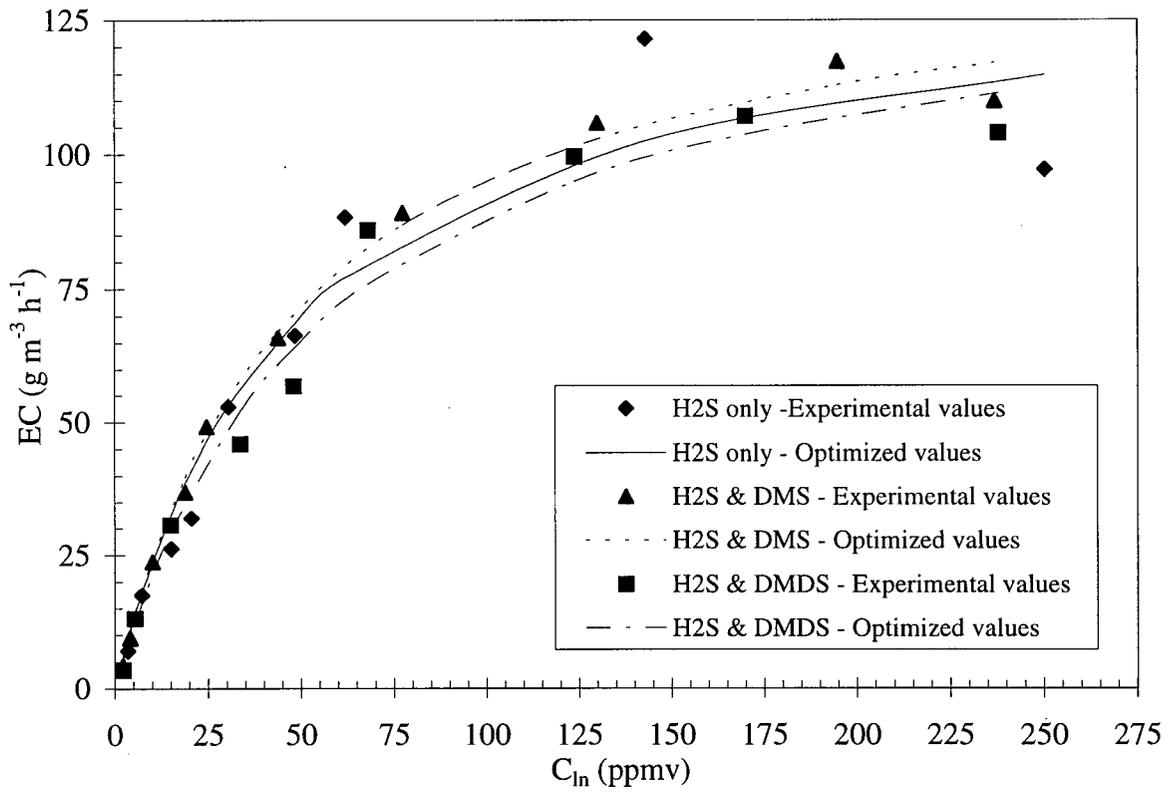
Figure 5.8. Hydrogen sulfide elimination capacity of hog fuel biofilter
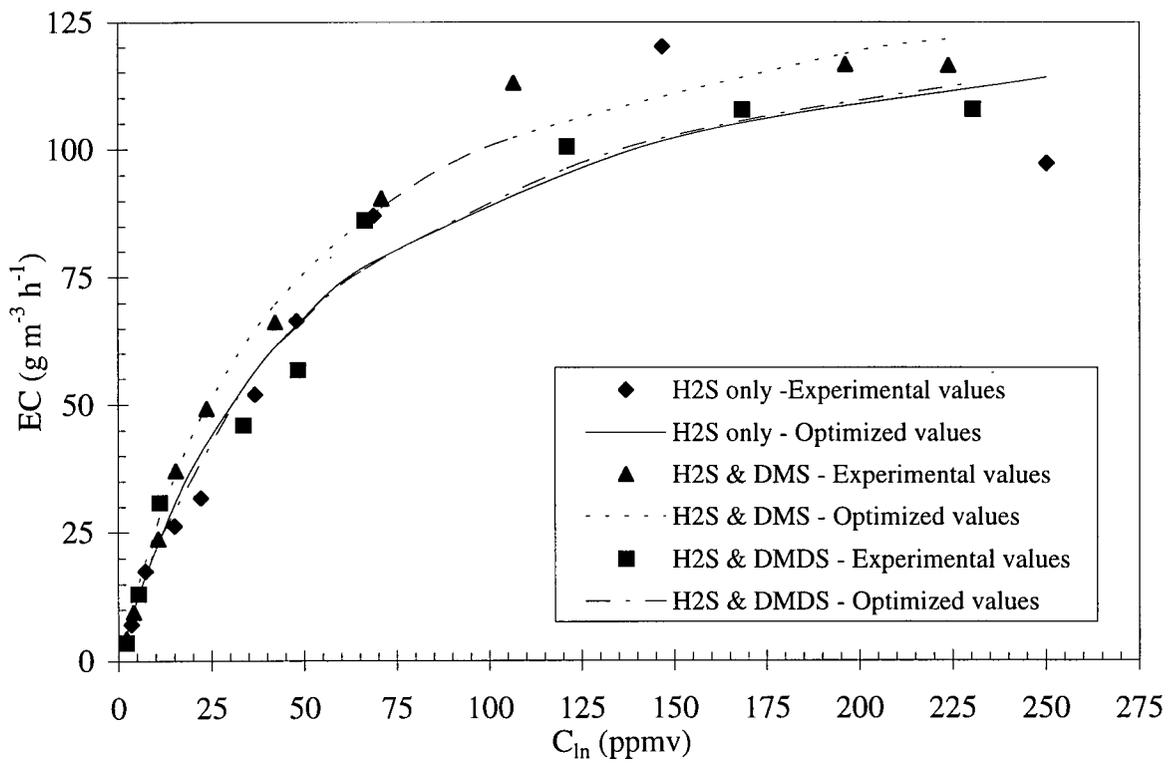

Figure 5.9. Hydrogen sulfide elimination capacity of mixture biofilter

seeding materials, and the lowest value in the range was obtained using peat seeded with *Thiobacillus sp.* and the highest utilizing *Thiobacillus sp.* and night soil sludge as seeding.

There were not any significant changes in the maximum removal rate of hydrogen sulfide for the three different biofilters either in the presence of dimethyl sulfide or dimethyl disulfide. Hydrogen sulfide elimination capacity was not affected by coexistence with either dimethyl sulfide or dimethyl disulfide in any of the three biofilters, confirming the earlier results that hydrogen sulfide biodegradation in biofilters is independent of the presence of organo-sulfur compounds mainly because of its easy biodegradability and enzyme specificity[30,31].

However, there was a slight increase in the V_{max} in presence of dimethyl sulfide or dimethyl disulfide as compared to the V_{max} when hydrogen sulfide was degraded as a single substrate, confirming the results of Hirai et al[31]. This increase in V_{max} may be because of the additional carbon source available from dimethyl sulfide or dimethyl disulfide, as reported by Cho et al[9]. They found that the growth of *Thiobacillus sp.* in degrading reduced sulfur species was stimulated by organic compounds in the presence of a reduced sulfur compound (thiosulfate). Table 5.2 indicates that in the compost biofilter there was an increase in K_m in the presence of dimethyl sulfide and an even greater increase in the presence of dimethyl disulfide. This could be interpreted to mean that these organo-sulfur gases are inhibitory to hydrogen sulfide removal. But in the case of the hog fuel biofilter the presence of dimethyl sulfide had no effect on K_m, although the presence of dimethyl disulfide did result in a higher K_m value. For the mixture biofilter the presence of dimethyl sulfide resulted in a lower value for K_m while dimethyl disulfide had little effect. Given the scale of the changes in K_m observed in the presence of dimethyl sulfide and dimethyl disulfide, and taking into account all the data relevant to K_m in Table 5.2 leads one to conclude that there was no significant effect of dimethyl sulfide and dimethyl disulfide on K_m and if there was, it was not a strong effect.

The behaviors of all of the three filtering media for the removal of two co-substrates (dimethyl sulfide, and dimethyl disulfide) treated in association with hydrogen sulfide were similar. However, the compost biofilter was less efficient than other two biofilters for dimethyl disulfide biodegradation. Dimethyl sulfide elimination efficiency (30-35%) was slightly better than dimethyl disulfide removal efficiency (< 30%) in all of the three biofilters. This was probably because of the

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enhancement of dimethyl sulfide degradation in presence of hydrogen sulfide as reported by earlier studies[30,31] on the biodegradation of dimethyl sulfide in association with hydrogen sulfide.

5.4.2. Experiment II. Biodegradation Macrokinetics of Dimethyl Sulfide

Biofilter acclimation with increasing dimethyl sulfide concentration from 3 to 25 ppmv was started immediately after the columns were packed. During the initial stages of this experiment the usual measurements of performance (% removal, elimination capacity and outlet concentration) could not be observed because of the unavailability of dimethyl sulfide during the initial start up period and the system was re-started after a break. So, only the four steady-state experimental runs performed to evaluate the bioremoval rates of dimethyl sulfide independently, as well as in association with hydrogen sulfide, methyl mercaptan and dimethyl disulfide are presented here.

The dimethyl sulfide concentration in the inlet waste air stream was varied from 3 to 25 ppmv in order to determine the macrokinetics of its biodegradation solely as well as in the presence of hydrogen sulfide, methyl mercaptan and dimethyl disulfide, and to illustrate the inhibition effects of these reduced sulfur gases on dimethyl sulfide removability. The biofilters were allowed to stabilize for 24 hours prior to analyzing the outlet concentration and changing to a new inlet concentration. Concentration profiles over the entire effective bed height (packed bed volume of 0.018 m^3) in all of the three biofilters were used in estimating the apparent macrokinetic parameters because dimethyl sulfide inlet loads were removed along the entire height of the filter bed (Figure 5.10).

Over the operating period of more than two months the biofilter media pH (Figure 5.11) did not show any significant changes in all of the three biofilters. Although sulfate is produced stoichiometrically as the end product in the biodegradation of dimethyl sulfide[26,27], the media pH was not reduced noticeably. This stability in media pH was attributed to the excellent pH buffering capacity of the dolomitic lime initially mixed with the filter media as a pH buffer. Although both hydrogen sulfide and dimethyl sulfide contain the single atom of sulfur in their molecules, the lower concentration of dimethyl disulfide ($\leq$ 25 ppmv) treated in biofilters as compared to very high hydrogen sulfide concentrations ($\leq$ 450 ppmv) definitely produced much
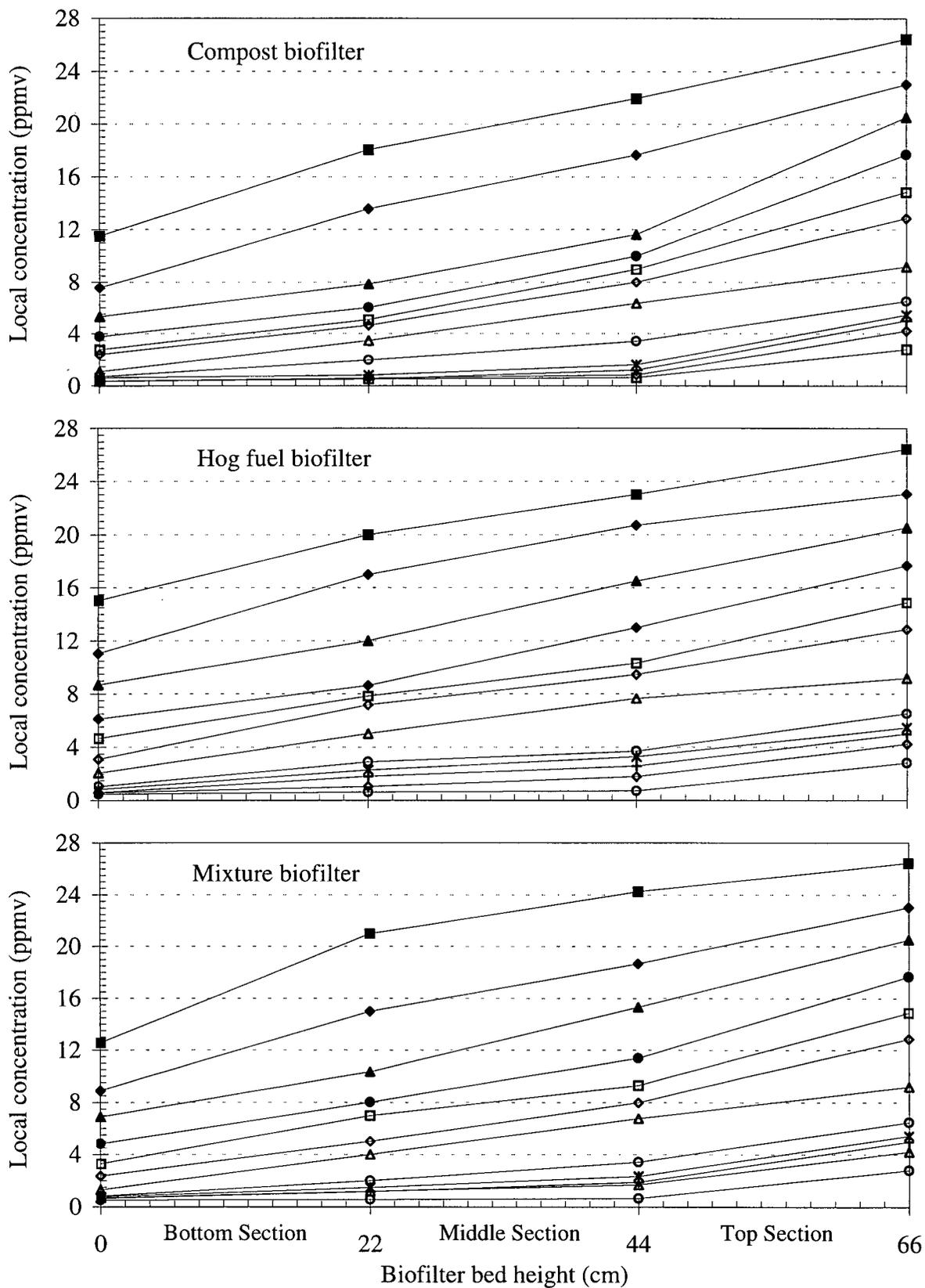
Figure 5.10. Axial concentration profile of dimethyl sulfide in biofilters. Different line markers represent different inlet concentration levels for each stage.

less sulfate as compared to the hydrogen sulfide degradation in biofilters, resulting in slight drop in media pH.

5.4.2.1. Dimethyl Sulfide Biodegradation in the Compost Biofilter

The dimethyl sulfide bioelimination capacity of the compost biofilter for four different operating conditions, when treating dimethyl sulfide alone ($C_{in\ other\ reduced\ sulfur\ gases}$ = 0 ppmv) and with co-supply of other reduced sulfur gases ($C_{in\ hydrogen\ sulfide}$ ≈ 23, $C_{in\ methyl\ mercaptan}$ ≈ 15, and $C_{in\ dimethyl\ disulfide}$ ≈ 7 ppmv), plotted as a function of the logarithmic mean concentration of dimethyl sulfide is depicted in Figure 5.12. The apparent macrokinetic parameters, V_{max} and K_m, for the biodegradation of dimethyl sulfide were calculated by performing non-linear regression between EC (g m^{-3} h^{-1}) and C_{ln} (ppmv), using the NONLIN Model of the SYSTAT software, according to equation 8, as described in Section 5.4.1.1. The maximum elimination rate and the saturation constant for the biodegradation of dimethyl sulfide, when treated singly, were calculated to be V_{max} = 5 g m^{-3} h^{-1} and K_m = 7.2 ppmv, from the optimization plot shown in Figure 5.13. The ellipse-shaped area near the center of the plot represents the region where the loss function is minimized, and any parameter value combination produces approximately the same loss function. The same methodology was employed for the simultaneous optimization of V_{max} and K_m for dimethyl sulfide biodegradation with a co-supply of hydrogen sulfide, methyl mercaptan, and dimethyl disulfide respectively, and the best combination values for V_{max} and K_m are summarized in Table 5.3.

Table 5.3. Apparent kinetic parameters for dimethyl sulfide bioelimination in biofilters

Filtering Media	Kinetic Parameter	Contaminant Feed Conditions				Mean ± SD
		DMS only	DMS + H$_2$S	DMS + MM	DMS + DMDS	
Compost	V_{max}	5.0	5.3	3.0	3.5	4.2 ± 1.1
	K_m	7.2	6.6	7.4	7.8	7.2 ± 0.5
Hog Fuel	V_{max}	3.8	4.0	2.1	2.1	3.0 ± 1.0
	K_m	6.5	6.0	9.4	8.3	7.6 ± 1.6
Mixture	V_{max}	4.6	4.4	2.4	2.3	3.4 ± 1.2
	K_m	7.3	6.1	7.9	7.9	7.3 ± 0.8

Units: V_{max} in g m^{-3} h^{-1}, and K_m in ppmv. SD = Standard deviation
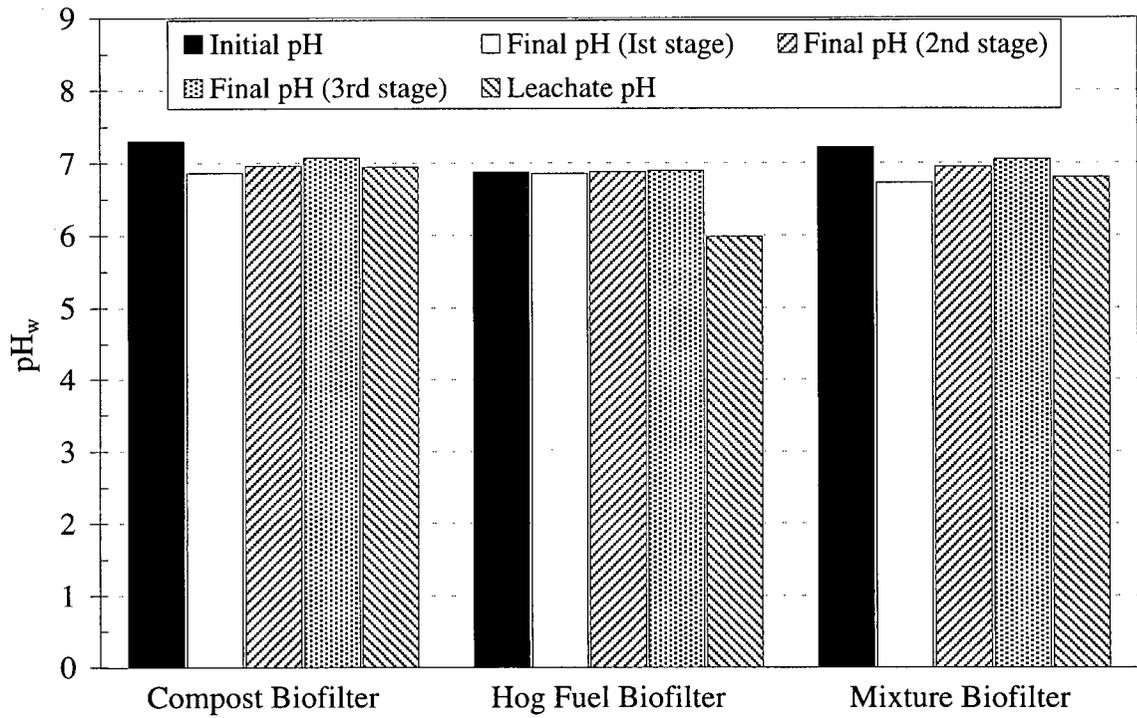
Figure 5.11. Biofilter media and leachate pH after degrading dimethyl sulfide
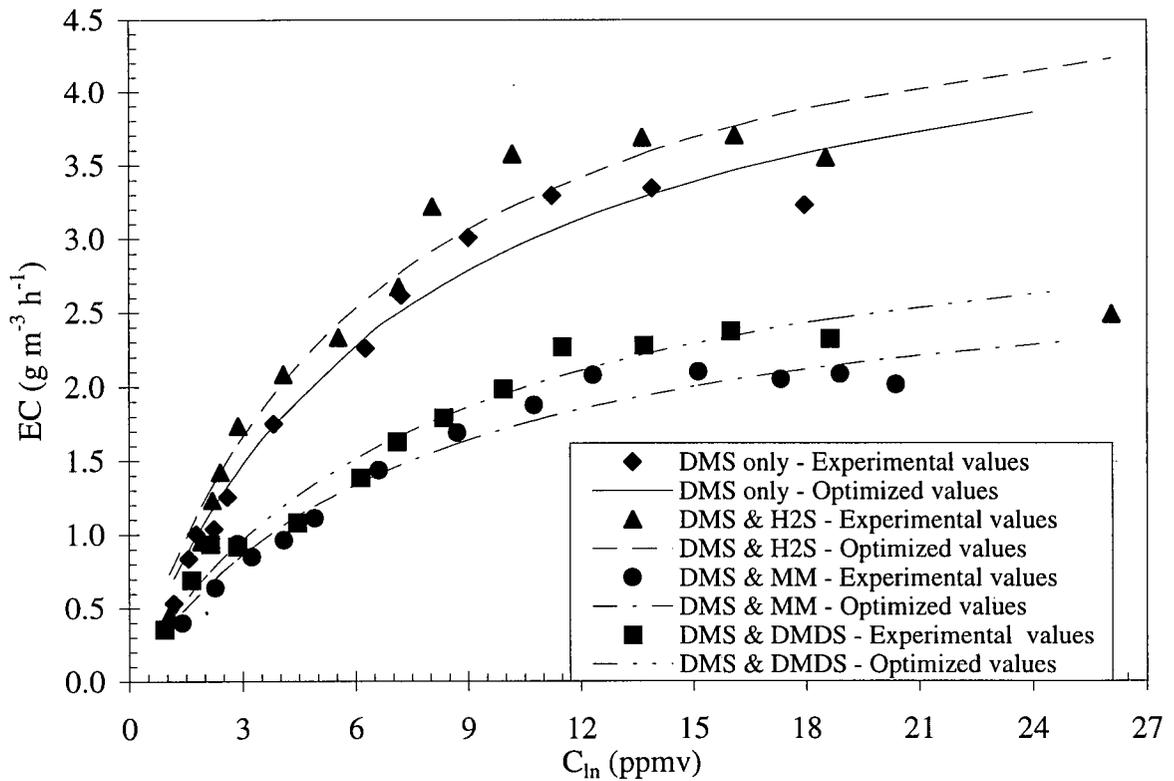
Figure 5.12. Dimethyl sulfide elimination capacity of compost biofilter
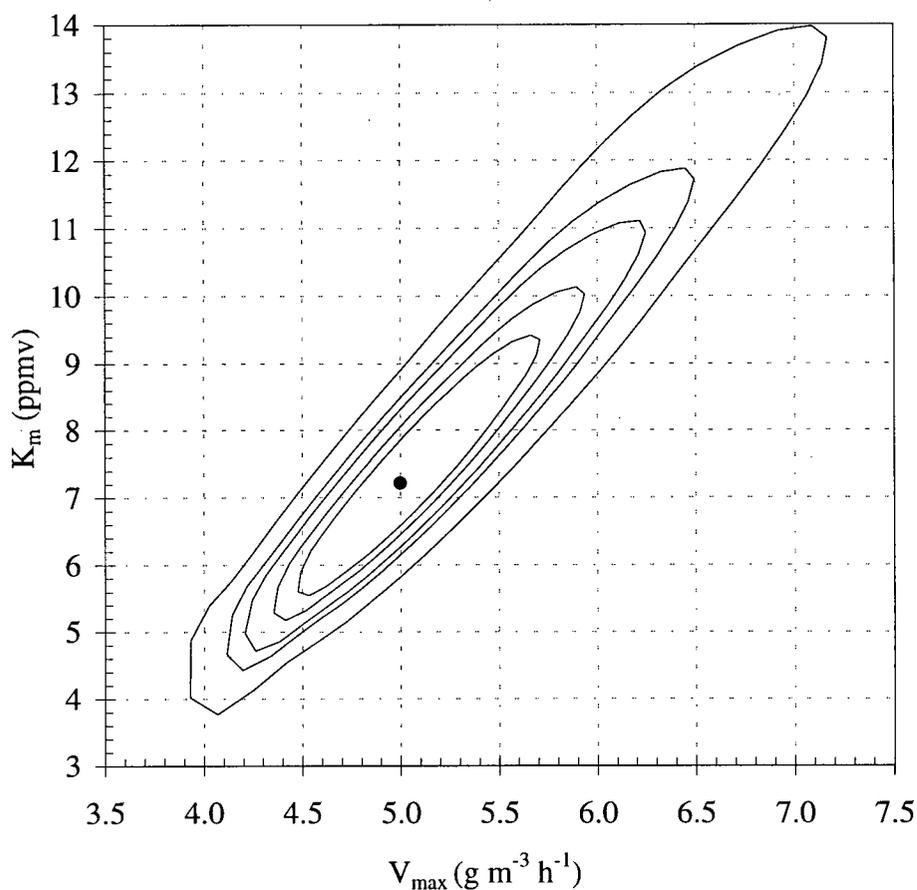
Figure 5.13. Simultaneous optimization of V_{max} and K_m
for dimethyl sulfide biodegradation in compost biofilter.
The best combination obtained is $V_{max} = 5.0$ g m^{-3} h^{-1} and
$K_m = 7.2$ ppmv

It is clearly observed (Figure 5.12) that the dimethyl sulfide elimination capacity is slightly increased in the presence of hydrogen sulfide, and at the same time K_m showed a decrease (Table 5.3) as the result of the enhancement of biomass affinity for dimethyl sulfide, if the physical meaning of K_m is assumed to be analogous to its meaning in enzymatic kinetics. Although the coexistence of methyl mercaptan and dimethyl disulfide did not have any significant impact on the K_m value, the elimination capacity was drastically reduced and a decrease in V_{max} by a factor of 1.65 and 1.45 occurred with the co-supply of methyl mercaptan and dimethyl disulfide, respectively.

Amongst the other three reduced sulfur gases used as co-substrates, hydrogen sulfide was almost completely removed in the first (top) section to the extent that its concentration in the effluent gas

was below the detection limit of the gas chromatograph. The removal efficiency of around 96-98% was achieved for methyl mercaptan in all the three filter media. Initially dimethyl disulfide was removed at 96+ %, however after two days the removal efficiency dropped to 90-92% and remained at this level for rest of the test period, in all the three biofilter media materials (Figure 5.14). This drop in the dimethyl disulfide % removal may be because of the higher dimethyl sulfide inlet concentrations that have a negative impact on the removability of dimethyl disulfide.

5.4.2.2. Dimethyl Sulfide Biodegradation in the Hog Fuel Biofilter

The elimination capacities of the hog fuel biofilter for dimethyl sulfide biodegradation, under the four different operating conditions described above, as functions of the logarithmic mean concentration of dimethyl sulfide at the biofilter inlet and outlet are shown in Figure 5.15. For all four experimental runs, the experimental results and the predicted values are in good agreement with R^2 values greater than 0.94. The maximum elimination rate for dimethyl sulfide, when fed individually, in the hog fuel biofilter was estimated to be 3.8 g m^{-3} h^{-1} with a biodegradation half-saturation constant of 6.5 ppmv. These values were obtained by performing the simultaneous optimization of V_{max} and K_m using the experimental data of EC and C_{ln}.   Maximum bioelimination capacities of the hog fuel biofilter for dimethyl sulfide in the presence of hydrogen sulfide, methyl mercaptan, and dimethyl disulfide respectively, were estimated using the same optimization technique in order to reduce the loss function, and the best combination values for V_{max} and K_m for these three different operating conditions are given in Table 5.3. As in the compost biofilter, the dimethyl sulfide bioelimination capacity was not adversely affected by a co-supply of hydrogen sulfide, instead the presence of hydrogen sulfide caused a small increase in V_{max} and a slight decrease in the K_m values. Contrary to the effects observed in the compost biofilter, K_m for dimethyl sulfide biodegradation was significantly increased, 45% in the presence of methyl mercaptan and 28% in the presence of dimethyl disulfide. Consequently, the maximum elimination capacity, V_{max}, was reduced by a factor of 1.8 with the co-supply of either methyl mercaptan or dimethyl disulfide.

The removal capacities for the three co-substrates (hydrogen sulfide, methyl mercaptan, and dimethyl disulfide) in hog fuel biofilter were very high, according to their ease in biodegradability, as in the compost biofilter (Figure 5.14).

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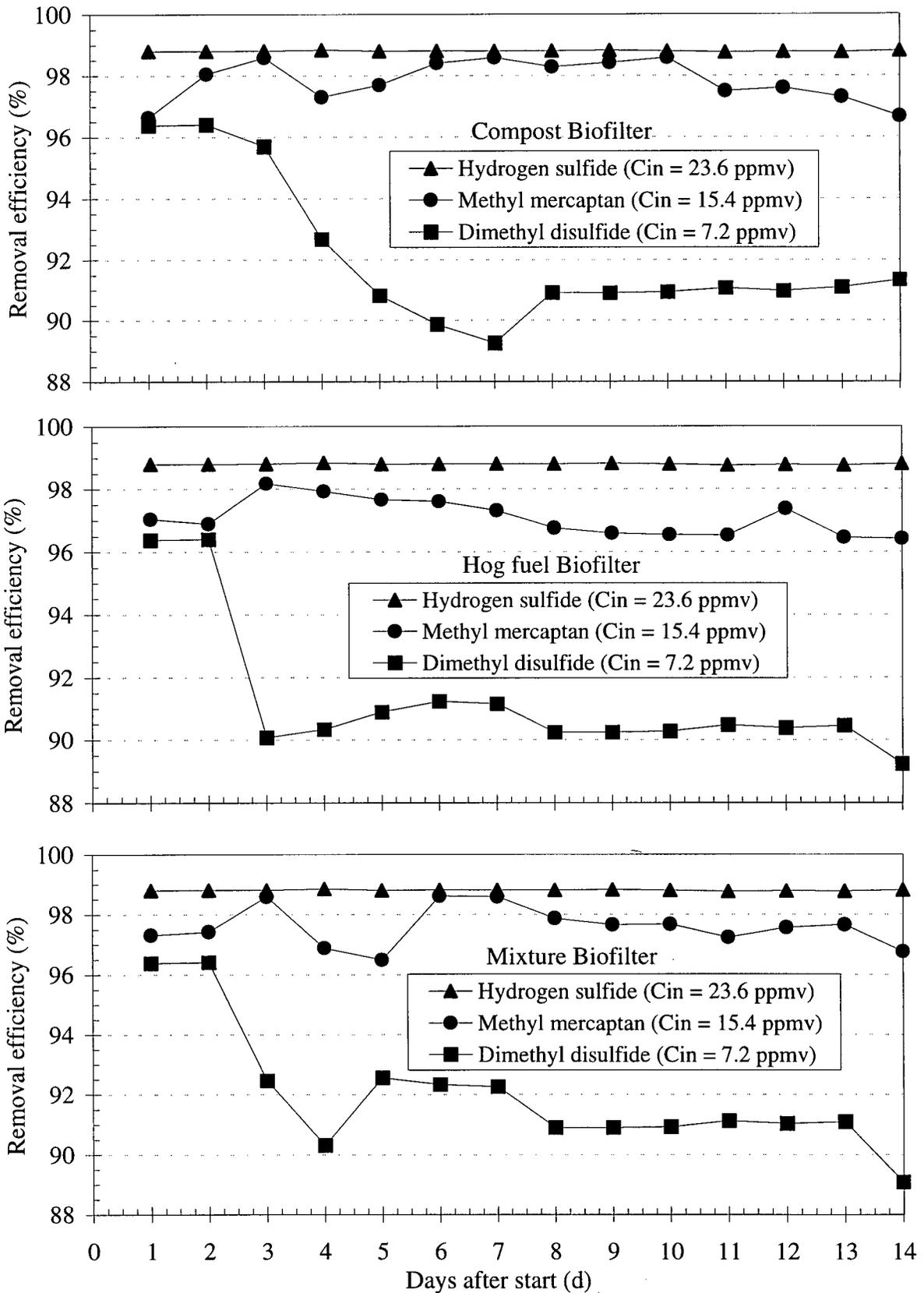
Figure 5.14. Bioelimination efficiency of hydrogen sulfide, methyl mercaptan
and dimethyl disulfide as co-substrates with dimethyl sulfide in biofilters

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5.4.2.3. Dimethyl Sulfide Biodegradation in the Mixture Biofilter

Dimethyl sulfide elimination capacities of the mixture biofilter plotted against the logarithmic mean concentration of dimethyl sulfide at the inlet and outlet of biofilter, when dimethyl sulfide was treated alone, and in the presence of hydrogen sulfide, methyl mercaptan, and dimethyl disulfide respectively, are presented in Figure 5.16. The experimental data and the predicted values are in close agreement ($R^2 > 0.95$). The maximum elimination rate for dimethyl sulfide alone in mixture biofilter is estimated to be 4.6 g m^{-3} h^{-1} with a K_m value of 7.3 ppmv. The maximum elimination capacities of the mixture biofilter for dimethyl sulfide biodegradation with coexistence of the other three co-substrates - hydrogen sulfide, methyl mercaptan, and dimethyl disulfide - were estimated by performing the simultaneous optimization of V_{max} and K_m. The best combination values for V_{max} and K_m are given in Table 5.3. As might be expected the maximum removal rates in the mixture biofilter are somewhat in between the compost and the hog fuel biofilter values, however when dimethyl sulfide was supplied in a mixture with any of the three co-substrates, the mixture biofilter behaved more like the compost biofilter. As in the case of the compost and the hog fuel biofilters, the presence of hydrogen sulfide decreased the K_m value for dimethyl sulfide bioelimination in the mixture biofilter too, but at the same time V_{max} was not increased. The co-existence of methyl mercaptan, or dimethyl disulfide had similar antagonistic effects on the bioelimination of dimethyl sulfide, with about a 10% increase in the K_m value. V_{max} was approximately half of its value obtained for dimethyl sulfide biodegradation as the sole substrate.

The mixture biofilter performed well in removing the other three co-substrates (hydrogen sulfide, methyl mercaptan, and dimethyl disulfide) and the removal rates were similar to those of the compost and the hog fuel biofilters (Figure 5.14).

The maximum elimination capacities for dimethyl sulfide in the three biofilter media (compost, hog fuel, and the mixture of compost and hog fuel) studied were between 3.8 and 5 g m^{-3} h^{-1}, depending upon the filter media used. These results compare favorably with those obtained in previous studies[16,30,31] in which V_{max} varied from 3.2 to 5.5 g m^{-3} h^{-1}, with an exceptionally high of 28.3 g m^{-3} h^{-1} reported by Smet et al.[17]. These comparative studies, however, were conducted using lab-scale peat and compost biofilters with different seeding materials and the high removal capacity was observed in a compost biofilter inoculated with highly specific microorganisms.

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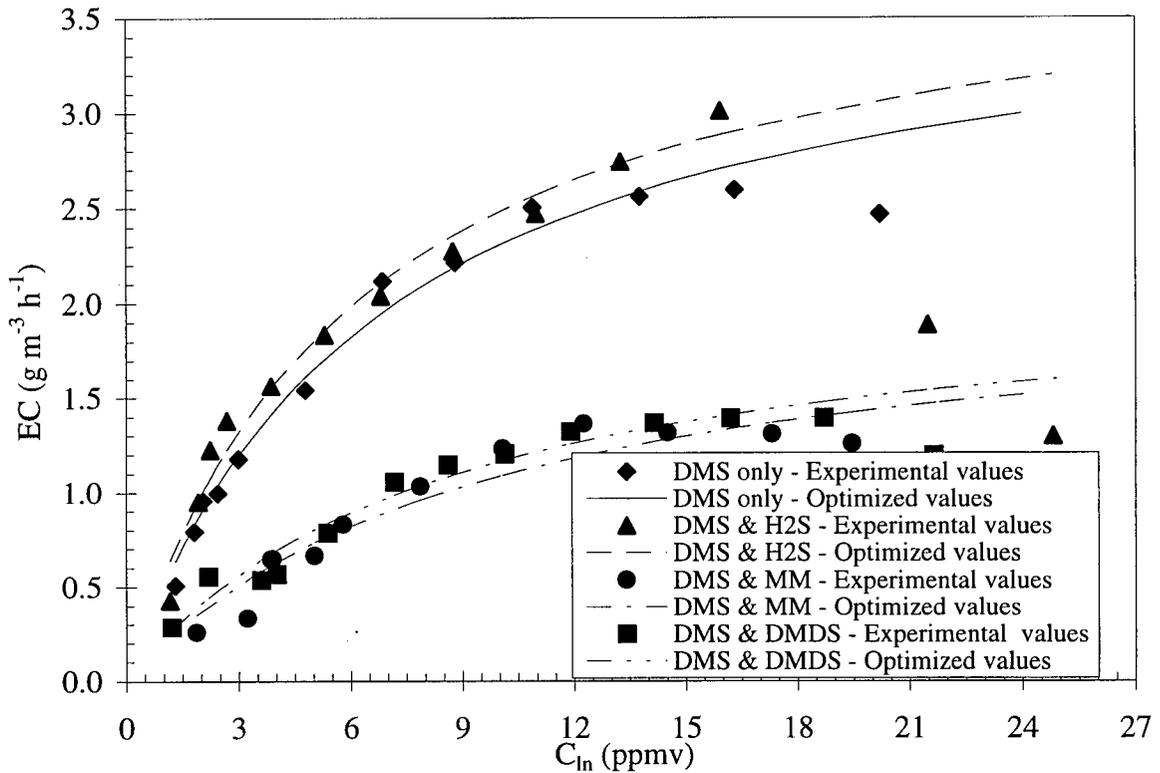
Figure 5.15. Dimethyl sulfide elimination capacity of hog fuel biofilter
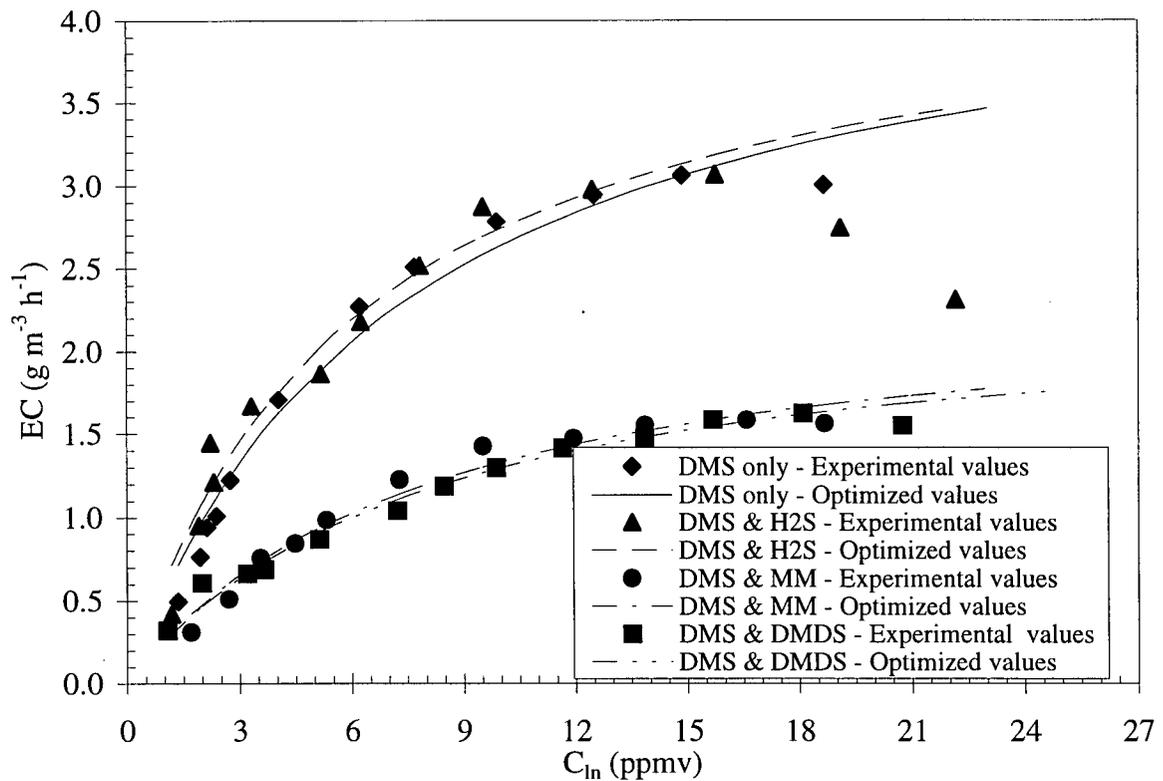

Figure 5.16. Dimethyl sulfide elimination capacity of mixture biofilter

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The three biofilter media, tested in our study, significantly varied in their capacity for the bioelimination of dimethyl sulfide. The highest V_{max} (5 g m^{-3} h^{-1}) was noted in the compost filtering medium as compared to 3.8 and 4.6 g m^{-3} h^{-1} in the hog fuel and the mixture filter media, respectively. The lower removal rates in the hog fuel biofilter could have been due to poor growth of microorganisms capable of degrading dimethyl sulfide, because all of the three biofilters were inoculated with the same waste activated sludge and operated under identical loading conditions. The results are in agreement with those reported by Smet et al.[17] that the elimination capacity of wood bark biofilter (0.21 g m^{-3} h^{-1}) for dimethyl sulfide was about one-half of that of a compost biofilter, and after inoculating both biofilters with highly specific microorganisms, the elimination capacity of the wood bark biofilter (1.46 g m^{-3} h^{-1}) was significantly lower, about 20 times less than that of the compost biofilter. A possible reason for wood waste/hog fuel filter media being an inhospitable habitat for the growth of dimethyl sulfide degrading microorganisms might be its low nutrient content, especially the available nitrogen (C/N$_{dry\ basis}$ = 325) as compared to the compost media (C/N$_{dry\ basis}$ = 27). However, this was not the case with hydrogen sulfide degradation where the three biofilter media materials behaved similarly. This perhaps might be because of the dominant microbial communities like autotrophs that obtain carbon from the waste air stream and utilize the hydrogen sulfide, but are not able to degrade organo-sulfur compounds viz., methyl mercaptan, dimethyl sulfide and dimethyl disulfide.

In all of the three biofilters the co-supply of hydrogen sulfide caused a slight decrease in K_m and consequently enhanced the biodegradation with a minor increase in V_{max}. In the presence of methyl mercaptan and dimethyl disulfide, the V_{max} for dimethyl sulfide biodegradation was significantly reduced by 30-50%, with a slight increase in K_m value in the three biofilter media used. The coexistence effects of dimethyl disulfide were similar to those of methyl mercaptan, because methyl mercaptan is the primary metabolic byproduct produced as a result of the reductive cleavage of dimethyl disulfide. This strong inhibition occurs when two or more pollutants, possessing different biodegradation rates are degraded by the same population of microorganisms. A close examination of the literature[30,31] reveals that dimethyl sulfide is more difficult to biodegrade than methyl mercaptan and dimethyl disulfide. The presence of methyl mercaptan in the waste air stream caused a more than 50% decrease in the biodegradation of dimethyl sulfide. The researchers involved have hypothesized the existence of two types of enzyme systems namely C-S bond and an S-H bond breaking enzymes. The C-S bond enzyme participates

in the first step of the oxidation of either methyl mercaptan or dimethyl sulfide and thus dimethyl sulfide degradation is allosterically inhibited by the presence of methyl mercaptan. The S-H bond enzyme takes part in hydrogen sulfide degradation and at the same time hydrogen sulfide oxidation may stimulate the activity of the C-S bond-cleaving enzyme thereby having positive impacts on the degradation of dimethyl sulfide. However, no attempts were made to isolate the microorganisms for their reduced sulfur degrading enzyme characterization.

In all of the three filtering media the removal patterns of the co-substrates (hydrogen sulfide, methyl mercaptan, and dimethyl disulfide) treated in association with dimethyl sulfide were similar with very high removal efficiency for hydrogen sulfide, to an undetectable level, and more than 90% for methyl mercaptan and dimethyl disulfide. Methyl mercaptan removal rates were better than those of dimethyl disulfide, confirming the earlier results[10,20,30] that the biodegradability of these reduced sulfur gases follows the same order as hydrogen sulfide > methyl mercaptan > dimethyl disulfide > dimethyl sulfide.

5.4.3. Experiment III. Biodegradation Macrokinetics of Dimethyl Disulfide

The biofilters were acclimated to dimethyl disulfide for two weeks by increasing the contaminant concentration gradually from 10 to 50 ppmv in order to establish steady state conditions as indicated by dimethyl disulfide removals remaining constant with time. Once the columns were fully acclimatized, the transient behavior of the biofilters in response to fluctuating dimethyl disulfide concentrations and waste airflow rates was evaluated (results discussed in Chapter IV), before commencing the evaluation of the bioelimination rates of dimethyl disulfide independently, as well as in the presence of other reduced sulfur gases. Three experimental tests, with dimethyl disulfide alone and in the presence of hydrogen sulfide and dimethyl sulfide, were performed to evaluate the bioremoval rates of dimethyl disulfide independently and to illustrate any inhibition effects of these other sulfur gases on the dimethyl disulfide biodegradation rate.

Macrokinetics for dimethyl disulfide biodegradation were estimated by varying the dimethyl disulfide inlet concentration from 5 to 45 ppmv in the waste air stream. Before sampling the outlet concentration, and changing the inlet concentration to a new level, the biofilters were allowed to stabilize for 24 hours. Hydrogen sulfide ($\approx$ 16 ppmv), and dimethyl sulfide ($\approx$ 9 ppmv) were co-supplied with dimethyl disulfide in order to detect any coexistence effects of these two

sulfur gases on the bioelimination of dimethyl disulfide. Concentration profiles over the entire effective bed height (packed bed volume of 0.018 m^3) in all of the three biofilters were used in estimating the apparent macrokinetic parameters because dimethyl disulfide inlet loads were removed along the entire height of the filter bed (Figure 5.17).

The media's initial pH, when the biofilter columns were packed, along with the final pH of media in each section, after a total operating period of more than four months (including the period for the analysis of biofilter dynamics and transient behavior) are shown in Figure 5.18. Although it has been reported[27] that sulfate is produced stoichiometrically as an end product in the biodegradation of dimethyl disulfide, the drop in media pH was not so much as in case of hydrogen sulfide degradation (Figure 5.4). Here the quantity of sulfur degraded as dimethyl disulfide was much lower than the amount of sulfur degraded as hydrogen sulfide because very high concentrations of hydrogen sulfide (up to 450 ppmv) were used as compared to dimethyl disulfide concentrations of less than 45 ppmv. Consequently the buffering capacity of the media was not exhausted within the period the biofilters were operated for the degradation of dimethyl disulfide.

5.4.3.1. Dimethyl Disulfide Biodegradation in the Compost Biofilter

The elimination capacities of the compost biofilter for dimethyl disulfide biodegradation; under three different operating conditions with dimethyl disulfide (1) as a sole contaminant, (2) in a mixture with hydrogen sulfide, and (3) in association with dimethyl sulfide; as a function of its logarithmic mean concentration are plotted in Figure 5.19. The experimental and predicted values are in close agreement with R^2 values greater than 0.95. Hydrogen sulfide, and dimethyl sulfide concentrations (approximately 16 and 9 ppmv, respectively) were kept constant throughout the experimental tests with step-increases in dimethyl disulfide concentration. The NONLIN Model of the SYSTAT software was used to estimate the apparent macrokinetic parameters, V_{max} and K_m for dimethyl disulfide biodegradation, through non-linear regression of EC (g m^{-3} h^{-1}) and C_{ln} (ppmv) according to equation 8. The V_{max} and K_m values for dimethyl disulfide biodegradation as a sole contaminant were found to be 16.9 g m^{-3} h^{-1} and 7.7 ppmv, respectively. The results of simultaneous optimization of these kinetic parameters are shown in Figure 5.20. The elliptical area in the center of the plot represents the region where the loss function is minimized, and any parameter value combination produces approximately the same loss function. The V_{max} and K_m values for dimethyl disulfide bioremoval in the presence of hydrogen sulfide and dimethyl sulfide,
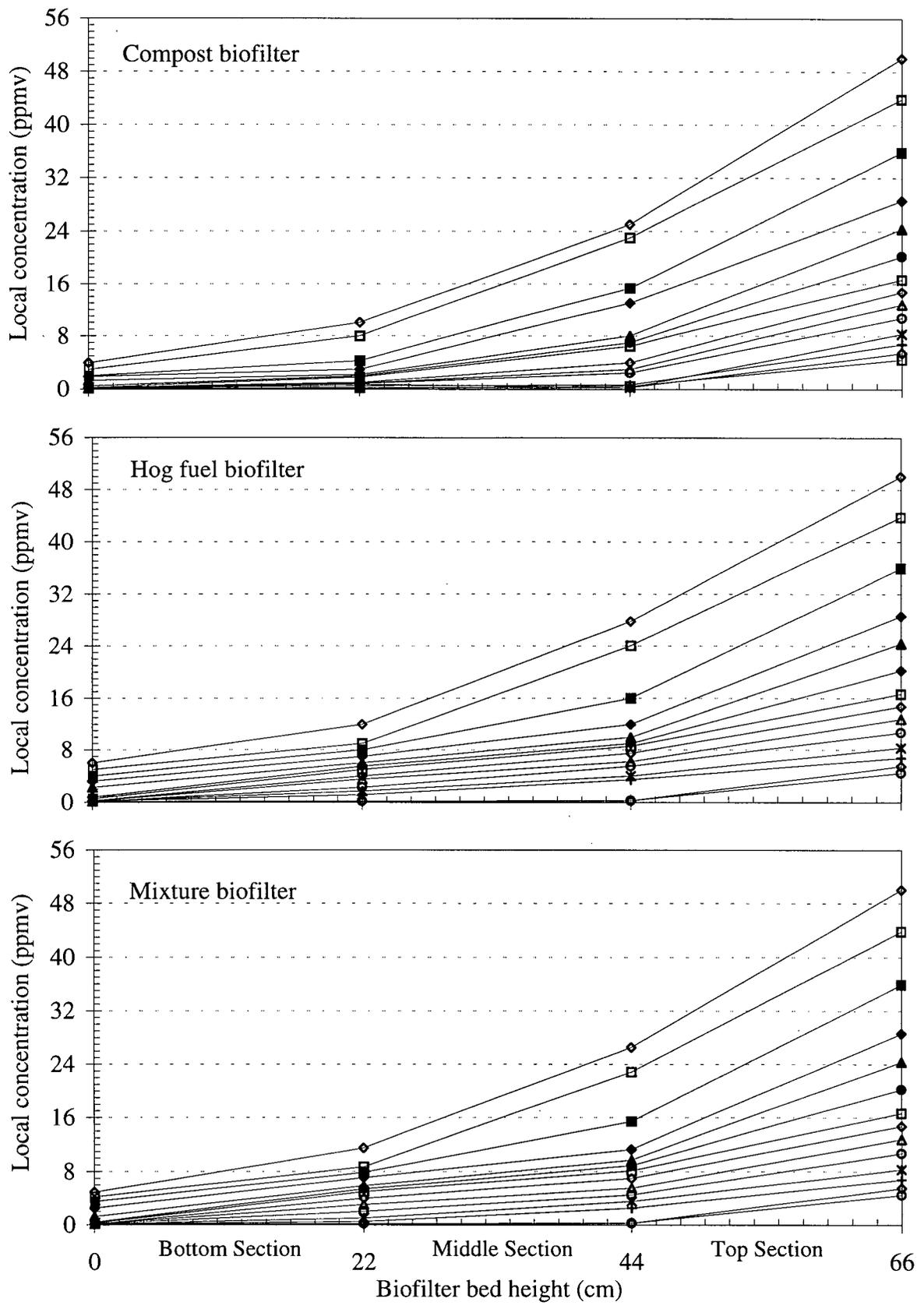
Figure 5.17. Axial concentration profile of dimethyl disulfide in biofilters. Different line markers represent different inlet concentration levels for each stage.
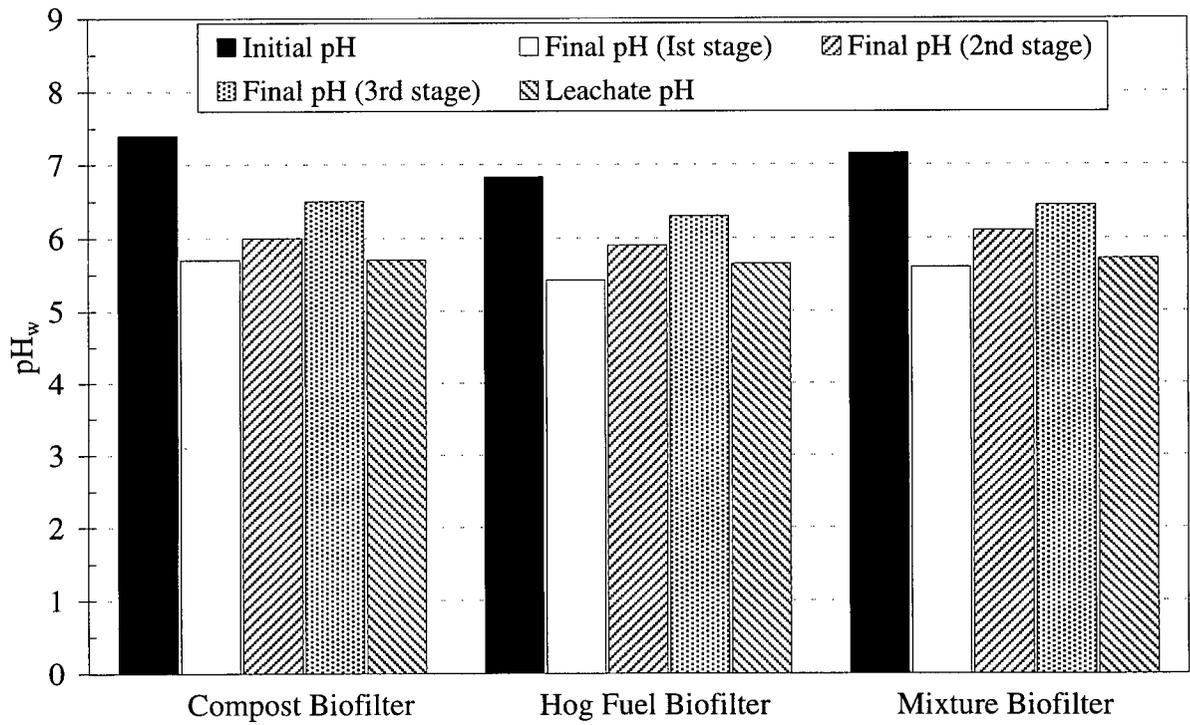
Figure 5.18. Biofilter media and leachate pH after degrading dimethyl disulfide
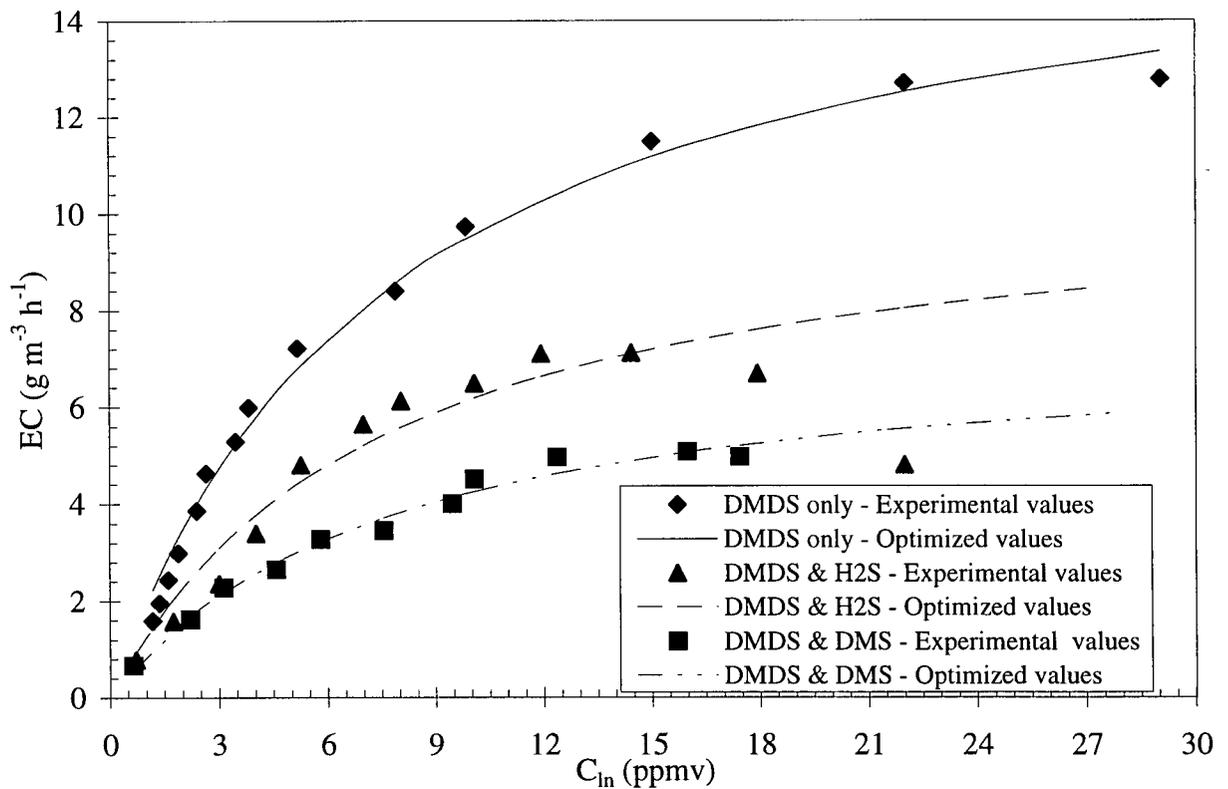

Figure 5.19. Dimethyl disulfide elimination capacity of compost biofilter
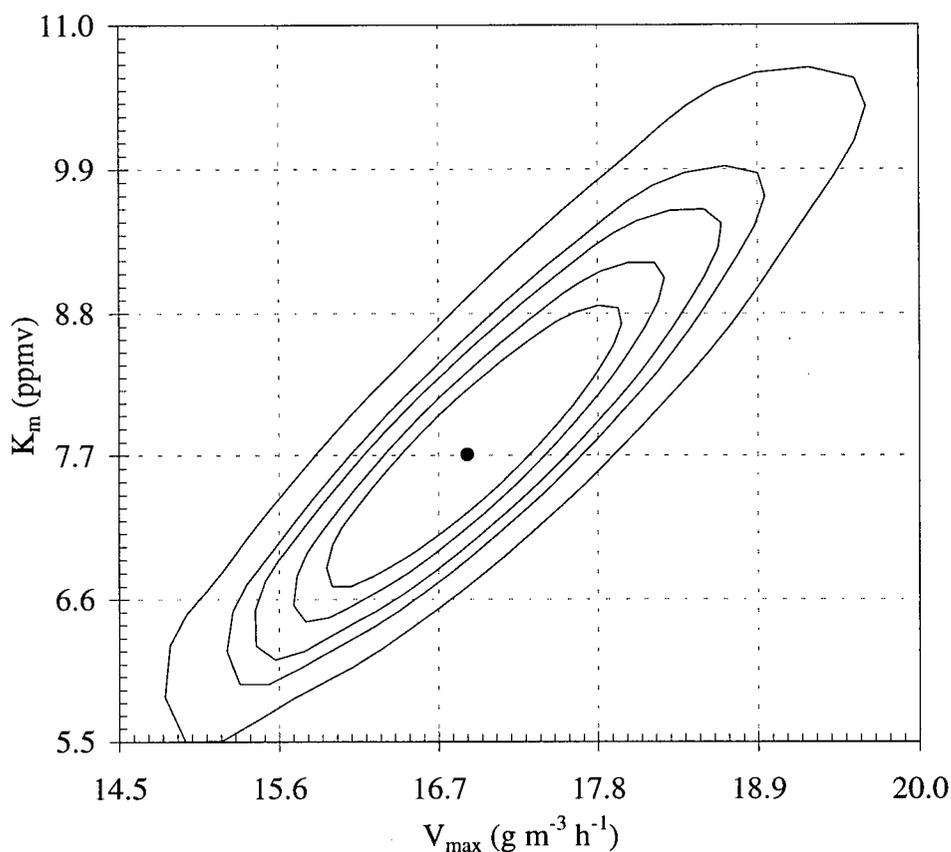
Figure 5.20. Simultaneous optimization of V_{max} and K_m
for dimethyl disulfide biodegradation in compost biofilter.
The best combination obtained is $V_{max} = 16.9$ g m^{-3} h^{-1} and
$K_m = 7.7$ ppmv

respectively were calculated employing the same methodology and are tabulated in Table 5.4 for comparison with those obtained when dimethyl disulfide was treated as the sole substrate. It is evident from Table 5.4 and Figure 5.19 that even though the K_m values for dimethyl disulfide degradation under the three operating situations nearly remained constant, the co-supply of hydrogen sulfide, and dimethyl sulfide caused a significant reduction in the V_{max} by 36 and 56%, respectively.

The removal efficiency for hydrogen sulfide as a co-substrate with dimethyl disulfide was very high and it was removed to such an extent that the amount in outlet gas stream was undetectable (Figure 5.21). Despite the fact that the inlet concentration of dimethyl sulfide in a mixture with dimethyl disulfide was very low (9 ppmv), its removal efficiency was incredibly low, between 25 and 30%
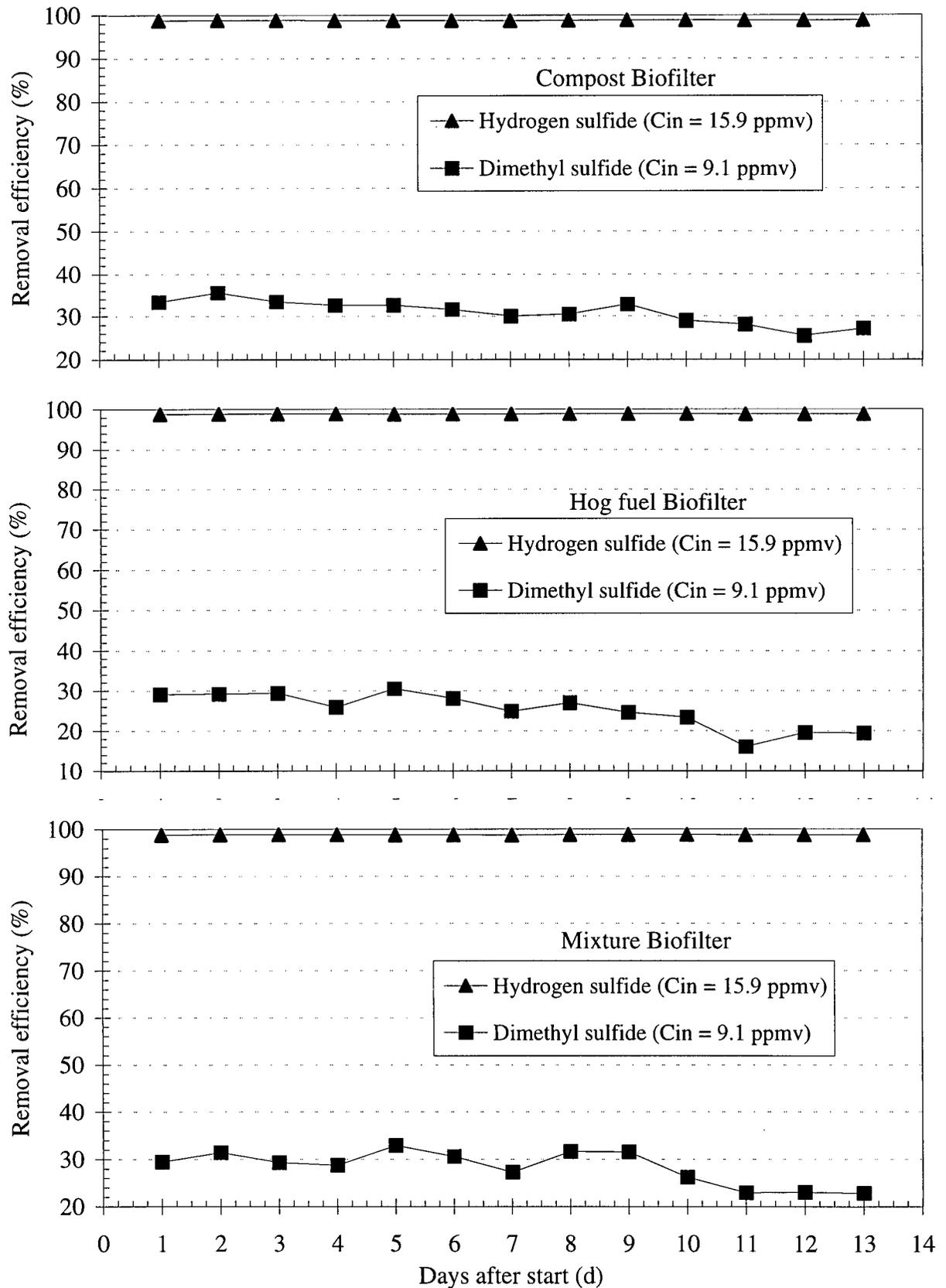
Figure 5.21. Bioelimination efficiency of hydrogen sulfide and dimethyl sulfide as co-substrates with dimethyl disulfide in biofilters

during the entire test. The dimethyl disulfide percent removal as a co-substrate with dimethyl disulfide was lower than that when treated in a mixture with hydrogen sulfide, because it has been reported that presence of hydrogen sulfide enhances the removability of dimethyl sulfide[31].

Table 5.4. Apparent kinetic parameters for dimethyl disulfide bioremoval in biofilters

| Filtering Media | Kinetic Parameter | Contaminant Feed Conditions | | | |
		DMDS only	DMDS + H$_2$S	DMDS + DMS	Mean ± SD
Compost	V$_{max}$	16.9	10.8	7.5	11.7 ± 4.8
	K$_m$	7.7	7.5	7.7	7.6 ± 0.2
Hog Fuel	V$_{max}$	12.3	8.4	6.1	8.9 ± 3.1
	K$_m$	5.0	6.2	6.5	5. 9 ± 0.8
Mixture	V$_{max}$	13.6	9.6	7.4	10.2 ± 3.1
	K$_m$	5.3	7.7	7.9	7.0 ± 1.4

Units: V$_{max}$ in g m^{-3} h^{-1}, and K$_m$ in ppmv. SD = Standard deviation

5.4.3.2. Dimethyl Disulfide Biodegradation in the Hog Fuel Biofilter

Biodegradation removal characteristics of dimethyl disulfide, when treated individually as well as in a mixture with hydrogen sulfide, and dimethyl sulfide, in the hog fuel biofilter are summarized in Figure 5.22. For all of the three experimental runs, the experimental and predicted values of EC, as a function of C$_{In}$, are in good agreement (R^2 > 0.94). The V$_{max}$ for dimethyl disulfide bioelimination, when treated singly, was estimated to be 12.3 g m^{-3} h^{-1} with a K$_m$ of 5 ppmv. The same methodology as described above for the compost biofilter was employed in the estimation of V$_{max}$ and K$_m$ values for dimethyl disulfide in the hog fuel biofilter. The maximum bioelimination capacities of the hog fuel biofilter for dimethyl disulfide in presence of the hydrogen sulfide, and dimethyl sulfide respectively, are given in Table 5.4. Contrary to the effects observed in the compost biofilter, K$_m$ for dimethyl disulfide biodegradation was considerably increased by 25-30% in the presence of hydrogen sulfide or dimethyl sulfide. As a result, the maximum elimination capacity, V$_{max}$, was significantly reduced by a factor of about 1.5 with the co-supply of hydrogen sulfide, and by 2 in the presence of dimethyl sulfide.

The bioremoval patterns for hydrogen sulfide, and dimethyl sulfide, as co-substrates with dimethyl disulfide, in hog fuel biofilter were similar to that of the compost biofilter with hydrogen sulfide

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removed completely to an undetectable level and dimethyl sulfide at a lower removal efficiency of 20-30% (Figure 5.21).

5.4.3.3. Dimethyl Disulfide Biodegradation in the Mixture Biofilter

In Figure 5.23 the bioelimination capacities of the mixture biofilter for dimethyl disulfide, for the three operational scenarios as described for the compost biofilter, are plotted against the logarithmic mean concentration of dimethyl disulfide. There is a good agreement between experimental and the predicted values with an $R^2 > 0.95$. The V_{max} for dimethyl disulfide (as a sole substrate) in the mixture biofilter was estimated to be 13.6 g m^{-3} h^{-1} with a K_m value of 5.3 ppmv. The maximum elimination capacities of the mixture biofilter for dimethyl disulfide biodegradation with a co-supply of hydrogen sulfide, and dimethyl sulfide were estimated by performing the simultaneous optimization of V_{max} and K_m using the experimental data of EC and C_{ln} obtained for these two experimental runs, and the values are summarized in Table 5.4. As in the hog fuel biofilter, the co-existence of either hydrogen sulfide or dimethyl sulfide caused an increase in the K_m values for dimethyl disulfide bioelimination in the mixture biofilter. Consequently, the maximum elimination capacity, V_{max}, dropped by factors of about 1.4 and 1.8 in presence of hydrogen sulfide, and dimethyl sulfide, respectively.

The elimination efficiencies for the co-substrates (hydrogen sulfide, and dimethyl sulfide) in the mixture biofilter were almost the same as those found in the hog fuel biofilter (Figure 5.21).

The maximum elimination capacities achieved for dimethyl disulfide biodegradation, as sole substrate, in the compost, hog fuel, and mixture biofilters were between 12.3 and 16.9 g m^{-3} h^{-1}. The elimination capacity values obtained in this study are, however, considerably higher than those reported in previous studies[8,11,15,30] which varied from 3.5 to 10 g m^{-3} h^{-1}, with an extreme low of 1 g m^{-3} h^{-1} reported by Smet et al.[17]. The differences in these elimination capacity values for dimethyl disulfide degradation may be a result of the different filter materials employed, the operating conditions selected, and/or the microorganisms involved. The three biofilter media materials used in our study significantly varied in their capacity to remove dimethyl disulfide, individually, with the compost biofilter achieving the highest V_{max} of 16.9 g m^{-3} h^{-1} as compared to 12.3 and 13.6 g m^{-3} h^{-1} in the hog fuel and mixture biofilters, respectively. The elimination rates were low in the hog fuel biofilter probably because of weak growth of dimethyl disulfide degrading
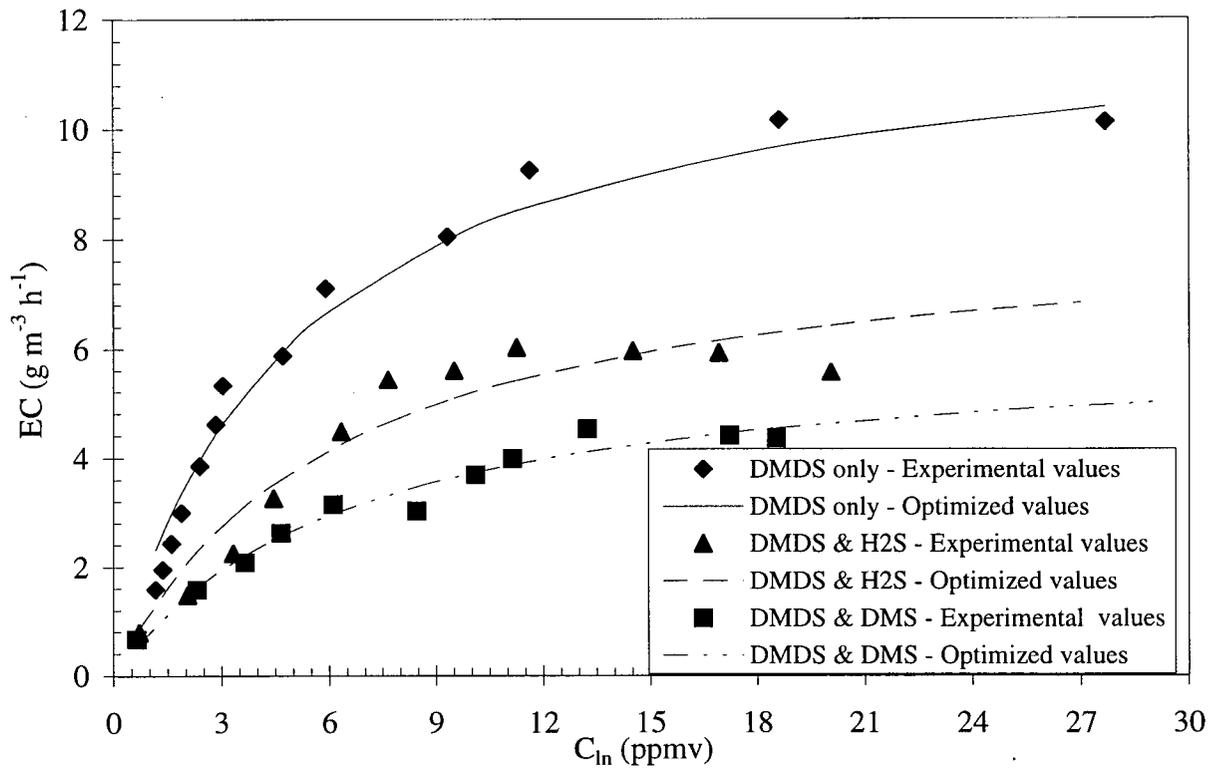
Figure 5.22. Dimethyl disulfide elimination capacity of hog fuel biofilter
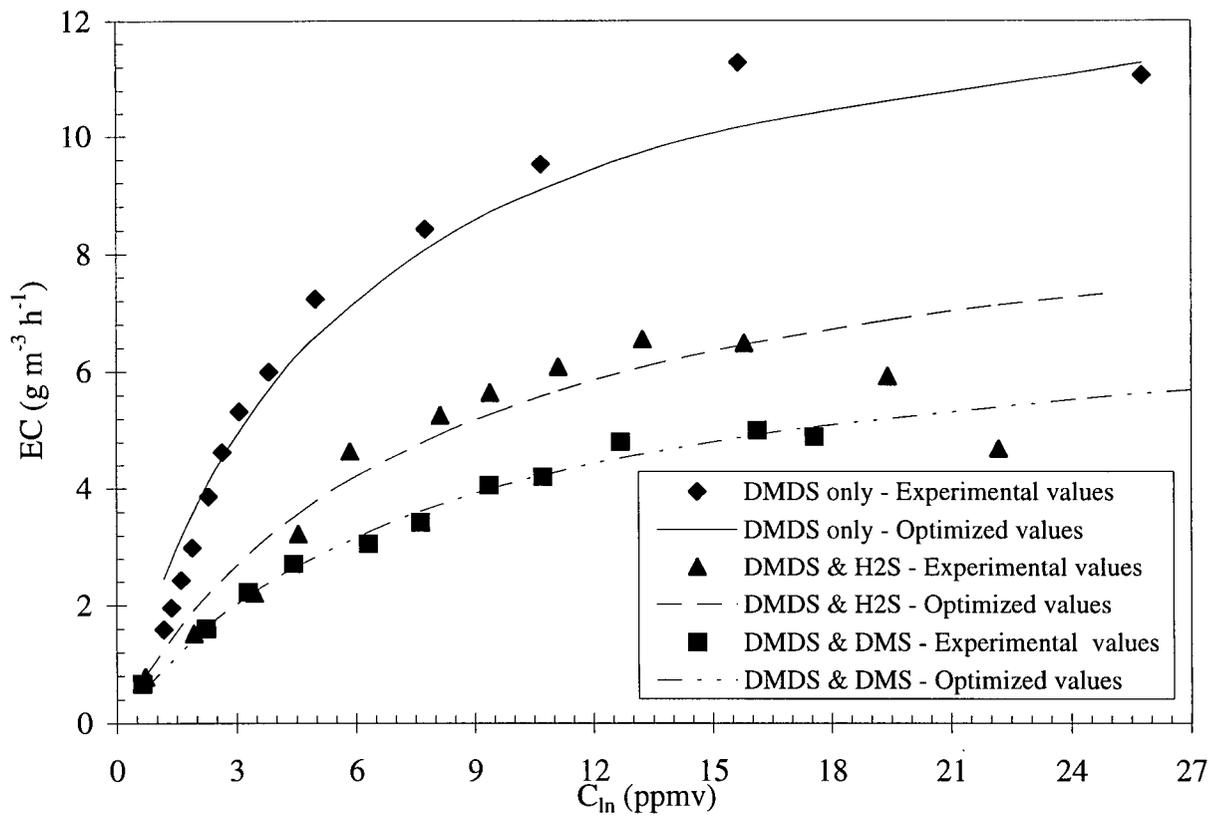
Figure 5.23. Dimethyl disulfide elimination capacity of mixture biofilter

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microorganisms, because all the three biofilters were initially inoculated with the same waste activated sludge and operated under identical loading conditions. These results acknowledge the earlier findings that the compost is a better carrier material than wood waste for the biofiltration control of methylated sulfur[17], because a compost biofilter achieved 100% removal efficiency up to an organic loading of 500 g m^{-3}d^{-1} while for a wood bark biofilter similar efficiencies were obtained only at organic loadings of less than 30 g m^{-3}d^{-1}. One of the possible reasons that wood waste/hog fuel seems to be an unfavorable habitat for the robust growth of microorganisms capable of degrading dimethyl disulfide could be its low nutrient content with a very high C/N ratio of 325 (dry basis) as compared to 27 for compost media.

The coexistence of hydrogen sulfide, and dimethyl sulfide caused a significant reduction in the V_{max} for dimethyl disulfide biodegradation in all of the three biofilters by 30-36% and 46-56%, respectively. The reduction in V_{max} was more pronounced in the compost biofilter than in the other two biofilters. The presence of either hydrogen sulfide or dimethyl sulfide, as a co-substrate with dimethyl disulfide, had more or less the same effects on the K_m value with no change in the compost biofilter and an increase in the hog fuel and the mixture biofilter. This strong inhibition happens when two or more contaminants with different biodegradability are degraded by the same population of microorganisms. Although, to our knowledge, there is no study dealing with the influence of other sulfur gases on the bioremoval of dimethyl disulfide, it may be worthwhile to compare these results with other studies on methyl mercaptan because methyl mercaptan is the primary metabolic byproduct in dimethyl disulfide biodegradation[25]. It has been reported that in peat biofilters the co-supply of hydrogen sulfide with methyl mercaptan resulted in a severe decrease (43-50%) in the V_{max} for methyl mercaptan biodegradation[31]. Those researchers have hypothesized that these co-existence effects are due to the relative ease in biodegradability of hydrogen sulfide and methyl mercaptan, coupled with the enzyme specificity of the resident microorganisms in biofilters for a particular sulfur gases.

The biodegradation patterns for the two co-substrates (hydrogen sulfide, and dimethyl sulfide) were similar in all of the three biofilters. Hydrogen sulfide was removed to an undetectable level and the removal efficiency for dimethyl sulfide ranged between 25 and 30%. Even though the dimethyl sulfide inlet concentration was low, it could not be effectively removed. Its removal efficiency was less than 30% when in association with dimethyl disulfide. This is because

dimethyl sulfide is very hard to biodegrade and it has been reported to be less degradable in comparison to other reduced sulfur gases[11,30,31].

5.4.4. Design Criteria for Biofilter Scale-Up

Contaminant removal to a desired outlet concentration can only be achieved for inlet loads less than some critical load for a particular filtering media at a fixed space velocity of the waste air stream through the biofilter column. Therefore, the inlet contaminant concentration plays an important role in the design of a biofilter, provided the packing materials and the operating conditions are constant. Any variation in the inlet concentration will result in a proportional change in the empty bed contact time or the space velocity of the waste air stream through the biofilter column. The maximum inlet concentration of each reduced sulfur gas that can be treated in order to attain a desired outlet concentration at a specific space velocity is calculated by using the estimated V_{max} and K_m given in Tables 5.2, 5.3 and 5.4 in equation 10. Figure 5.24 illustrates the relationship between the maximum allowable inlet concentration to achieve the desired outlet concentrations at different space velocities for hydrogen sulfide removal in compost, hog fuel and the mixture biofilter, respectively. It is clear from Figure 5.24 that as a higher space velocity (i.e., lower empty bed residence time) is utilized, a lower hydrogen sulfide inlet concentration can be treated in compliance with the desired outlet concentration. The maximum hydrogen sulfide inlet concentration of 596 and 692 ppmv (equivalent to maximum inlet loads of 82.9 and 96.2 g m^{-3} h^{-1}) will be allowed at a space velocity of 100 h^{-1} (equivalent to empty bed residence time of 36 s) in a compost biofilter if the hydrogen sulfide outlet concentrations were limited to 0.1 and 1 ppmv, respectively. However, under the same operating conditions (C_{out} = 1 ppmv and SV = 100 h^{-1}), a slightly lower hydrogen sulfide concentration of 673 and 651 ppmv would be allowed in the hog fuel and the mixture biofilters, respectively because of their higher saturation constants (Table 5.2).

Similar correlations between the maximum allowable inlet concentrations of dimethyl sulfide and dimethyl disulfide and the waste air space velocities through the biofilter columns are shown in Figures 5.25 and 5.26. It is clear as the inlet concentration increases the waste air space velocity decreases. A maximum dimethyl sulfide inlet concentration of 6.8, 5.2 and 5.9 ppmv (equivalent to maximum inlet loads of 1.7, 1.3 and 1.5 g m^{-3} h^{-1}) would be allowed in the compost, hog fuel and mixture biofilters respectively, at a space velocity of 100 h^{-1} (τ of 36 s) to
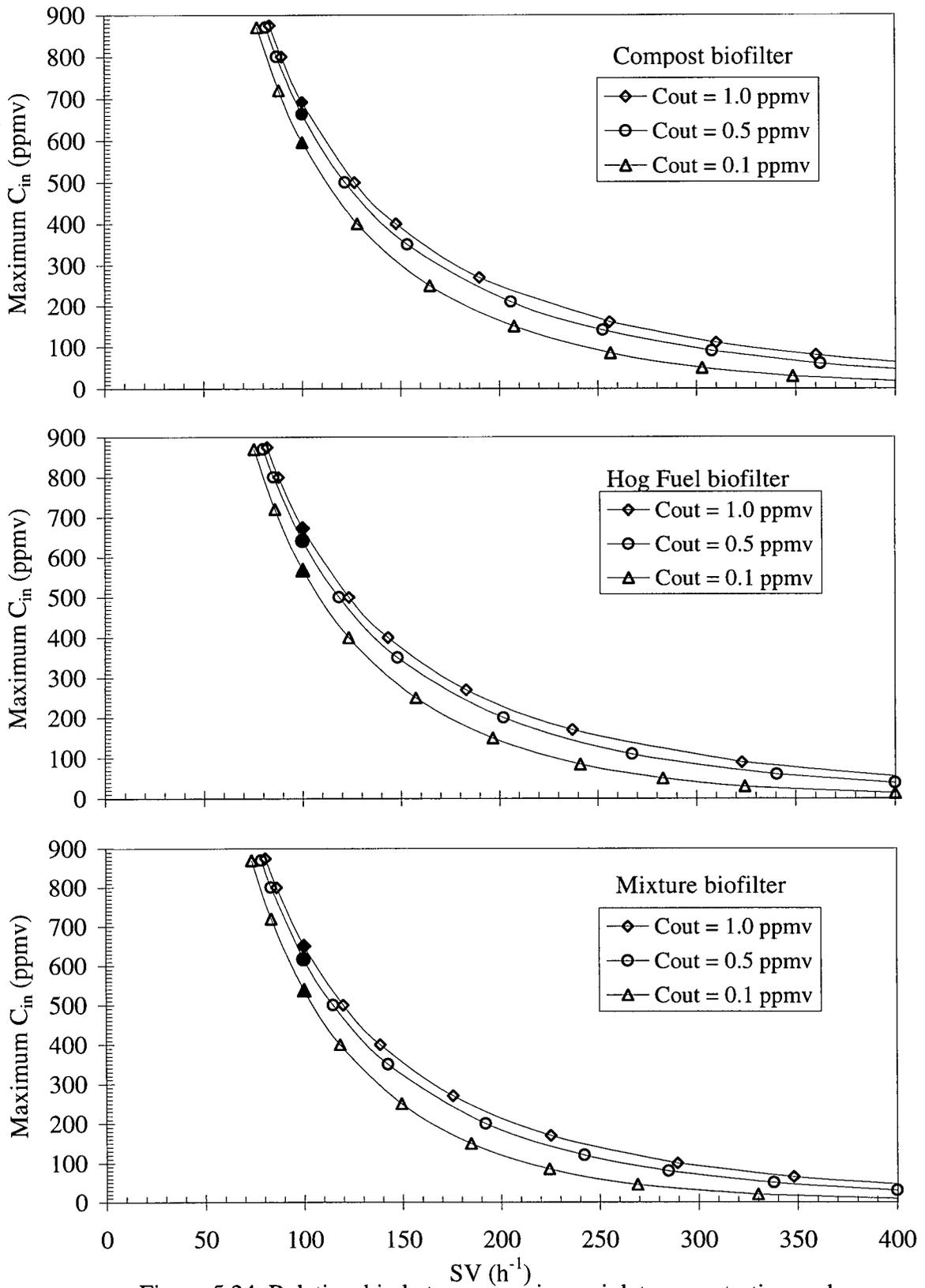
Figure 5.24. Relationship between maximum inlet concentration and
space velocity for hydrogen sulfide removal in biofilters.
(Solid symbols denote the SV of 100 h^{-1})

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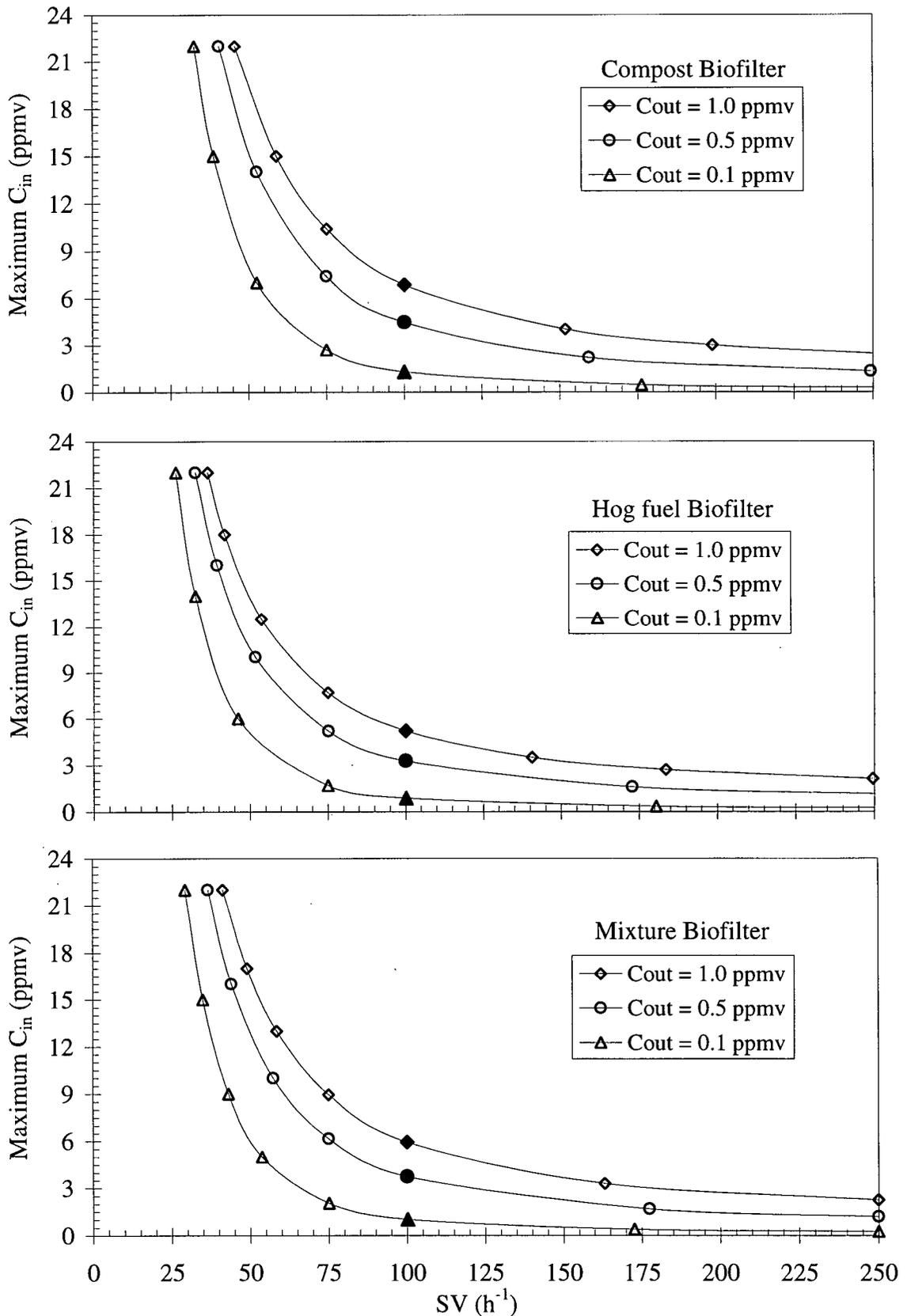
Figure 5.25. Relationship between maximum inlet concentration and space velocity for dimethyl sulfide removal in biofilters. (Solid symbols denote the SV of 100 h^{-1})
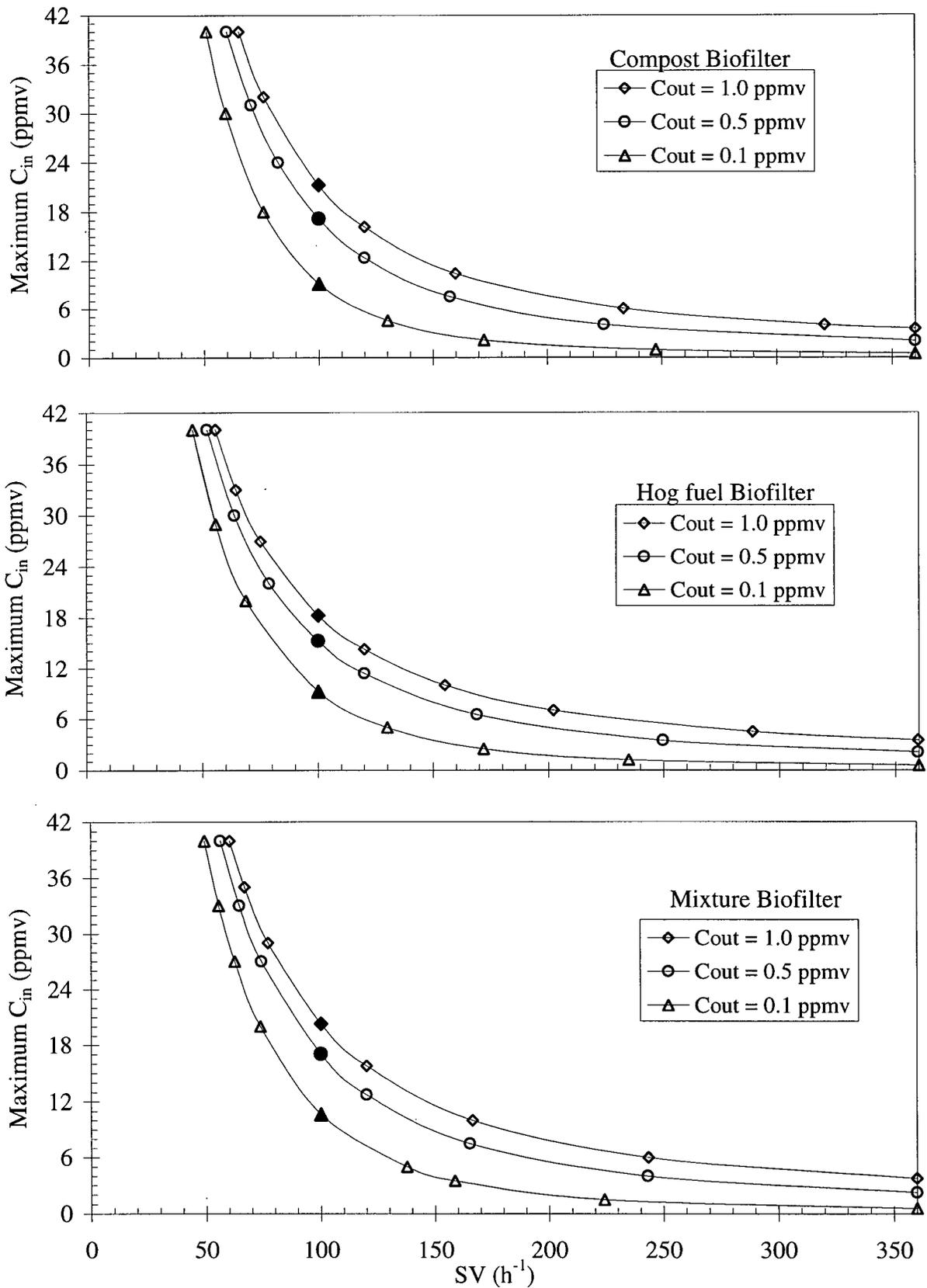
Figure 5.26. Relationship between maximum inlet concentration and space velocity for dimethyl disulfide removal in biofilters. (Solid symbols denote the SV of 100 h^{-1})

accomplish the desired outlet concentration of 1 ppmv. However, under the same operating conditions higher dimethyl disulfide concentrations of 21.3, 18.2 and 20.3 ppmv would be allowed in the compost, hog fuel and the mixture biofilters, respectively because of their higher elimination capacities for dimethyl disulfide as compared to dimethyl sulfide.

Similarly, in the presence of co-substrates the allowable maximum inlet concentration of dimethyl sulfide or dimethyl disulfide to achieve the same outlet concentration of 1 ppmv at a SV of 100 h^{-1} would be much lower because in the presence of co-substrates the V_{max} for dimethyl sulfide or dimethyl disulfide is significantly reduced (Table 5.3 and 5.4).

This implies that for treating a given inlet concentration of dimethyl sulfide or dimethyl disulfide in a mixture of reduced sulfur gases a lower space velocity (higher empty bed residence time) would be required than if each were treated alone. This is conceivable because as the gas contact time increases, more time is available for the removal of dimethyl sulfide/dimethyl disulfide once the inhibiting co-substrate(s) are removed in the upper sections of the biofilter columns. However, such is not the case with hydrogen sulfide because the coexistence of organo-sulfur gases had no noticeable effect on its removal levels in all the three biofilters.

Using the same scale-up methodology, Table 5.5 summaries the design specifications of a biofilter for the treatment of reduced sulfur gases from "Washer Hood Vent" stream of a typical pulp mill. Because of the easy degradability of hydrogen sulfide the footprint for the biofilter to treat waste gas stream of 37,500 m^3 h^{-1} containing 5 ppmv hydrogen sulfide is considerably low (119 and 129 m^2) as compared to one treating 15 ppmv of dimethyl sulfide (1601 to 1939 m^2) or 3 ppmv of dimethyl disulfide (438 to 403 m^2). However, these gases are emitted in a mixture that will further increase the size of biofilter as the co-existence of other reduced sulfur gases significantly decrease the removal rates of dimethyl sulfide and dimethyl disulfide in compost and hog fuel biofilters.

Table 5.5. Biofilter design example for washer hood vent of a typical pulp mill.

Design Parameters			Hydrogen Sulfide		Dimethyl Sulfide		Dimethyl Disulfide	
			Compost Biofilter	Hog fuel Biofilter	Compost Biofilter	Hog fuel Biofilter	Compost Biofilter	Hog fuel Biofilter
Gas Flow	$(m^3\ ton^{-1})$	=	3750	3750	3750	3750	3750	3750
Mill Capacity	$(ton\ d^{-1})$	=	240	240	240	240	240	240
C_{in}	(ppmv)	=	5	5	15	15	3	3
C_{out}	(ppbv)	=	4.7	4.7	1	1	5.6	5.6
K_m	(ppmv	=	43.9	47.9	7.2	6.5	7.7	5.0
V_{max}	$(g\ m^{-3}\ h^{-1})$	=	136.1	136.8	5.0	3.8	16.9	12.3
M	(g)	=	34	34	62	62	94	94
T	(° C)	=	25	25	25	25	25	25
Q	$(m^3\ h^{-1})$	=	37500	37500	37500	37500	37500	37500
C_{ln}	(ppmv)	=	0.72	0.72	1.56	1.56	0.48	0.48
β	$(g\ m^{-3})$	=	0.00139	0.00139	0.00254	0.00254	0.00384	0.00384
SV	(h^{-1})	=	314.8	290.3	23.4	19.3	85.6	93.0
V	$(m^3\ bed)$	=	119.1	129.2	1601.9	1939.3	438.3	403.3
H	(m)	=	1	1	1	1	1	1
A	(m^2)	=	**119.1**	**129.2**	**1601.9**	**1939.3**	**438.3**	**403.3**

Gas flow rate per ton of pulp produced is taken from Table A.2 (Appendix A), and the mill capacity is assumed as 10 tons per hour.

Inlet concentration of the pollutants is taken from Table A.2 and the outlet concentration from Table A.1 (Appendix A) as the odor threshold limit for each contaminant.

The values of V_{max} and K_m for the bioremoval of hydrogen sulfide, dimethyl sulfide and dimethyl disulfide in the two biofilter media are taken from Table 5.2, 5.3 and 5.4 (Chapter V).

The maximum biofilter bed height is limited to 1 meter to avoid excessive pressure loss and channeling due to compaction.

$C_{ln} = [(C_{in} - C_{out})/ln(C_{in}/C_{out})]$

$\beta = [(M*10^{-3})/\{22.4*(273+T)/273\}]$

$SV = [\{V_{max}/(\beta*(C_{in} - C_{out}))\}* \{C_{ln}/(K_m+C_{ln})\}]$

$V = [Q/SV]$

$A = [V/H]$

5.5. CONCLUSIONS

The current chapter has considered media effectiveness and bioelimination macrokinetics for hydrogen sulfide, dimethyl sulfide and dimethyl disulfide, singly as well in mixtures, utilizing three different biofilter media materials. The results are well described by a saturation kinetics model modified for plug flow behavior of biofilters, with the assumptions of steady state, negligible dispersion, and rapid contaminant transfer between phases. The maximum elimination capacities for hydrogen sulfide as the sole contaminant in a compost, hog fuel and a mixture biofilter were 136.1, 136.8 and 138.3 g m^{-3} h^{-1}, respectively. These results compare favorably with those obtained in previous studies[9] in which the maximum elimination capacity ranged from about 120 to 327 g m^{-3} h^{-1}. The maximum elimination capacity for dimethyl sulfide, when treated alone, in the three biofilter media materials used was between 3.8 and 5 g m^{-3} h^{-1}. The results are well in agreement with the previous studies[16,30,31] in which the maximum elimination capacity for dimethyl sulfide ranged from 3.2 to 5.5 g m^{-3} h^{-1} with an exceptional high of 28.3 g m^{-3} h^{-1} reported by Smet et al[17]. The maximum elimination capacities achieved for dimethyl disulfide biodegradation, as the sole substrate, in compost, hog fuel, and the mixture biofilters were between 12.3 and 16.9 g m^{-3} h^{-1}. The elimination capacity values obtained in this study are, however, considerably higher than those reported in previous studies[8,11,15,30] which varied from 3.5 to 10 g m^{-3} h^{-1}, with an extreme low of 1 g m^{-3} h^{-1} reported by Smet et al[17]. The differences in these elimination capacity values may be as a result of the different filter materials employed, the operating conditions selected, and the microorganisms involved.

Within the experimental error, the estimated maximum removal rates (Table 5.2) for hydrogen sulfide in all the three biofilters, under three different operating conditions, are comparable and do not vary significantly. However, the three biofilter media materials used in this study significantly varied in their capacity to remove dimethyl sulfide and dimethyl disulfide, with the compost biofilter achieving the highest V_{max} in comparison to hog fuel and the mixture biofilters. The elimination rates were low in the hog fuel biofilter probably because of the weak growth of microorganisms capable of degrading methyl sulfides on that material because all of the three biofilters were initially inoculated with the same waste activated sludge and operated under identical loading conditions. These results confirm the earlier findings that compost is a better carrier material than wood waste for the biofiltration control of methylated sulfur[17], because the compost biofilter achieved 100% removal efficiency up to an organic loading of 500 g $m^{-3}d^{-1}$ while

for wood bark biofilter similar efficiencies were obtained at the organic loadings less than 30 g m^{-3}d^{-1}. One of the main reasons for a wood waste/hog fuel filter material's being an unfavorable habitat for the robust growth of microorganisms capable of degrading methyl sulfides could be its low nutrient content with a very high C/N ratio of 325 (dry basis) as compared to 27 for the compost media.

The presence of dimethyl sulfide or dimethyl disulfide, as co-substrates, had no impact on the removal capacity of hydrogen sulfide, confirming the findings of previous studies[30,31] that because of its ease of biodegradation and the enzyme specificity of the resident microbial population, hydrogen sulfide bioelimination in biofilters is independent of the coexistence of organo-sulfur species. In general one can conclude that if there were any inhibitory effects of dimethyl sulfide and dimethyl disulfide, acting through a slight increase in the value of K_m, on the removal rate of hydrogen sulfide they were rather small.

In all of the three biofilters coexistence of hydrogen sulfide had no adverse effects on the bioelimination of dimethyl sulfide rather it slightly enhanced the biodegradation of dimethyl sulfide. However, the co-supply of methyl mercaptan and dimethyl disulfide caused a significant decrease (30-50%) in the rate of removal of dimethyl sulfide. Similar inhibitory effects were observed for dimethyl disulfide degradation with the co-supply of hydrogen sulfide and dimethyl sulfide causing a significant reduction by 30-56% in V_{max} with a slight increase in K_m. Given the magnitude of the changes in K_m observed in the presence of co-substrates for dimethyl sulfide and dimethyl disulfide degradation in biofilters, and considering all the data relevant to V_{max} in Tables 5.3 and 5.4 leads one to conclude that these co-substrates are inhibitory to dimethyl sulfide and/or dimethyl disulfide removal. From the variations in V_{max} (see Tables 5.3 and 5.4) the possible type inhibition seems to be noncompetitive, because the noncompetitive inhibitors are not substrate analogs and the net effect of this type of inhibition is a reduction in V_{max}. However, the noncompetitive inhibition model given by equation 9 could not be used to explain the kinetic relationship between the competing substrates as the K_m value also varied in all the tests. This highlights the necessity for improved definition of bioremoval kinetics of reduced sulfur gases in biofilters with special emphasis on competition kinetics of mixed contaminant biodegradation.

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CHAPTER VI

OVERALL CONCLUSIONS AND FUTURE CONSIDERATIONS

Investigation regarding the aerobic biodegradation of reduced sulfur gases - hydrogen sulfide, methyl mercaptan, dimethyl sulfide and dimethyl disulfide - in compost and hog fuel based biofilters are reported and discussed. Particular emphasis has been placed on the biofilter media mineralization and its operating life, transient response of biofilters to fluctuating contaminant loading, and biofilter media effectiveness in removing reduced sulfur gases from a waste air stream. The following overall conclusions can be made:

- Amongst the three biofilter media materials investigated, hog fuel was found to be harder to degrade thus having a longer useful life (2310 days) in biofilters as compared to compost (533 days) and the mixture of compost and hog fuel (1155 days).

- Media decomposition was significantly increased in the presence of reduced sulfur gas polluted air, as a result of increased bioactivity by sulfur-oxidizing bacteria and other microorganisms, thereby reducing the media half-life by more than 50%.

- Biofilters were found to adapt to new operating conditions rapidly, after step changes in contaminant concentration or waste airflow, with short recovery times of about 2-8 h in case of hydrogen sulfide and 8-12 h in case of methyl mercaptan and dimethyl disulfide degradation.

- Contaminant concentration spikes in the waste air stream demonstrated major substrate inhibition causing temporary deactivation of the process culture that occurred with short-term exposure of biofilters to hydrogen sulfide concentrations of 615 ppmv or methyl mercaptan concentrations of 158 ppmv. However, the removal efficiency gradually increased as the microorganisms adapted to these conditions and finally reached the initial level, prevalent before the concentration spike, within 1.5-5 h.

- Biofilters were found to be capable of withstanding downtime periods with rapid recovery to full performance when such starvation ceased. The re-acclimation time of about 5 days for biological activity after the longest starvation period of three months was much shorter than literature reported initial start-up periods of 10-12 days for hydrogen sulfide degradation. In the case of methyl mercaptan or dimethyl disulfide the re-acclimation time after the longest starvation period of one week was about a day, much shorter than the initial start-up times of 5-6 days. Extended periods of starvation resulted in longer re-acclimation periods, so does the idle phase as compared to no-contaminant-loading phase.

- The hydrogen sulfide elimination capacity of the three filter media materials was essentially the same at 136.1, 136.8 and 138.3 g m^{-3} h^{-1} in compost, hog fuel and the mixture biofilter respectively; and was not affected by the presence of either dimethyl sulfide or dimethyl disulfide as the co-substrates.

- Dimethyl sulfide biodegradation was not influenced by the presence of hydrogen sulfide in all the three biofilters, however, it was adversely affected by the co-supply of methyl mercaptan or dimethyl disulfide. Dimethyl sulfide elimination capacities in the compost, hog fuel and the mixture biofilter were reduced from 5, 3.8 and 4.6 g m^{-3} h^{-1} when treated singly to 3.0, 2.1 and 2.4 g m^{-3} h^{-1} in presence of methyl mercaptan; and to 3.5, 2.1 and 2.3 g m^{-3} h^{-1} in presence of dimethyl disulfide.

- The biofilter elimination capacity for dimethyl disulfide was significantly inhibited by the co-existence of hydrogen sulfide or dimethyl sulfide. The elimination capacities were reduced from 16.9, 12.3 and 13.6 g m^{-3} h^{-1} to 10.8, 8.4 and 9.6 g m^{-3} h^{-1} in presence of hydrogen sulfide and to 7.5, 6.1 and 7.4 g m^{-3} h^{-1} with the co-supply of dimethyl sulfide in the compost, hog fuel and the mixture biofilter, respectively.

Finally it can be concluded that hog fuel is the best amongst the three media materials tested, because of its longer useful life and similar performance to that of compost and the mixture biofilter under transient conditions in treating fluctuating contaminant loadings. The lower bio-elimination capacity for organo-sulfur species (that means a bigger foot print) as compared to the

other two media materials can be compensated by the longer operating life thereby reducing the operating costs.

The discussion of the observed differences in elimination capacities between the systems indicated the importance of the different physico-chemical properties such as water solubility, chemical bonding, etc. of these reduced sulfur gases and emphasized the intrinsic biological removal limitations that control the elimination capacities. The Michaelis-Menten type kinetic model used in this research work adequately described the bioelimination rates of reduced sulfur gases, however, the model tested for noncompetitive inhibition when applied to the removal of mixed pollutant experiments resulted in huge differences between the experimental observations and model predictions. These findings highlighted the areas for future consideration as follows:

- Microbiological analysis of the three media materials to address the intrinsic biological removal limitations and nutrient deficiency, if any, especially in hog fuel being low in nitrogen.

- Improved definition of the bioremoval kinetics of reduced sulfur gases in biofilters with special emphasis on competition kinetics of mixed contaminant biodegradation, and mass transfer effects between the phases.

This thesis reports various important features of the biofiltration of reduced sulfur gases from waste air streams, that hopefully will contribute to the better understanding of the principles and operation of biofiltration process for the control of odorous sulfur gases.

APPENDIX A

FORMATION AND CHARACTERISTICS OF KRAFT PULP MILL ODOROUS EMISSIONS

Hydrogen sulfide and methyl mercaptan are gases at ambient temperatures, whereas dimethyl sulfide and dimethyl disulfide are low boiling volatile liquids. Hydrogen sulfide and methyl mercaptan can dissociate in aqueous solutions, and the dissociation is pH dependent. Dimethyl sulfide and dimethyl disulfide do not ionize and their volatility is therefore independent of pH and is governed by the pure component vapor pressure, concentration in the solution and an activity coefficient. Table A.1 summarizes the physical characteristics of reduced sulfur gases.

$$H_2S \underset{}{\overset{k_1}{\rightleftharpoons}} HS^- + H^+ \underset{}{\overset{k_2}{\rightleftharpoons}} S^{2-} + 2H^+$$

$$CH_3SH \overset{k}{\rightleftharpoons} CH_3S^- + H^+$$
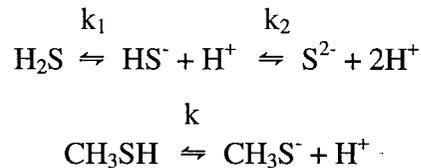
Hydrogen sulfide is formed by stepwise reactions, starting with the hydrolysis of sodium sulfide as follows:

$$Na_2S + H_2O \rightleftharpoons NaHS + NaOH$$

$$NaHS \rightleftharpoons Na^+ + HS^-$$

$$NaHS + H_2O \rightleftharpoons NaOH + H_2S$$
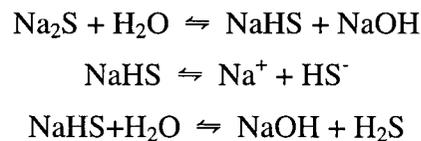
When the concentration of NaOH is high the pH will be high and the formation of NaHS is limited. However, as the cook proceeds, the pH drops and NaSH is produced. At pH 8 the formation of HS$^-$ predominates, but as the pH drops further gaseous hydrogen sulfide may be released. These hydrogen sulfide releases can be reduced up to 90% by maintaining the pH above 12 during the blow.

Methyl mercaptan is produced during the digestion process by a reaction of the hydrosulfide ion (HS$^-$) of the white liquor and the methoxyl groups of lignin (CH$_3$O-lignin) as follows:

$$HS^- + CH_3O\text{-lignin} \rightarrow CH_3SH + \text{lignin-}O^-$$
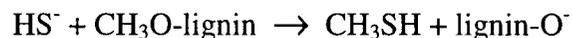
Methyl mercaptan is released at lower pH and its formation is completely dissociated at a pH above 12. The dissociated mercaptide (CH_3S^-) further reacts with the methoxyl lignin to form dimethyl sulfide.

$$CH_3S^- + CH_3O\text{-lignin} \rightarrow (CH_3)_2S + \text{lignin-}O^-$$

Table A.1. Physical characteristics of reduced sulfur gases.

Property	Hydrogen sulfide	Methyl mercaptan	Dimethyl sulfide	Dimethyl disulfide
Formula	H_2S	CH_3SH	$(CH_3)_2S$	$(CH_3)_2S_2$
Dissociation constant at 100 °C	$k_1 = 2.1 \times 10^{-7}$ [1] $k_2 < 1 \times 10^{-14}$ [1]	$k = 4.3 \times 10^{-11}$ [1]	Not dissociated	Not dissociated
Boiling point (° C)	-60.7 [2]	6.2 [2]	37.3 [2]	109.7 [2]
Vapor pressure (kPa)	1875 at 20 °C [3]	205 at 21.1 °C [3]	68.5 at 20 °C [3]	3.81 at 25 °C [3]
Vapor density (air = 1)	1.2 [3,4]	1.66 [3]	2.1 [3]	3.24 [3,4]
Lower explosive limit (% v/v)	4.0 [3,4] 4.3 [5]	3.9 [3,5]	2.2 [3] 2.25 [5]	1.1 [3]
Upper explosive limit (% v/v)	44.0 [3,4] 45.5 [5]	21.8 [3,5]	19.7 [3]	16.0 [3]
Solubility in water (g/L)	0.67 at 0 °C [2] 4.13 at 20 °C [4]	2.33 at 20 °C [4] 39 at 25 °C [6]	Insoluble [4] 17.1 at 20 °C [6]	Insoluble [4] 3.4 at 25 °C [6]
Odor threshold (ppbv)	130 [3] 0.029 – 900 [4] 0.5 – 10 [7]	2.1 [4] 0.02 – 40 [7]	0.99 – 20 [7]	0.78 – 3.6 [3] 1.3 [4] 0.026 – 0.09 [7]
Rat 4-h inhalation LC_{50} (ppmv)	444 [8]	675 [8]	250 [8]	805 [8]
Occupational 8-h exposure limit (ppmv)	10 [9]	0.5 [9]	-	-

The numbers in the square brackets represent the references.

In presence of oxygen methyl mercaptan undergoes oxidative coupling, and the product of the oxidative coupling of two molecules of methyl mercaptan is dimethyl disulfide. This reaction occurs in the black liquor oxidation stage of the recovery process.

$$4CH_3SH + O_2 \rightarrow 2(CH_3)_2S_2 + 2H_2O$$
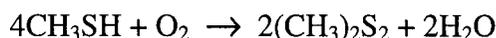
Overall the amounts of odorous materials released in the kraft pulping process is dependent up on the wood species used, pulping conditions employed, nature of subsequent processing, and the quantities of various streams. Table A.2. (adapted from Springer, 1993) summarizes the typical characteristics of waste air streams emitted from various pulping processes.

References:

1. Edde, H., *Environmental Control for Pulp and Paper Mills.* Noyes Publications, New Jersey. **1984**.

2. Weast, R.C. (Ed.) *CRC Handbook of Chemistry and Physics.* 68th ed., CRC Press, Boca Raton, Florida, **1987**.

3. CHEMINFO, *Database compiled by the Canadian Center for Occupational Health and Safety.* Issue 95-2, May **1995**.

4. CESARS (Chemical Evaluation Search and Retrieval System), *Database compiled by the Ontario Ministry of the Environment and the Michigan Department of Natural Resources.* Issue 95-2, May **1995**.

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6. Beckwith, W.F., Estimation of explosive limits of noncondensible gas mixtures. *Tappi J.* **1974;** 57, 147.

7. Ruth, J.H., Odor threshold and irritation levels of several chemical substances: A review. *Am. Ind. Hyg. Assoc. J.* **1986**; 47, 142-151.

8. Tansy, M.F., Kendall, F.M., Fantasia, J., Landin, W.E. and Oberly R., Acute and subchronic toxicity studies of rats exposed to vapors of methyl mercaptan and other reduced sulfur compounds. *J. Toxicol. Env. Hlth.* **1981**; 8, 71-88.

9. Guide to Occupational Exposure Values –1994. *Compiled by the American Conference of Governmental Industrial Hygienists.* Cincinnati, **1994.**

10. Springer, A.M., *Industrial Environmental Control: Pulp and Paper Industry.* Tappi Press, Atlanta. **1993**.

Table A.2. Typical gas characteristics and reduced sulfur concentrations from kraft pulp mill processes

Emission Source	Gas flow rate (m³/ton)	Temperature (°C)	Moisture content (%)	Hydrogen sulfide (ppmv)	Methyl mercaptan (ppmv)	Dimethyl sulfide (ppmv)	Dimethyl Disulfide (ppmv)
Batch Digester							
- Blow gases	3 - 6,000	65 - 100	30 - 99	0 - 1,000	0 - 10,000	100 - 45,000	10 - 10,000
- Relief gases	0.3 - 100	25 - 60	3 - 20	0 - 2,000	10 - 5,000	100 - 60,000	100 - 60,000
Continuous Digester	0.6 - 6	75 - 150	35 - 70	10 - 300	500 - 10,000	1,500 - 7,500	500 - 3,000
Washer Hood Vent	1,500 - 6,000	20 - 45	2 - 10	0 - 5	0 - 5	0 - 15	0 - 3
Washer Seal Tank	300 - 1,000	55 - 75	15 - 35	0 - 2	10 - 50	10 - 700	1 - 150
Evaporator Hotwell	0.3 - 12	80 - 145	50 - 90	600 - 9,000	300 - 3,000	500 - 5,000	500 - 6,000
Black Liquor Oxidation	500 - 1,500	70 - 80	30 - 40	0 - 10	0 - 25	10 - 500	2 - 95
Recovery Furnace	6,000 - 12,000	120 - 180	25 - 35	0 - 1,500	0 - 200	0 - 100	2 - 95
Smelt-dissolving Tank	500 - 1,000	70 - 110	35 - 45	0 - 75	0 - 2	0 - 4	0 - 3
Lime Kiln Exhaust	1,000 - 1,600	65 - 95	25 - 35	0 - 250	0 - 100	0 - 50	0 - 20
Lime Slaker Vent	12 - 30	65 - 75	20 - 25	0 - 20	0 - 1	0 - 1	0 - 1

APPENDIX B

METHODOLOGY FOR BIOFILTER MEDIA ANALYSIS

BULK DENSITY

Bulk density (ρ_b, g/mL) is the ratio of the mass of biofilter media to the bulk volume of the filter media. The bulk volume includes the volume of solids and the pore space. The biofilter material bulk density was determined by weighing a sample of known volume at field conditions.

PARTICLE DENSITY

Particle density (ρ_p, g/mL) of filtering material refers to the density of the solid particles collectively, and is a ratio of the total mass of the solid particles to their volume, excluding pore spaces between particles. Biofilter particle density was estimated using a "Pycnometer Method". After weighing the dry pycnometer, including the stopper, in air, about 50 g biofilter material was put inside the pycnometer. Pycnometer along with the media was again weighed, after cleaning the outside and neck of the pycnometer. The pycnometer was halfway filled with distilled water, while washing into the flask any material adhering to the inside of the neck. Entrapped air was removed by gentle boiling of the water for several minutes with frequent gentle agitations of the contents to prevent loss of biofilter material by foaming. After cooling the pycnometer and its contents to room temperature, enough distilled water was added so as to fill the pycnometer. Pycnometer was thoroughly cleaned after inserting the stopper and seating it carefully. The pycnometer along with the contents was again weighed and temperature of the contents noted. Finally the pycnometer was thoroughly washed after removing the biofilter media material. The pycnometer was filled with the distilled water at the same temperature as before, thoroughly dried after inserting the stopper and weighed along with the contents. The particle density was calculated as follows:

$$\rho_p = \left[\frac{\rho_w \cdot \{W_s \cdot (1 - M_c) - W_a\}}{\{W_s \cdot (1 - M_c) - W_a\} - \{W_{sw} - W_w\}} \right]$$

where, ρ_w is the density of water at observed temperature (g/mL); W_s is the weight of pycnometer plus media sample (g); M_c is the moisture content of biofilter material; W_a is the weight of pycnometer filled with air (g); W_{sw} is the weight of pycnometer filled with media and water (g); and W_w is the weight of pycnometer filled with water (g).

POROSITY

Biofilter media total porosity (S_t, %) was calculated from the bulk and particle densities of the media material. The ratio of the bulk density to particle density is the fraction of the total volume occupied by solids, and this value subtracted from unity and multiplied by 100 gives the percent volume occupied by pores, and was calculated by:

$$S_t = \left[1 - {\rho_b}\big/{\rho_p}\right] \cdot 100$$

MOISTURE CONTENT

Moisture content (M_c, %) of the biofilter materials was measured by gravimetric method as the weight loss on heating to 105 °C for 24 hours. Water content was obtained by dividing the difference between wet and dry sample masses by the mass of wet sample, multiplied by 100.

$$M = \left[\frac{(\text{weight of wet sample} + \text{tare}) - (\text{weight of dry sample} + \text{tare})}{(\text{weight of wet sample} + \text{tare}) - (\text{tare})}\right]$$

ORGANIC MATTER (LOSS ON IGNITION)

The biofilter organic matter content more specifically the percent ash content or loss on ignition (LOI %) was measured as the weight loss after heating a dry sample for 1 hour at 550 °C, and LOI was calculated as follows:

$$M = \left[\frac{\{(\text{weight of dry sample} + \text{tare})\text{before ignition}\} - \{(\text{weight of dry sample} + \text{tare})\text{after ignition}\}}{\{(\text{weight of dry sample} + \text{tare})\text{before ignition}\} - (\text{tare})}\right]$$

MEDIA pH$_w$

The pH values of the samples were determined with the use of a pH meter (Cole Parmer, USA). Samples were saturated with distilled water to bring the liquid to sample ratio equal to 10, and covered with parafilm paper to prevent equilibration with ambient carbon dioxide. Samples were thoroughly mixed for 10 minutes by rotary shaker. Samples were allowed to stand for about 10 minutes before measuring the pH. The measured pH was recorded as media pH in water or pH$_w$.

TOTAL CARBON

Total carbon (TC, %) content of the biofilter media materials was determined with the use of Shimadzu Total Organic Carbon Analyzer, Model TOC-5050, equipped with Solid Sample

Module, Model SSM-5000 (Shimadzu Corporation, Kyoto, Japan). The analytical equipment uses combustion method for the determination of total carbon at 900 °C furnace temperature. The carrier gas used is high purity oxygen, and the maximum sample weight used was 1 g (wet basis). Ceramic (alumina) sample boats are used to hold the weighed samples for introduction into the TC furnace. When the sample is introduced into the furnace, the total carbon component in the sample is combusted to carbon dioxide. The carrier gas along with the combustion products is then carried to a sample cell set in a non-dispersive infra-red (NDIR) gas analyzer where carbon dioxide is detected. The NDIR analyzer outputs a detection signal, which generates a peak whose area is calculated by a data processor. The peak area is proportional to the TC concentration of the sample and expressed as percent after comparing with the pre-developed internal calibration curve. Glucose (40% TC) was used as the standard sample for the making the calibration curve.

TOTAL NITROGEN

The biofilter media total nitrogen (TN, %) content was determined by using LECO FP-228 Nitrogen Determinator, Model 601-700 (Leco Corporation, Michigan USA). The weighed sample (150 mg nominal) was encapsulated in a tin capsule prior to analysis. The encapsulated sample was then placed into the FP-228 and combusted in resistence furnace in an oxygen rich environment at 950 °C. The products of combustion are carried through scrubbers to a thermal conductivity cell for nitrogen measurement. The final result is directly displayed as percent nitrogen after comparing with the internal calibration standard. The standard compound used for calibration was disodium ethylenediamine tetraacetate (EDTA) containing 9.57% total nitrogen.

PARTICLE SIZE DISTRIBUTION

The biofilter media particle size distribution was obtained by sieving the media sample manually. A series of 6 sieve plates with opening size of 4.76, 4.00, 2.83, 2.00, 1.40, and 0.85 mm were used.

References:

1. Klute, A., *Methods Of Soil Analysis: Physical And Mineralogical Methods*; American Society of Agronomy: Wisconsin, 1986; 2nd edition.
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DESIGN FEATURES OF HUMIDIFICATION AND BIOFILTER COLUMNS

Biofilter Columns

Humidification Column

Gas Diffuser System
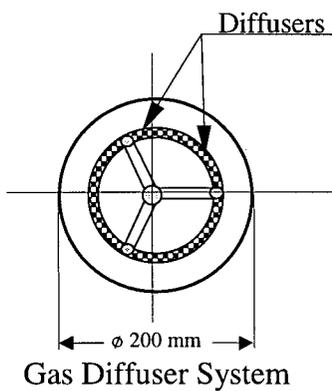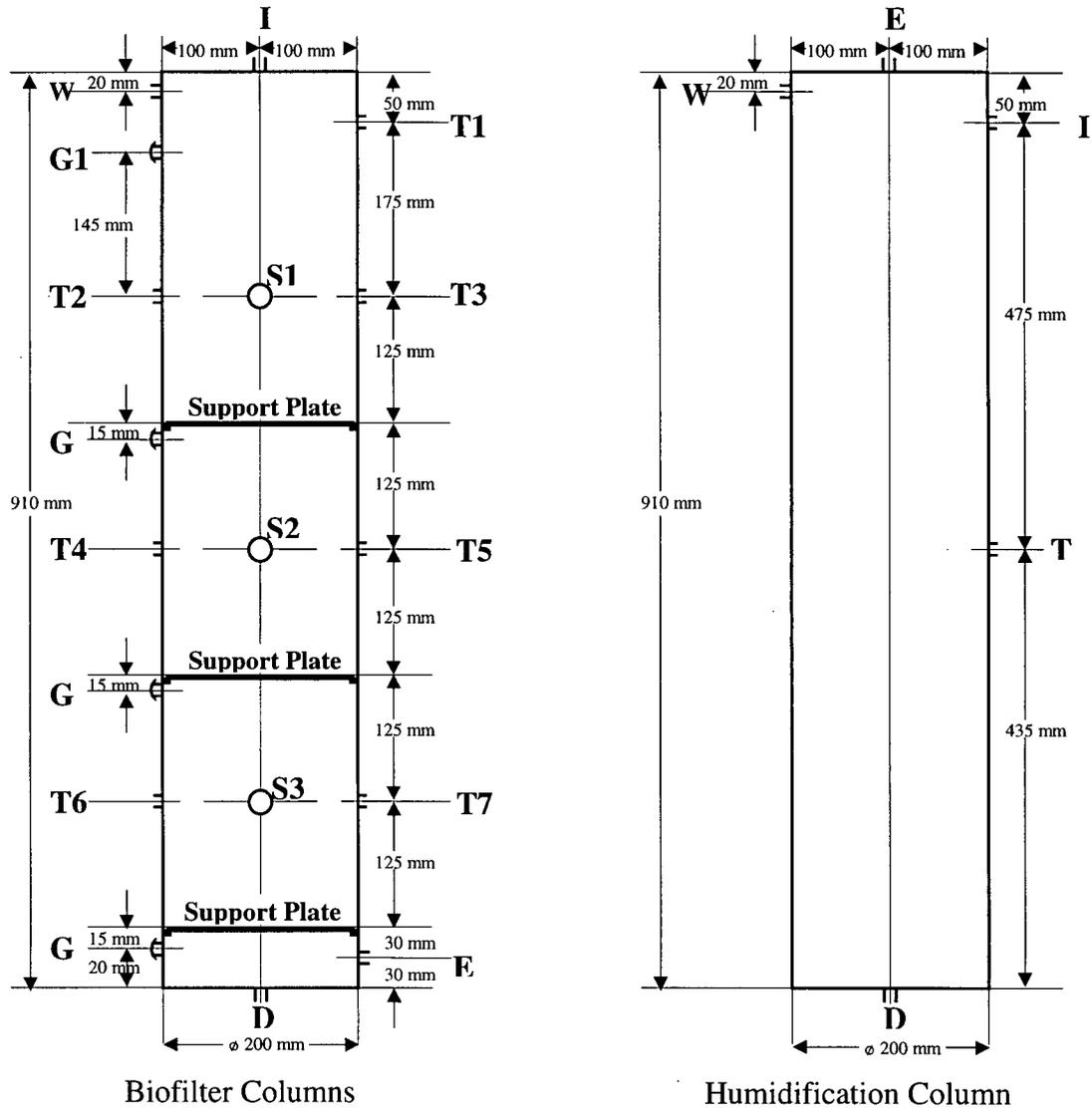
Fitting Specifications		
D	Drain	12 mm
E	Gas Outlet	12 mm
G1, G2, G3, G4	Gas Sampling Ports	12 mm
I	Gas Inlet	12 mm
S1, S2, S3	Media Sampling Ports	25 mm
T1, T2, T3, T4	Thermocouple	12 mm
T5, T6, T7	Thermocouple	12 mm
W	Water Inlet	12 mm

Figure C.1. Design specifications of humidification and biofilter columns

APPENDIX D

SAFETY FEATURES OF EXPERIMENTAL SETUP

The entire experimental unit was housed in a fully enclosed fume hood. For detecting any TRS leaks the experimental set-up was equipped with a "TRS sensing and fail-safe shutdown system". The system was designed for any possible TRS buildup in the fume hood either due to a power failure that would shut down the exhaust fan, thus ceasing the air changes in the hood or due to mechanical failure of the exhaust fan and/or leaks in the biofiltration system itself. Under both conditions the solenoid valves regulated by the TRS gas sensor/controller halt the TRS gas supply from the gas cylinders. In the first case (i.e., power failure) the entire system along with the exhaust fan shuts down, because the solenoid valves are normally closed and open only when energized. In the later case e.g., the mechanical failure of the exhaust fan or leaks from the biofiltration system resulting in buildup of TRS concentrations in the fume hood, the TRS gas sensor installed inside the fume hood senses the TRS concentrations and sends the signal to TRS controller/monitor.

There are two levels of signals: "warning" signal at 5 ppmv and "alarm" with shut down of the solenoid valve at 10 ppmv. The TRS monitor displays the TRS concentration on its LCD. If the concentration equals or exceeds 10 ppm the TRS controller stops the TRS gas supply by closing the solenoid valves, initiates the audio alarm and the "red light bulbs", installed at the top of fume hood and on the doors in the hall way, until concentration drops below 10 ppm.

Figure D.1 shows the schematics of experimental set-up layout and the leak detection and shut down safety system.
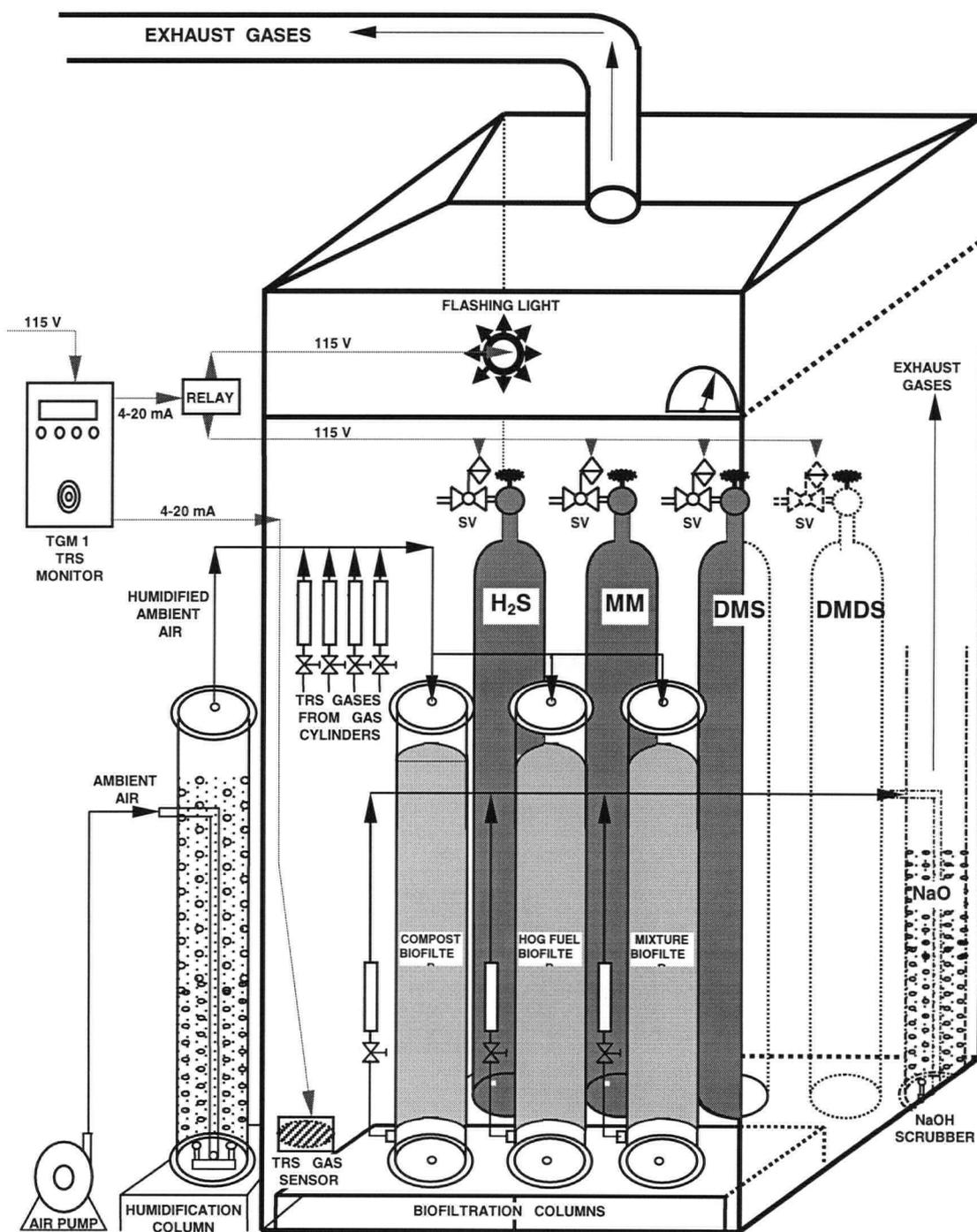
Figure D.1. Experimental set-up layout and safety instruments

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APPENDIX E

## GAS CHROMATOGRAPH CALIBRATION CURVES
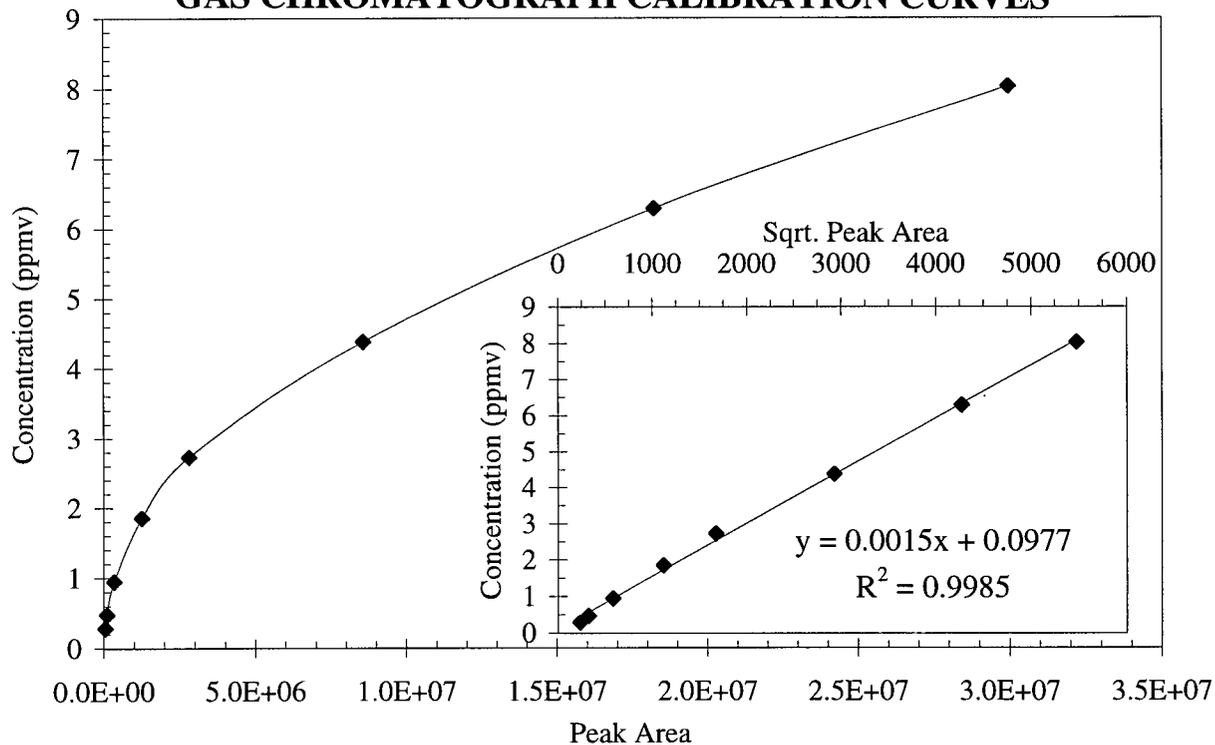
Figure E.1. Calibration curve for hydrogen sulfide
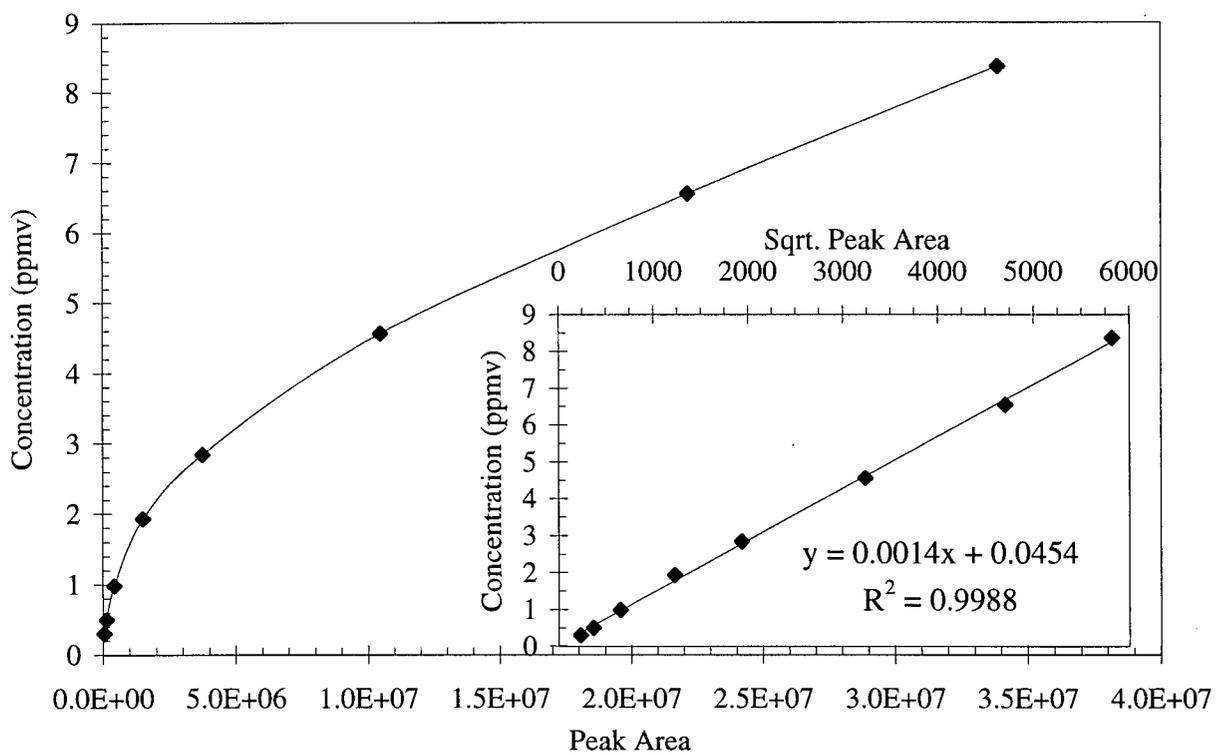

Figure E.2. Calibration curve for methyl mercaptan
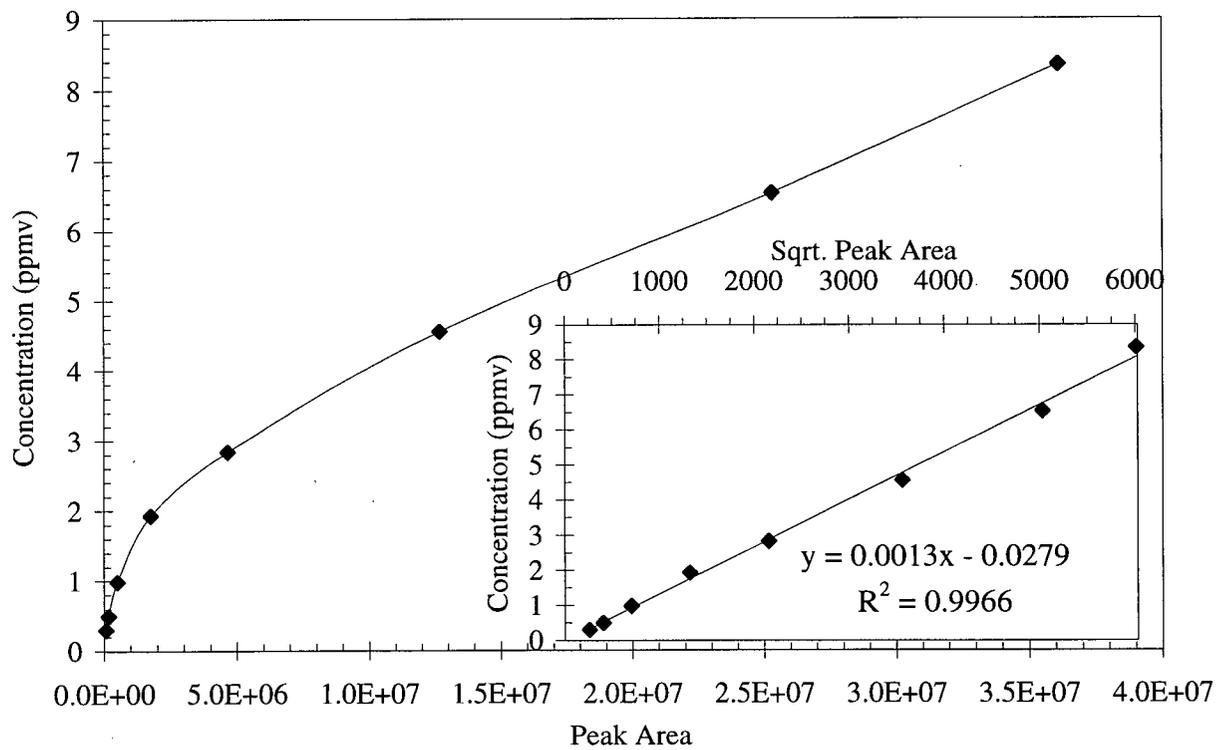
Figure E.3. Calibration curve for dimethyl sulfide
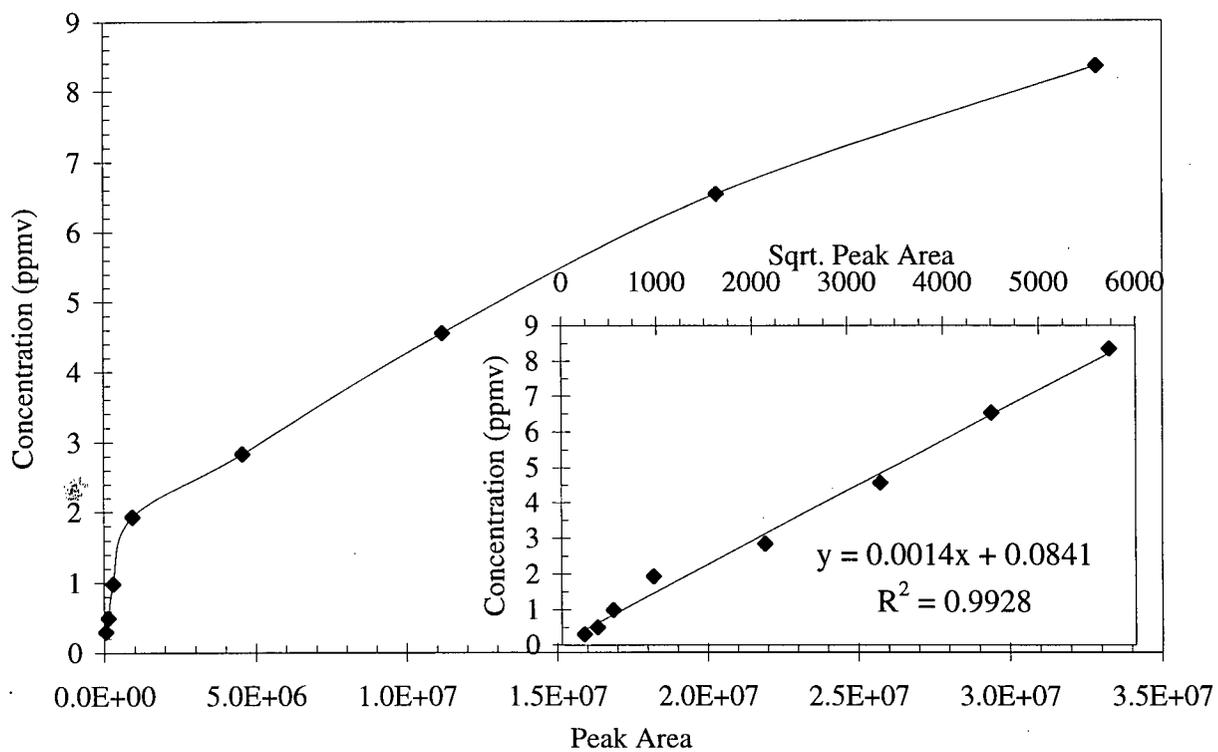
Figure E.4. Calibration curve for dimethyl disulfide

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