BIOFILTRATION OF BTEX WASTE GASES

by

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To my parents

Lebt' nicht in uns des Gottes eigne Kraft,
Wie könnt uns Göttliches entzücken? Goethe

As kind
het hulle my vertel
as jy
stip na die son kyk
word jy blind.

Blind?
Op 'n manier,
miskien –
maar die son self
laat die son sien.

(IL de Villiers, Gelykenisse en ander verse, Tafelberg)

Declaration

The experimental work described in this thesis was carried out in the Department of Microbiology and Biochemistry, University of the Free State, Bloemfontein, from January 1997 to November 1999 and in the School for Environmental Sciences and Development: Microbiology, Potchefstroom University for Christian Higher Education, Potchefstroom from January 2000 to November 2003. The study was conducted under the supervision and co-supervision of Dr. Chris A. du Plessis and Prof. Karl-Heinz J. Riedel.

These studies represent original work undertaken by the author and has not been otherwise been submitted in any form for any degree or diploma to any other university. Where use has been made of the work of others it is duly acknowledged in the text.

Johannes M. Strauss - B.Sc (Hons)

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Language and style used in this dissertation are in accordance with the requirements of the journal of Applied Microbiology and Biotechnology

This dissertation represents a compilation of manuscripts, where each chapter is an individual entity and some repetition between chapters has, therefore, been unavoidable.

Summary

A comparison of biofilter performance under different temperature conditions is of particular importance for the application and commercialization of biofiltration technology due to the fact that many waste gas streams are at elevated temperatures. The efficacy of higher temperature biofiltration reactors, therefore, has important practical and cost implications as it directly impacts on the need and cost for gas cooling prior to biofiltration treatment. In this study the performance of toluene degrading mesophilic (25°C) and thermophilic (50°C) composted pine bark biofilters were evaluated. The effect of oxygen concentrations on reactor performance was also evaluated, and comparisons made for both temperature conditions. Toluene, as part of the benzene, toluene, ethylbenzene and xylene (BTEX) group, are important solvents and constitutes a large percentage of petroleum. These compounds, mainly due to their solubility as well as being confirmed or suspected carcinogens, have been classified as environmental priority pollutants by the US Environmental Protection Agency with increasingly stringent regulations to avoid their release.

Investigations were performed at loading rates ranging from 9 to 54 g m^{-3} h^{-1}, retention times of 0.25 to 3.9 minutes, and at various bed heights. Comparison of the performance using empirical models indicated that higher removal efficiencies could be obtained under thermophilic conditions, although a slightly longer retention time was required to obtain the same efficiency. Under thermophilic conditions toluene removal efficiencies exceeding 90% were obtained when the reactor was subjected to retention times in excess of 0.6 minutes (36 seconds) and loading rates below 54 g m^{-3} h^{-1}. Under mesophilic conditions similar efficiencies could be obtained with a retention time of 0.32 minutes (19 seconds) and loading rates below 42 g m^{-3} h^{-1}. The influence of oxygen at a single loading rate and retention time indicated reduced performance at oxygen concentrations below 5% for both operating temperatures. A previously developed diffusion reaction model was further applied to this comprehensive dataset and through a process of subset model parameter optimization and parameter sensitivity analyses, both reactor condition performances were simulated with a high degree of accuracy at steady state conditions. Simulated

results further emphasized that higher elimination rates of toluene could be obtained at thermophilic temperatures.

BTEX substrate interactions, using this toluene-acclimatized biofilter consortium, were further investigated at a single loading rate of 18 g m^{-3} h^{-1} and retention times ranging from 0.5 to 3 minutes. The mesophilic results obtained were modelled using Michaelis-Menten kinetics and an explicit finite difference scheme to generate V_m and K_m parameters, of which the ratio can be used as an indication of the catalytic efficiency in order to quantify substrate interactions occurring within the biofilter. Toluene was found to enhance the catalytic efficiency for *p*-xylene, while catabolism of all other compounds was inhibited competitively by the presence of toluene. All BTEX compounds could be degraded by the microbial consortium even in the absence of toluene. The catalytic efficiency of the reactor for the compounds was in the order: ethylbenzene > benzene > *o*-xylene > *m*-xylene > *p*-xylene. The catalytic efficiency of the microbial consortium for toluene was reduced by the presence of all other BTEX compounds, with the greatest inhibitory effect caused by the presence of benzene, while *o*-xylene and *p*-xylene caused the least inhibitory effect.

This BTEX substrate interaction study was further extended to include the thermophilic conditions at a similar loading to that of the mesophilic study, in order to compare results from both temperature conditions. Overall toluene degradation rates under mesophilic conditions were found to be superior to degradation rates of individual BEX compounds. With the exception of *p*-xylene, higher removal efficiencies were achieved for individual BEX compounds compared to toluene under thermophilic conditions. Overall BEX compound degradation under mesophilic conditions was ranked as ethylbenzene > benzene > *o*-xylene > *m*-xylene > *p*-xylene. Under thermophilic conditions overall BEX compound degradation was ranked as benzene > *o*-xylene > ethylbenzene > *m*-xylene > *p*-xylene. With the exception of *o*-xylene, the presence of toluene in paired mixtures with BEX compounds resulted in enhanced removal efficiencies of BEX compounds, both under mesophilic and thermophilic conditions. A substrate interaction index was calculated to compare removal efficiencies at a retention time of 0.83 minutes (50 seconds). A reduction in toluene removal efficiency (negative interaction) in the presence of individual BEX compounds was observed under mesophilic conditions, while enhanced toluene

removal efficiency was achieved in the presence of other BEX compounds, with the exception of *p*-xylene under thermophilic conditions.

This study illustrated the potential of biofiltration as an emerging technology, especially at elevated temperatures, but emphasized the complexity of interactions that might occur between individual compounds that could influence the performance of the reactors when treating mixed pollutant gas streams.

Opsomming

'n Vergelyking in biofiltrasie verwydering by verskillende temperature is van besondere belang tydens die toepassing en kommersialisering van biofiltrasie tegnologie. Biofiltrasie, wat aansienlike praktiese en koste implikasies het, kan verder verrykende toepassings hê sou hierdie tegnologie suksesvol toegepas kon word op afval gas stome wat vrygestel word by verhoogde temperature. Die verrigting vir 'n tolueen degraderende mesofiele (25°C) en termofiele (50°C) gekomposteerde dennebas biofilter, asook die effek wat suurstof konsentrasies op reaktor effektiwiteit by verskillende temperatuur kondisies het, word geevalueer. Tolueen, wat deel is van die benseen, tolueen, etielbenseen en xyleen (BTEX) groep, is belangrike oplosmiddels en beslaan 'n groot persentasie van petroleum. Hierdie stowwe, meestal as gevolg van hulle oplosbaarheid, is deur die Amerikaanse Omgewings Beskermings Agentskap as prioriteit besoedel stowwe verklaar, en is ook of bevestigde of moontlike karsinogene.

Ondersoek is gedoen by verskillende lading hoeveelhede tussen 9 tot 54 g m^{-3} h^{-1}, retensie tye tussen 0.25 tot 3.9 minute, asook verskillende bed hoogtes. Vergelyking in die verrigting, deur gebruik te maak van empiriese modelle, het aangedui dat hoër verwydering verkry kon word tydens termofiliese kondisies, maar dat 'n langer retensie tyd tipies benodig word om dieselfde hoeveelheid verwydering te kan verkry. Tydens termofiele kondisies is 'n verwydering van meer as 90% verkry met 'n retensie tyd van langer as 0.6 minute (36 sekondes) en 'n lading snelheid van laer as 54 g m^{-3} h^{-1}. Vir mesofiele kondisies kon dieselfde verwyding verkry word met 'n retensie tyd van 0.32 minute (19 sekondes) en lading hoeveelhede van minder as 42 g m^{-3} h^{-1}. Die effek wat suurstof by 'n enkele lading en retensietyd by beide temperatuur kondisies gehad het, het aangedui dat verlaagde verwydering verkry word wanneer die konsentrasie laer as 5% daal. 'n Voorheen ontwikkelde diffusie reaksie model is verder toegepas op hierdie volledige reeks data en deur 'n proses van model optimisering en parameter sensitiwiteit analieses, is die verrigting gesimuleer tydens reelmatige stand kondisies met 'n hoë mate van akkuraatheid. Gesimuleerde resultate het verder gestaaf dat hoër verwydering snelhede vir tolueen verkry kon word tydens termofiele kondisies.

BTEX substraat interaksies vir hierdie toluene-geakklimatiseerde biofilter konsortium is verder ondersoek by 'n enkele lading snelheid van 18 g m^{-3} h^{-1} en retensie tye tussen 0.5 tot 3 minute. Die mesofiele resultate verkry is gemodelleer deur gebruik te maak van Michaelis-Menten kinetika en eksplisiete beperkte verskil skemas om V_m en K_m parameters te genereer, waarvan die verhouding gebruik kan word as 'n aanduiding van die katalitiese effektiwiteit en die kwantifisering van die substraat interaksies wat plaasvind binne die biofilter. Daar is bevind dat toluene die katalitiese effektiwiteit van *p*-xyleen verhoog, terwyl katabolisme van al die ander verbindings kompeterend geïnhibeer word deur die teenwoordigheid van tolueen. Al die BTEX verbindings kon wel gedegradeer word deur hierdie mikrobiese konsortium selfs wanneer tolueen afwesig was. Die reaktor se katalitiese effektiwiteit vir die verbindings is gevind om in die orde: etielbenseen > benseen > *o*-xyleen > *m*-xyleen > *p*-xyleen te wees. Die katalitiese effektiwiteit vir tolueen is verlaag met die teenwoordigheid van die ander BTEX verbindings, met die grootste invloed veroorsaak deur die teenwoordigheid van benseen, terwyl *o*-xyleen en *p*-xyleen die minste effek gehad het.

Hierdie BTEX substraat interaksie studie is verder uitgebrei ten einde termofiele kondisies in te sluit by dieselfde ladings snelheid, en om dus 'n vergelyking te kon tref tussen die resultate. Daar is bevind dat toluene degradasie snelhede tydens mesofiele kondisies beter is as degradasie snelhede vir individuele BEX verbindings. Met die uitsondering van *p*-xyleen, kon hoër verwydering verkry word vir individuele BEX verbindings vergeleke met toluene tydens termofiele kondisies. Met alles in ag geneem is bevind dat BEX verbinding degradasie tydens mesofiele kondisies in die volgorde etielbenseen > benseen > *o*-xyleen > *m*-xyleen > *p*-xyleen plaasvind, terwyl vir termofiliese kondisies die volgorde benseen > *o*-xyleen > etielbenseen > *m*-xyleen > *p*-xyleen was. Met die uitsondering van *o*-xyleen, is verhoogde BEX verbinding verwydering tydens beide kondisies verkry wanneer toluene teenwoordig was met gepaarde BEX verbindings. 'n Substraat interaksie indeks is ook bepaal om die effektiwiteit by 'n bepaalde retensie tyd van 0.83 minute (50 sekondes) te vergelyk. 'n Verlaging in tolueen verwyderings effektiwiteit (negatiewe interaksie) in die teenwoordigheid van individuele BEX verbindings is waargeneem, terwyl verhoogde toluene verwyderings effektiwiteit verkry is in die teenwoordigheid van ander BEX verbindings, met die uitsondering van *p*-xyleen tydens termofiele kondisies.

Die studie het die potensiaal vir biofiltrasie as 'n groeiende tegnologie uitgewys, veral by verhoogde temperature. Die kompleksiteit van die interaksies wat mag voorkom tussen individuele verbindings en wat die effektiwiteit van die reaktore kan beïnvloed tydens die behandeling van gemengde verbinding gas strome, is verder beklemtoon.

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1. General introduction

In recent times, remediation issues have become increasingly important. This is mainly due to a number of factors that include increased public and environmental awareness of pollution hazards, increasingly stringent legislation and penalties, workplace safety concerns, and trade agreements that require companies to ensure certain minimum environmental standards in order to be able to trade in certain regions of the world. These factors have forced technologists to examine the neglected possibilities for efficient and economic waste treatment.

During the last few decades, biotreatment processes have found increasingly widespread application for the treatment of wastewater, and more recently, the treatment of waste gas streams. Biological waste gas treatment techniques has been established as a reliable, cost-effective technology for controlling low-concentrations of biodegradable waste gases originating from a wide range of industries and public sectors (Leson and Winer 1991, Swanson and Loehr 1997, Wani et al. 1997, Ergas and Kinney 2000). In comparison with traditional and chemical technologies, biological methods have many advantages. These include negligible energy consumption, low investment and operating costs and the absence of environmental nuisances such as the transfer of pollutants to another phase or the subsequent release of hazardous or toxic wastes. The most common form of biological waste gas treatment systems are biofilters. In biofiltration the waste gas to be treated is forced through a support media bed onto which microorganisms are attached as a biofilm. The constituents of the waste gas transfers from the air phase to the liquid phase (includes water and biofilm) and biodegraded to innocuous compounds. It is believed that gas mass transfer limitations inherent in liquid phase bioreactors are significantly decreased in gas phase bioreactors, thereby increasing conversion rate. Rapid and complete biodegradation can be accomplished whilst an optimal microbial growth environment is maintained inside the biofilter. The underlying mechanisms which allow biofilters to work are, however, complex.

Benzene, toluene, ethylbenzene and xylene (BTEX) are important industrial solvents and constitute a large percentage of petroleum. A large amount of these compounds are released into the atmosphere or are encountered in soil and groundwater sites resulting from industrial activities related to refining, transportation, use, and disposal of petroleum products (Cozzarelli et al. 1990). These compounds are of considerable concern mainly due to their solubility relative to other petroleum hydrocarbons and are transported with groundwater in a downwards gradient from contaminated sources. These compounds have also been classified as environmental priority pollutants by the US EPA (1977), and are either confirmed or suspected carcinogens (Dean 1985).

Developing bioreactor technologies through comprehensive research in an aim to elucidate, quantify and optimise the interacting processes to efficiently degrade BTEX compounds have, therefore, been of interest.

1.1. Scope and structure of thesis

Chapter 2 provides background information regarding biological waste gas treatment systems, placing emphasis on the microbiological and operational parameters that govern the behaviour and optimal performances of these systems. In order to further contribute to a better understanding of the biofiltration process, the biodegradation of toluene and BTEX compounds both at mesophilic (25°C) and thermophilic* (50°C) temperatures were studied in a toluene acclimatised biofilter system. The research involved the following:

- Development of empirical models (Chapters 3 and 5) to describe the reactor performances in terms of loading rate, retention time and bed height. The influence of oxygen on removal efficiency was also evaluated. The research enabled the comparison of results obtained for mesophilic and thermophilic conditions due to the differences in solubility expected. These chapters provide valuable information required for scale-up and design of biofiltration plants and

* Thermophilic conditions have been identified to be at temperatures of 50°C and higher. Although this study explored temperatures on the border line, a temperature of 50°C allowed a better homogeneity of humidity (Matteau and Ramsay 1999) and enabled continuous temperature control.

represent the most comprehensive research describing these operational parameters thus far.

- Development of methods to illustrate substrate interactions directly from biofilter results without the need for free-cell and monoculture experimentation. Although the biochemistry of the aerobic degradation of individual BTEX compounds is fairly well understood (Smith 1990) and studied, substrate interactions as observed in biofilter systems containing diverse microbial consortia can lead to uncertain results when treating mixtures. A method to quantify substrate interactions as observed for BTEX compounds in a toluene-acclimatized biofilter, operated at mesophilic temperatures, are reported (Chapter 4). A more comparative overview evaluating these interactions for mesophilic and thermophilic acclimated biofilters are also reported (Chapter 6). These results represent a better understanding of the intricate interactions taking place and provide valuable information for multiple compound bioreactor degradation development.
- The development of a diffusion reaction model to describe the steady state behaviour of both a mesophilic and thermophilic biofilter (Chapter 7). The model considers the reactors to be comprised of finite sections for which mass balances are determined and solved using mathematical modeling. This data represented could prove useful in order to optimise design and performance during bioreactor scale-up.
- In Chapter 8 the overall findings are placed into perspective, appropriate conclusions drawn and possibilities for future research elucidated.

1.2. References

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2. Biological systems for the treatment of waste gases

2.1. Introduction

For more than a century, the human population has been growing rapidly, with concurrent increases in energy demands and pollution of the atmosphere, the hydrosphere, and lithosphere. This reality has stimulated man's consciousness on environmental issues, urging for cleaner technologies.

Most industries generate waste gases that contain odorous organic or inorganic compounds, often polluting the environment, even at very low concentrations. These include wastewater treatment facilities, composting operations, the food processing industry etc., and the main contributor, the chemical production industry (Edwards and Nirmalakhandan 1996, Ottengraf 1986). This necessitated the implementation of environmental protection programmes which serve as guidelines for waste disposal and discharge in most countries (van Groenestijn and Hesselink 1993). To meet the emission standards laid down, various techniques for waste gas treatment have been developed. These include physico-chemical (thermal and catalytic oxidation, filtration, carbon adsorption, liquid absorption, condensation and electrostatic precipitation) or biological techniques (biofiltration, bioscrubbing, biotrickling filtration) for the treatment of waste gases containing volatile organic compounds (VOCs), particulate matter, or inorganic compounds such as NO_x and SO_x. The concentration and gas flow rate of the pollutant often determines the treatment method option. Physico-chemical treatment techniques are generally applied for the treatment of waste gases containing pollutant concentrations higher than 1-5 g m^{-3}, while adsorption on activated carbon and biotreatment processes are considered more economical for lower pollutant concentrations (van Groenestijn and Hesselink 1993).

Biotreatment processes are increasingly being applied in the treatment of waste gases. Low capital and operational costs, simplicity and the fact that it is considered an environmentally friendly process make this an attractive alternative

treatment option. Biotreatment processes are based on the ability of microorganisms to oxidise various organic and sometimes inorganic pollutants to carbon dioxide, water and biomass, thus serving as an energy and carbon source for the continued maintenance and growth of the microbial population. The process is, however, dependent upon the transfer of the waste gas pollutants to an aqueous phase.

The aim of this literature review is thus to provide background information regarding biological systems for the treatment of waste gases with emphasis on the microbiological and operational parameters that govern the behaviour of these systems.

2.2. Waste gas treatment techniques

Two forms of air emission control strategies can be differentiated, i.e. source- and secondary control. Source control involves the reduction of pollutants through raw product substitution, reduction or recycling which may reduce the quality of the product or increase the costs. Secondary control, however, involves the treatment of the pollutant after it has been produced and of which the specific action is dictated by economical and ecological constraints. This is based on the nature of the compound(s) being treated, the concentration, the flow rate, and the mode of emission of the gaseous waste stream. Combinations of various technologies may often be required to reduce the pollutants to meet regulatory standards (Devinny et al. 1999). The most commonly used secondary techniques include: condensation; incineration; adsorption; absorption; and biological treatment methods. For the purpose of this literature review emphasis will be placed on biological treatment options.

2.3. Biological methods

Gas phase biological reactors utilise microbial metabolic reactions to treat waste gases. Biological treatment is effective and economical for the treatment of low

concentrations of contaminants in large volumes (Devinny et al 1999). Gaseous pollutants are sorbed into an aqueous phase prior to biodegradation by microorganisms (mainly bacteria). Through oxidative, and occasionally reductive reactions, the contaminants are converted to carbon dioxide, water, and organic biomass. The overall reaction, which is exothermic, can be written as follows:

$$\text{Organic pollutant} + \text{Oxygen} \xrightarrow{\textit{Microorganisms}} CO_2 + H_2O + \text{Heat} + \text{Biomass}$$

These waste gases may be either organic or inorganic compounds and are used by the microorganisms as energy and carbon sources for maintenance and growth by the population. In general, the microorganisms used for biological treatment are naturally occurring. These microbial populations may be dominated by one particular species or may be consortia of various species to biodegrade the contaminant synergistically. Normal ecological relationships (predation, parasitism, etc.), that are important for balance within the system, would also take place.

A prerequisite for successful biological gas treatment is that the compounds to be removed are biodegradable and non-toxic. The most successful removal in gas phase bioreactors can be obtained for low molecular weight and highly water-soluble organic compounds. Furthermore, simple bond structures are biodegraded more readily than complex structures, which may be more energy consuming. Organic compounds such as alcohols, aldehydes, ketones and some simple aromatics demonstrate excellent biodegradability. Some compounds that show moderate to slow biodegradation include phenols, chlorinated hydrocarbons, polyaromatic hydrocarbons, and highly halogenated hydrocarbons. Inorganic compounds such as hydrogen sulphide and ammonia are also biodegraded well (Table 1).

Table 1 Biodegradability of Various Contaminants in a Biofilter (Adapted from Devinny et al. 1999)

Contaminant	Biodegradability	Contaminant	Biodegradability
Aliphatic hydrocarbons		***Oxygenated carbon compounds***	
Methane	1	Alcohols	3
Pentane	1	Ethanol	3
Isopentane	1	Butanol	3
Hexane	2	2-Butanol	3
Cyclohexane	1	1-Propanol	3
Acetylene	1	2-Propanol	3
		Aldehydes	3
Aromatic hydrocarbons		Formaldehyde	3
Benzene	2	Acetaldehyde	3
Phenol	3	*Carbonic acids (esters)*	3
Toluene	3	Butyric acid	3
Xylene	2	Vinyl acetate	2
Styrene	2	Ethyl acetate	3
Ethylbenzene	3	Butyl acetate	3
		Isobutyl acetate	3
Chlorinated [b] hydrocarbons		Ethers	1
Carbon tetrachloride	1	Diethyl ether	1
Chloroform	1	Dioxane	1
Dichloromethane	3	Methyl tert-butyl ether	1
Tetrachloroethane	1[a]	Tetrahydrofuran	3
Trichloroethane	1[a]	Ketones	3
Vinyl chloride	1	Acetone	3
Chlorotoluene	1	Methyl ethyl ketone	3
		Methyl isobutyl ketone	3
Sulphur-containing [b] carbon compounds			
Carbon disulphide	2	***Inorganic [b] compounds***	
Dimethyl sulfide	2	Ammonia	3
Dimethyl disulfide	2	Hydrogen sulphide	3
Methyl mercaptan	1	Nitrogen oxide	1
Thiocyanates	1		
Nitrogen-containing carbon compounds			
Amines	3		
Aniline	3		
Nitriles	1		
Pyridine	1		

[a] Indicates that cometabolism or anaerobic treatment has been identified within a biofilter
[b] Indicates that a change in filter bed pH may occur with treatment of these compounds. This change may negatively affect performance.

Note : 1 = some biodegradability; 2 = moderate biodegradability; 3 = good biodegradability

2.4. Historical review of biofiltration

Microbial biodegradation capabilities have mainly been exploited for the treatment of wastewater and solid waste from various manufacturing facilities. However, as far as could be established, the first proposal to use biological methods to treat odorous compounds was as early 1923 (van Groenestijn and Hesselink 1993), but it was in the mid-fifties that biologically active reactors were first implemented to treat odorous compounds in low concentrations. Some of the earliest known biofilter systems (1953) were constructed as open pits filled with porous soil for the treatment of odorous sewer gases in Long Beach, California (Pomeroy 1957; Carlson and Leiser 1966).

In the 1970s, interest in biofilters increased in response to increasingly stringent air quality regulations. Research into more advanced biofilters capable of handling higher loads of odorous and volatile organic compounds were mainly developed in Germany and the Netherlands. Most of the designed biofilters were open and had better air distribution capabilities with improved structural support media (e.g. bark, wood chips, polystyrene balls etc.). Though these changes improved biofilter performance, dry-out, compaction, and some acidification of the media was still observed (Devinny et al. 1999).

In the years to follow, biofiltration research of odorous-, volatile organic compounds, and even mixtures, progressed rapidly in Europe and slowly in North America. Various inorganic filter bed support media (e.g. granular activated carbon, ceramics, perlite etc.) were also evaluated in order to improve bed porosity, while increasing the life expectancy of the filter bed. This demonstrated the effectiveness of biofilter technology being a cost-effective, reliable means of controlling low concentrations of biodegradable waste gases. At present various companies are commercially marketing this technology, thereby improving the biofilter designs and enhancing biofilter performance. Currently research is also directed towards a better understanding of the complete biofiltration process which includes: pollutant biodegradation pathways; mixed pollutant treatment; transient behaviour; nutrient limitation; biomass control; and process modelling.

2.5. Biological treatment for waste gases

The most commonly used reactors for biological gas phase treatment are biofilters, biotrickling filters and bioscrubbers. These systems can be distinguished by the behaviour of the liquid phase, which is either continuously moving or stationary in the contact apparatus, or by the state of the microorganisms, that are either freely dispersed in the aqueous phase or immobilised on a support material (Table 2) (Ottengraf 1987). In compost production plants, sewage plants and for agricultural applications there is a preference for biofilters and trickling filters, while biofilters and bioscrubbers are preferred for other industrial applications (Ottengraf 1987). The following sections outline these techniques.

Table 2 Classification of Bioreactors for Waste Gas Purification (Ottengraf 1987)

Reactor type	Microorganisms	Liquid phase
Biofilter	Fixed	Stationary
Biotrickling filter	Fixed	Flowing
Bioscrubber	Suspended	Flowing

2.5.1. Biofilters

Biofilters are essentially reactors in which a humid polluted waste gas stream is passed through a porous packed bed onto which a consortium of pollutant-degrading microorganisms are naturally immobilised (Fig. 1). The microorganisms grow in a biofilm on the surface of the support media or are suspended in the water phase that surrounds the support media. As the waste gas passes through the bed, the pollutants sorb into the biofilm and support media, where they are biodegraded (Devinny et al. 1999). To enable suitable mass transfer of the waste gas, support media with a high specific surface are generally used. These include active natural substances like compost and peat, which not only supply additional nutrients to the microorganisms but also contain a consortium of bacteria, thereby shortening bed acclimatisation time. To prevent high pressure drops and channelling, inorganic compounds such as perlite (Shareefdeen et al. 1993), polystyrene (Deshusses et al. 1995), polyurethane foam (Shareefdeen et al. 1993; Moe and Irvine 2001), and glass beads (Zilli et al. 1996), to name a few, are

added, or alternatively also used as primary support media. For certain applications, activated carbon or other buffer compounds are also added to minimise fluctuations of pollutant concentrations (Weber and Hartmans 1995) or to stabilise the pH of the filter bed. Biofilters are especially suitable for the treatment of poorly water-soluble pollutants with a Henry's Law coefficient of less than 10 (Kennes and Thalasso 1998).

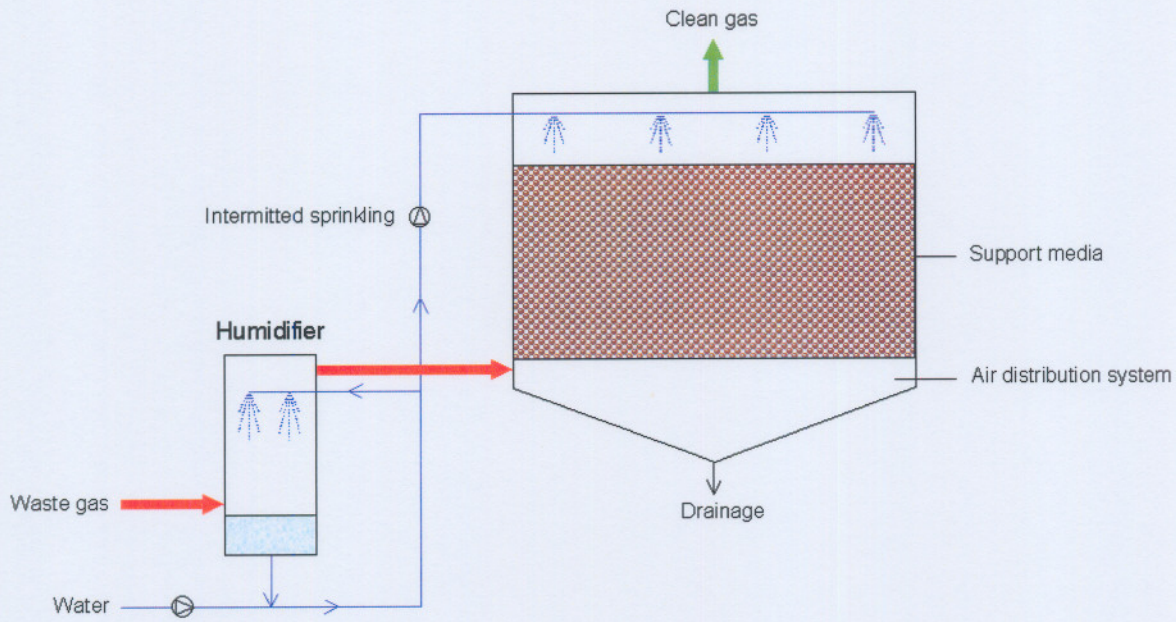

Fig. 1 Generalised schematic diagram of a biofilter system

2.5.2. Biotrickling filter

Waste gas treatment in biotrickling biofilters involves the use of a biological filter continuously fed with a liquid medium, packed with an inorganic support material on which microorganisms are immobilised (Fig. 2). The waste gas passes through the filter bed, co- or countercurrently to the liquid phase, which supplies the microorganisms with nutrients. Additional nutrients (inorganic), fresh water, acid or base may be added to the recirculating liquid ensuring a suitable environment for optimal pollutant removal (Devinny et al. 1999). Support media reported in literature include plastic or ceramic structured media (Diks et al. 1994b; Pedersen and Arvin 1995; Weber and Hartmans 1996), unstructured celite (Speitel and

McLay 1993), activated carbon (De Heyder et al. 1994; Kirchner et al. 1987) or mixtures of different materials.

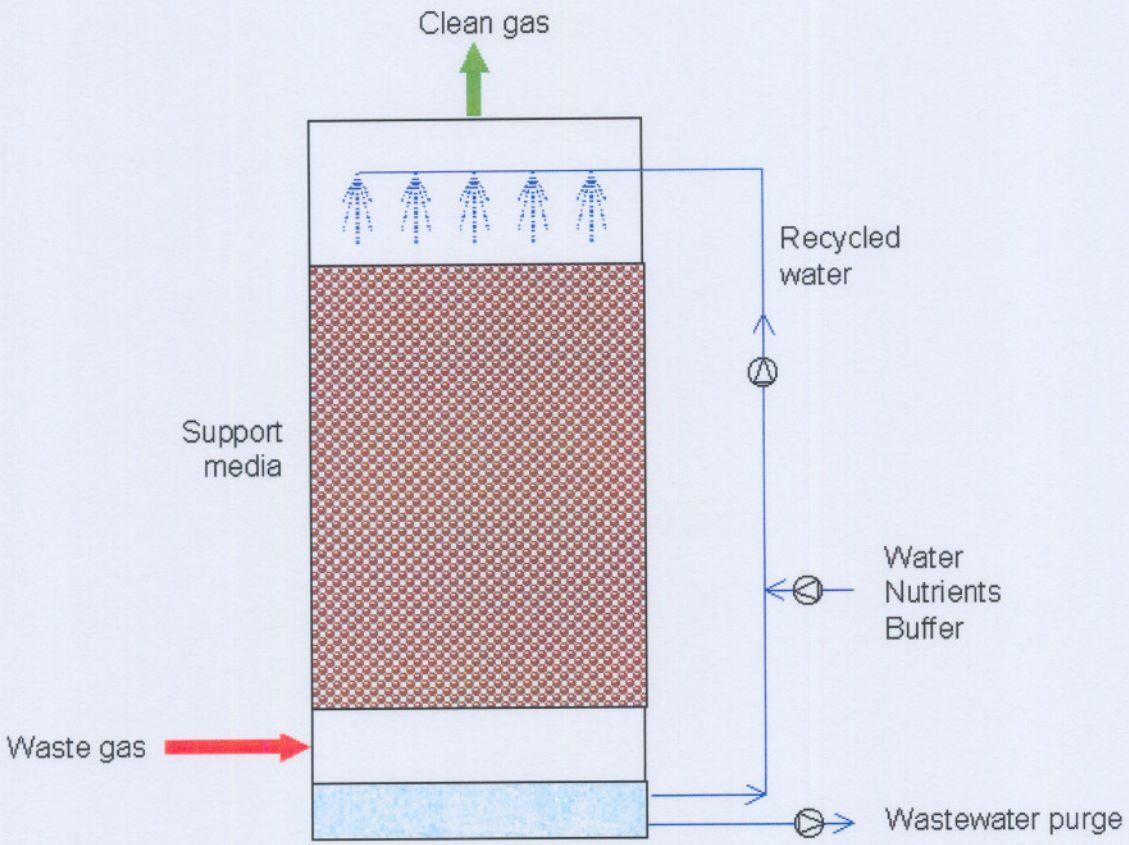

Fig. 2 Generalised schematic diagram of a biotrickling filter

2.5.3. Bioscrubber

A bioscrubber generally consists of a scrubber compartment and a biological treatment system. In the scrubber compartment, water droplets flow countercurrently with the waste gas where continuous mass transfer of pollutants and oxygen from the waste gas to the liquid phase takes place (Fig. 3). Absorption may be achieved in a packed column, spray tower, or a bubble column. Pollutants absorbed in the water will then be oxidised through microbial activity and eliminated from the liquid phase in a separate biological treatment system (e.g. activated sludge systems). The regenerated water phase is then recirculated to the scrubber compartment. Nutrients, buffers and titrants can be added and the liquid can be refreshed and discharged in order to remove undesired products or

inhibitory compounds. In addition, temperature, pH and ionic strength can be monitored and controlled easily.

This technology is particularly effective when the waste gas pollutants are highly water-soluble. Bioscrubbing is therefore of interest for gaseous pollutants with a Henry's Law coefficient of less than 0.01 (Kennes and Thalasso 1998).

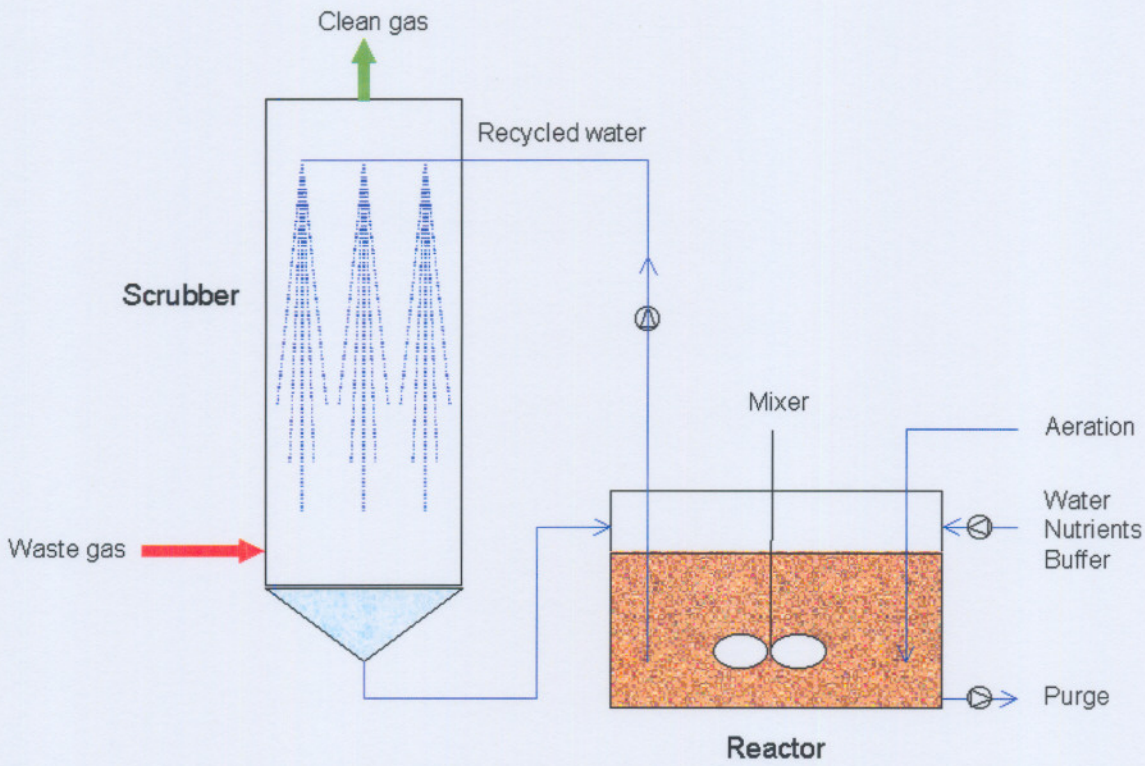

Fig. 3 Generalised schematic diagram of a bioscrubber system

2.6. Advantages and disadvantages

In Table 3 the advantages and disadvantages of the three described biological treatment systems are summarised. The main characteristics and application areas are also indicated.

Table 3 Characteristics, application area, advantages and disadvantages of biofiltration, bioscrubbing and biotrickling filtration for waste gas treatment (adapted from van Groenestijn and Hesselink 1993)

Biofiltration	
Characteristics	**Advantages**
▪ Immobilised biomass ▪ Immobile water phase ▪ Single reactor	▪ High gas/liquid surface area ▪ Easy operation and start-up ▪ Low operation costs
Application area	**Disadvantages**
▪ Concentration target compounds < 1.0 g m^{-3} ▪ Henry's coefficient < 10	▪ Poor control of reaction conditions ▪ Slow adaptation to fluctuating concentration in gas ▪ Large area required
Bioscrubbing	
Characteristics	**Advantages**
▪ Suspended biomass mostly ▪ Mobile water phase ▪ Two reactors	▪ Better control of reaction conditions (pH, nutrients) ▪ Possibilities to avoid accumulation of products ▪ Compact equipment ▪ Low pressure drop
Application area	**Disadvantages**
▪ Concentration target compounds < 5 g m^{-3} ▪ Henry's coefficient < 0.01	▪ Low surface area for mass transfer ▪ Wash out of slow growing microorganisms ▪ Stagnation periods of a few days detrimental ▪ Disposal of excess sludge ▪ Complicated start-up procedure ▪ Extra air supply needed at high degradation rates ▪ High investment, maintenance and operational costs
Biotrickling filtration	
Characteristics	**Advantages**
▪ Immobilised biomass ▪ Mobile water phase ▪ Single reactor	▪ Comparable to bioscrubbing ▪ Better retention of slow growing microorganisms ▪ Single reactor
Application area	**Disadvantages**
▪ Concentration target compounds < 0.5 g m^{-3} ▪ Henry's coefficient < 1.0	▪ Low surface area for mass transfer ▪ Disposal of excess sludge ▪ Complicated start-up procedure ▪ High operational costs

2.7. Technology effectiveness

There is no waste gas treatment technology (conventional or biological) that can effectively and economically be applied to each and every industrial and commercial application. In practice the effectiveness of a technology can often be defined by the gas flow rates and the concentrations of the pollutant(s) at which adequate cost-effective treatment can be expected (Fig. 4).

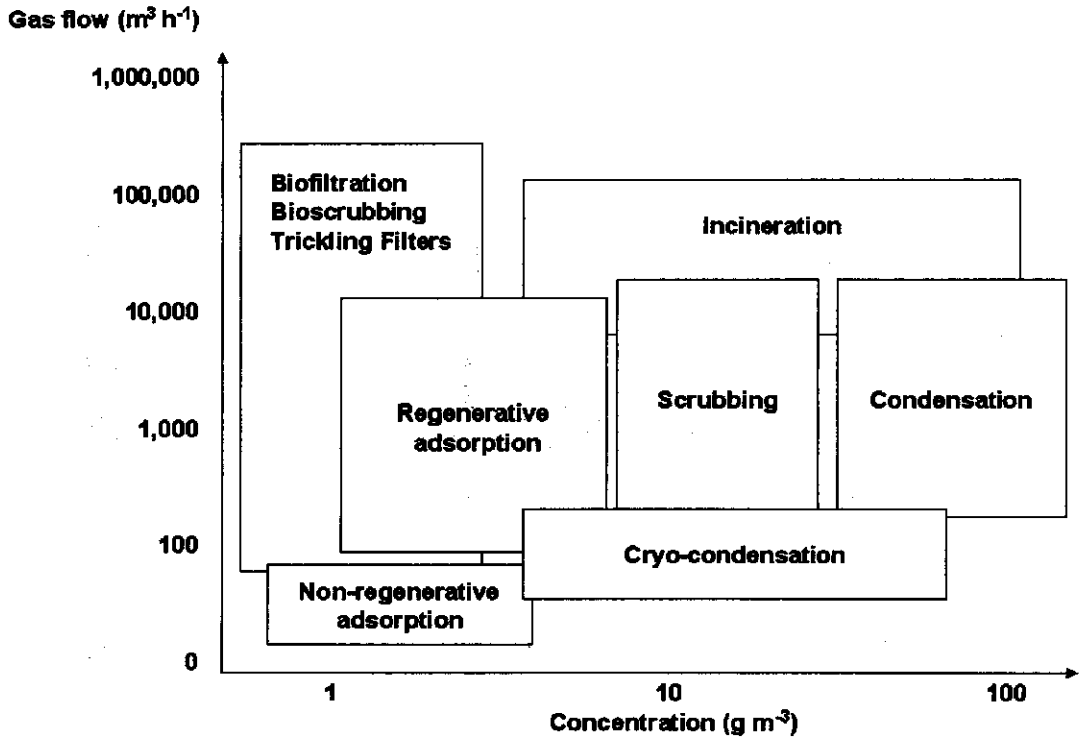

Fig. 4 Application of various waste gas control technologies based on flow rates and concentrations of the pollutant to be treated (Adapted from Devinny et al. 1999)

The advantages of conventional waste gas treatment techniques, compared to biological systems, are that more complete elimination of particles and successful treatment of inorganic compounds can be achieved. Such inorganics include HCl, HF, Cl_2, HCN and NO_x. Reliability and the possibility of valuable pollutant recovery are also advantages of such systems. On the other hand, most conventional systems only transfer the pollutant from one phase to another, thus requiring

additional treatment. A major disadvantage is the higher operating costs often associated with conventional waste gas treatment technologies.

Biological systems present the advantage of completely degrading pollutants into innocuous or less-contaminating products with minimal secondary pollutant waste streams. The biggest disadvantage is, however, that it may be ineffective at high pollutant concentrations or when the pollutant is poorly degradable.

2.8. Recent developments of biofilters to improve the removal of hydrophobic pollutants.

2.8.1. Activated carbon

Weber and Hartmans (1995) have studied the application of activated carbon addition for a biofilter treating toluene. They observed that mixing activated carbon with compost in the biofilter did not result in better buffering capacity, but that placement of an activated carbon filter ahead of the biofilter resulted in better overall performance (also previously suggested by Ottengraf et al. 1986). They attributed this difference to the presence of water in the filter since the pollutant first has to diffuse through a water film to reach the activated carbon.

2.8.2. Two-liquid-phase systems

Poppe and Schippert (1992) demonstrated the advantages of adding a water-immiscible organic solvent to the liquid phase to aid in the removal of hydrophobic compounds in a two-stage bioscrubber. By adding organic solvents with high boiling points in a range of 10 – 30% of the total volume, 100 to 1000 times larger amounts of hydrophobic compounds were absorbed in the scrubber compartment. The first bioscrubber was conventional, while the second contained the organic solvent. Each stage included a biological regeneration reactor. In the first stage

mainly hydrophilic compounds were removed, while hydrophobic compounds passed and were eliminated in the second stage.

The transfer of pollutants from the gaseous phase to the liquid phase can be significantly improved by the addition of a solvent. However, since the biodegradation occurs in the liquid phase, the efficiency of the process is dependent on the exchange of pollutant between the solvent and the liquid (water), i.e. the solvent / water mass transfer rate. The influence of parameters such as gas/solvent, gas/water and solvent/water exchange areas, mass transfer coefficients and partition coefficients on the pollutant removal efficiency was studied by Cesário et al. (1995). This was initially done by comparing the performance of three solvent-containing systems (liquid-impelled loop reactor, packed bed reactor, mixed settler) with systems featuring direct gas-water transfer. Three compounds with different gas/water partition coefficients were evaluated, i.e. hexane (71 kg m^3 gas / kg m^3 water), dichloromethane (0.1 kg m^3 gas / kg m^3 water) and acetone (0.0016 kg m^3 gas / kg m^3 water). Because this theoretical study was aimed at characterising the different systems in terms of mass transfer, the biological conversion was assumed to be non-limiting. It was concluded that the use of an organic solvent is advantageous only if the specific exchange solvent/water is large enough to compensate for the additional transport resistance introduced by the solvent.

2.8.3. Membranes

A schematic view of a membrane bioreactor to illustrate the principle of the system is represented in Fig. 5. Organic pollutants in the waste gas diffuse through the membrane into the water phase, where microorganisms that are present in this phase, can degrade the pollutants. In time, microorganisms will form a biofilm on the membrane, enabling biodegradation. This biofilm is supplied with inorganic carbon and oxygen from the gas phase and with water and nutrients through the liquid phase. The separate water phase also enables the removal of toxic degradation products allowing the application of a wider range of waste gases

(Reij et al. 1995). Membrane bioreactors may prove to be more advanced than bioreactors but also require greater capital expenditure.

Different types of membranes have been proposed for the removal of poorly water-soluble compounds, i.e. dense silicone membranes that are semipermeable (Freitas dos Santos et al. 1995) and microporous hydrophobic membranes which have very large (specific) surface areas (Beeton et al. 1991; Reij and Hartmans 1996; Reij et al. 1995). Dense silicone membranes have a higher mass transfer resistance than microporous hydrophobic membranes. For dense silicone membranes the contaminants have to dissolve in the membrane material and diffuse through this material, whereas in the microporous membranes diffusion is in the air filled pores of the membrane.

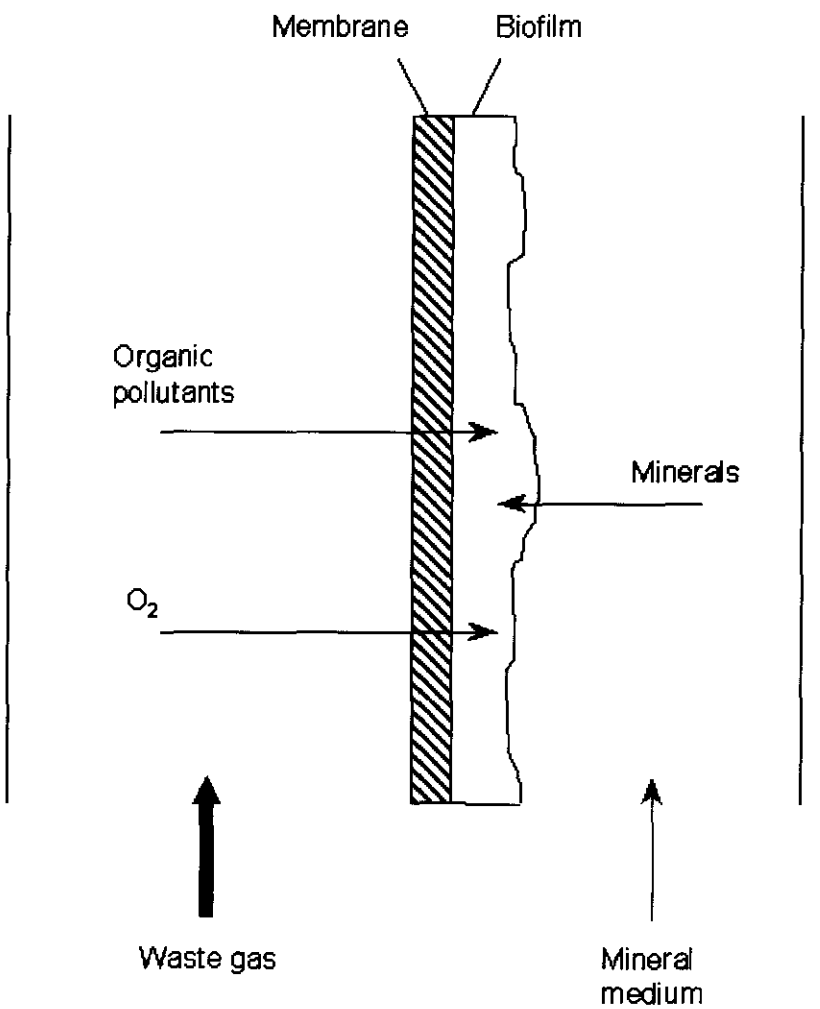

Fig. 5 Generalised schematic representation of membrane bioreactor principle

2.8.4. Fungi

In biofilters the aerial hyphae of fungi form a very large specific surface area that is in direct contact with the waste gas flowing through the filter. The pollutants are, therefore, in direct contact with the microorganism without an intermediate aqueous phase. This is especially advantageous for the elimination of hydrophobic contaminants (Weber et al. 1995). Fungi are also tolerant to low water activities and acidification (van Groenestijn et al. 2001).

Majcherczyk et al. (1990) proposed the use of a biofilter inoculated with white-rot fungi growing on straw to biodegrade a wide range of hydrophobic and hydrophilic compounds. The fungi, when growing, secrete oxidative enzymes that catalyse the degradation of lignin. These extracellular enzymes are non-specific and are able to degrade many aromatic compounds as well. Due to the very large surface area and the broad substrate specificity, the biofilter can treat waste gas containing a variety of pollutants. A removal efficiency of 95 - 100% from a styrene (1.2 g m^3 inlet gas concentration), lignosulphonate vapour, H_2S and ammonia waste gas stream was observed. More recently, Woertz et al. (2001) and van Groenestijn et al. (2001) further investigated the use of fungal biofiltration systems. Woertz et al. (2001) reported on the removal of nitric oxide (NO) using a black, dimorphic fungus *Exophiala lecanii-corni* using toluene as the sole carbon and energy source. The reactor removed 93% of an inlet containing 250 ppmv NO at an empty bed contact time of 1 minute supplied with 90 g m^{-3} h^{-1} toluene. A greater than 95% toluene removal efficiency was maintained, while a maximum elimination capacity of 270 g m^{-3} h^{-1} was reported. High volumetric elimination capacities for toluene (80 – 125 g m^{-3} h^{-1}) were also reported by van Groenestijn et al. (2001). The introduction of mites was furthermore suggested as an interesting tool for preventing filter bed clogging while maintaining high elimination capacities in these reactors.

2.9. Microbiological and operational parameters

2.9.1. Substrates

Biofilters have been used to treat a wide variety of both organic and inorganic compounds produced from various installations worldwide. These compounds include odorous waste gases from the food processing industry, wastewater treatment facilities, composting operations, rendering plants and VOCs from industrial operations to name a few (Wani et al. 1997). Selected biofilter elimination values for various compounds are represented in Table 4.

2.9.2. Microorganisms and inoculation

Several groups of microorganisms (fungi and bacteria) are known to be involved in the biodegradation of waste gases in biofilters. The microbial population is generally made up of autotrophic microorganisms that feed on the inorganic compounds and heterotrophic microorganisms that utilise the organic compounds (waste gas to be treated) as sources of carbon and energy. The diversity of the active microbial consortium, however, mainly depends on the composition of waste gas treated. The continued growth and survival of the microorganisms are dependent upon the physical and chemical characteristics of the support media, water, oxygen, mineral nutrients, waste gas composition, pH and the temperature (sections 2.9.3 and 2.9.4).

Support media of natural origin (e.g. compost) contains a wide variety of microorganisms able to initiate the reactions required for the elimination of simple pollutants. The removal efficiency is generally enhanced following the growth of active strains and the acclimatisation of the microorganisms to the waste gas. Faster start-up can be achieved by inoculation of the support medium with either specialised or non-specialised microorganisms (Acuña et al. 1999). The following inoculants are generally used:

Table 4 Biofilter elimination values (adapted from Devinny et al. 1999)

Contaminant(s)	Biofilter support medium	Critical load ($g\ m^{-3}\ h^{-1}$)	Maximum elimination capacity ($g\ m^{-3}\ h^{-1}$) (% removal)
Acetone	Compost based	229	229 (90%)
Acetone	Compost based	N/A	164
Acetone	Compost based	20-25	8
Benzene	Compost based	1	23
Benzene	Compost based + GAC	N/A	41-55
BTEX	Carbon coated foam	N/A	14-30
BTEX	Sand	N/A	15-44
BTEX	Carbon	N/A	50-60
BTX	Compost / Perlite	35-40	30
1,3-butadiene	Ceramic	N/A	
Butanol	Compost based	30-40	70-80
Butyl acetate	Compost based	~10	40
Butyl acetate	Compost based	25-30	35
Butyric acid	Compost based	N/A	30
Dimethyl disulphide	Compost/pine mulch	10	10-12
Dimethyl disulphide	Wood bark	8-10	11-20
Dimethyl disulphide	Compost based	N/A	70 (84%)
Dioxan	Compost based + GAC	N/A	11-13
Ethanol	Granular carbon	N/A	156
Ethanol	Compost based	80	150
Ethanol / 2-propanol	Compost based	N/A	57
Ethene	GAC	N/A	10
Ethyl acetate	Compost based	8-10	25
Ethyl acetate	Compost based	180	200
Ethylene	Ceramic	8-12	40-50
Gasoline vapors	Granular carbon	N/A	avg. 64, max. 119
Hexane	Compost based	1	5
Hydrogen sulfide	Compost	100	130
Isobutyl acetate	Compost based	45	75
Isopentane	Compost based	2	8
Jet fuel, JP-4	Peat	N/A	4-19
Jet fuel, JP-4	Sand	N/A	12
Jet fuel, JP-4	Compost	N/A	65
Methane	Glass rings	10-13	15-18
Methanol	Compost based	42	N/A
Methanol	Compost / perlite	10-20	301
Methanol	Compost based	N/A	18
Methanol	Compost based	30-35	70
Methanol	Compost / perlite	50-80	100-120
MEK	Compost based	75-100	120
MIBK	Compost based	15-18	25-30
MEK/MIBK	Compost based	N/A	40/18
1-propanol	Compost based	120	150
α-Pinene	Compost / perlite or compost/GAC	N/A	35
Styrene	Perlite	62	62
Styrene	Peat	60-75	100
Toluene	Peat	N/A	4-40
Toluene	Compost	N/A	100
Toluene	Compost based	8	15
Toluene	Compost based	<10	20-25
Toluene	Compost	30-40	45-55
Xylene	Compost based	10-15	25

- Activated sludge

  Activated sludge from wastewater treatment plants may serve as a good source of microorganisms for the treatment of easily biodegradable pollutants. Activated sludge contains an immense variety of rugged microorganisms which have been exposed to the typical wastes of man.

- Material from adapted biofilters

  Material from biofilters, which already eliminate poorly biodegradable compounds, can be mixed with support media from a new filter. The old material thus serves as inoculum.

- Pure cultures or consortia of specialised microorganisms

  The use of pure cultures or consortia of specialised microorganisms have been widely reported in literature. The addition of an acclimatised microorganism will therefore shorten the start-up period.

2.9.3. Support media

Support media are the key components of biological treatment systems, therefore serving multiple functions. The most important physical characteristics the support media should have are (Kinney et al. 1997; Swanson and Loehr 1997; Kennes and Thalasso 1998):

- high surface area for optimum microbial development and immobilization;
- low bulk density; and
- high void fraction to limit, or avoid, pressure drops and clogging problems

Furthermore, the presence of a large number of different microorganisms naturally present on the support media as well as a balanced chemical composition may be an advantage, thereby enhancing microbial adaptation and activity inside the bioreactor. The choice of support media for different biological treatment systems should be based on the following criteria:

- Inorganic nutrient content

  High nitrogen, phosphorous, potassium and sulfate contents, as well as trace minerals, are required for the establishment of a dense process culture. In general, nutrients are supplied onto the support medium during preparation only, but in some cases it needs to be added on a regular basis.

- Organic content

  In some instances an alternative food source (available in compost for example) will be required during biofilter shutdown (process rotation or weekends) or discontinuous waste gas feed.

- Chemical and inert additives

  Support media should prevent compaction of the filter bed and minimise the pressure drop. Inert-additives, also referred to as bulking agents, such as polystyrene beads, wood and perlite are used for this purpose. Optimal pH can also be obtained by the addition of limestone or crushed shells which buffer produced acidity.

- Water content

  Water should be readily available for the microbial activity to utilise, especially during dry periods.

- pH

  Neutral pH values are required for optimal bacterial growth.

- Sorption characteristics, porosity

  Support media should have a large surface area for both microbial immobilisation and pollutant mass transfer. Pollutants are transferred (sorbed) into the pore water and biofilm on the support media and also directly onto the support media itself. This sorption is, however, a function of the water content, the pollutant characteristics and the nature of the support media.

- Bacterial attachment

  Support media should provide a suitable niche for microorganisms. Rough, porous and hydrophilic support media are more readily colonised by microorganisms. Rough surfaces protect organisms from hydraulic shear, while porous media enable them to survive in unfavourable conditions.

- Mechanical properties

  A stable structured filter bed is required for continued operational use. No clogging, shrinkage or compaction should therefore occur. Furthermore the support media at the bottom of the bed must be able to bear the weight of the media above.

- Packing cost and lifetime

  Support media should provide good removal efficiencies over a long-term period. The cost of the support media should be minimal compared to the investment costs, and its contribution to the overall operating cost should remain minimal.

2.9.4. Micro-environmental conditions

- Moisture content

  Moisture content of the filter bed is the single most critical factor determining the effectiveness of a biofilter (Leson and Winer 1991). The reason for this is that microorganisms require water to carry out their natural metabolic functions and is, therefore, essential to ensure optimal microbial activity (Ottengraf 1986; Wani et al. 1997). Optimal moisture levels vary with different support media which is mainly dependent upon the surface area and porosity (Hodge et al. 1991). Filter moisture content for optimal operation of the biological filter should be maintained between 30 – 60% by weight, depending on the type of support media used. For compost and peat biofilters a moisture content of 40 – 50% (Ottengraf 1986) and 40 – 60% (Wani et al. 1997) respectively, is recommended. Reported studies have indicated that biofiltration systems

require at least 90% humidity in the inlet gas stream when the inlet gas stream is not warmer than the filter bed (van Lith et al. 1997; Auria et al. 1998; Gostomski et al. 1997; Chou and Cheng 1997; Corsi and Seed 1995, Tang and Hwang 1997). In many practical situations prehumidification is often not sufficient and water needs to be added to the top of the reactor (Krailas et al. 2000). In biofilters with too low moisture content fungi are expected to dominate the bacterial population. Too high moisture contents (>60%) should, however, be avoided as it decreases the gas/liquid surface area and may lead to mass transfer problems in biofilters (Ottengraf 1986; Gostomski et al. 1997). It may also inhibit the oxygen transfer to the biofilm which may promote the development of anaerobic zones within the filter bed, resulting in odorous emissions, increasing back pressures and reduced removal efficiency (Hodge et al. 1991; Williams and Miller 1992).

- Temperature

  Temperature is one of the most important factors influencing the growth and survival of organisms. Microorganisms are adapted to perform their metabolic functions within a certain temperature range. There are broadly three distinguishable temperature classes of microorganisms: psychrophilic microorganisms with low-temperature optima (< 20°C); mesophilic microorganisms with midrange temperature optima (20 - 40°C) and thermophilic microorganisms with high-range temperature optima (40 - 68°C). It has been reported that biological reaction rates roughly double for each 10°C rise in temperature up to a maximum temperature at which the microbe functions optimally (Wani et al. 1997; Wright et al. 1997). Biological treatment systems are most often studied at mesophilic conditions (Lee et al. 1996, Wani et al. 1997). Cooling of the unsaturated inlet waste gas (e.g. by humidification) may, therefore, in some cases be necessary. It should also be kept in mind that biodegradation is an exothermic reaction and may contribute to a temperature increase (Kennes and Thalasso 1998). While a warmer environment generally supports more active microorganisms, the physico-chemical effects at higher temperatures are usually unfavourable. For most gases, the Henry's Law coefficient rises with temperature. This results in lesser water solubility of the pollutant with the effect that less carbon will be

available for the microorganisms. Hence, the physical effects should be considered, especially for contaminants with a high Henry's Law coefficient (Devinny et al. 1999).

- Oxygen content

  The microbial populations in biological treatment systems are predominantly aerobic, requiring oxygen to metabolise the constituents of waste gases. In most biological treatment systems, when the active microbial biofilm is relatively thin, oxygen supply to the microorganisms is adequate. Oxygen limitation is, however, most likely to occur in the case of high pollutant loadings of easily biodegradable hydrophilic compounds, especially where thick biofilms exists. This would often result in the production of partially oxidised by-products, such as carboxylic acids (Devinny and Hodge 1995), odourous aldehydes, acidic and other intermediates (Deshusses et al. 1996).

- pH

  Each organism has a pH range, narrow or broad, within which growth is possible, and usually has a defined pH optimum. Movement outside this range will thus inhibit or kill microorganisms thereby having a severe effect on the microbial activity of a biological treatment system (Leson and Winer, 1991; Yang and Allen 1994). Although rapid changes in pH are damaging to most species, microbial ecosystems may adapt to slow changes in pH. Species tolerant to the new conditions would, therefore, replace those that are not. It has been well documented that bacteria prefer a neutral pH, while fungi tend to be acid-tolerant ($\leq$ pH 5.0) (Brock and Madigan 1991). The pH of new filter media should thus be determined before inoculation. Furthermore, the type of waste gas (e.g. H_2S, dichloromethane) treated may form acidic intermediates that would require neutralization. Treatment with chemical buffers (e.g. lime) or the addition of neutralising agents (e.g. crushed shells) to the support media before bioreactor start-up, may be necessary (Lee et al. 1996).

- Nutrients

  As discussed, microorganisms utilise the pollutants present in waste gas as a carbon source (energy). This is, however, not the only requirement for growth. Mineral nutrients such as nitrogen, phosphorous potassium, sulfur, calcium, magnesium, sodium, iron and many more, together with trace minerals and/or vitamins are required. For good performance of any biological treatment systems sufficient levels of these nutrients have to be available. Compost as a support medium has the important advantage that most such nutrients are already present. The use of synthetic support media, however, often requires the addition of these nutrients. Several studies have also indicated that the addition of nutrients or nutrient supplementation to biofilters improved the degradation rates due to a better nutrient balance and pH stabilisation (Lee et al. 1996; Weckhuysen et al. 1993).

2.9.5. Biomass control methods

Biomass accumulates in biofilters when growth from waste gas carbon exceeds the endogenous decay and respiration. During periods of high loading and mineral nutrient abundance, the biomass may clog the filter bed support media, resulting in large pressure drops and air channelling through the filter bed. Pressure drops in turn increase the duty on blower equipment, while air channelling reduces the specific contact area for pollutant mass transfer. As clogging increases, anaerobic zones may also develop with the subsequent production of odorous compounds. Several studies and techniques have, therefore, been developed to prevent excessive biomass formation.

2.9.5.1. Backwashing

The most frequently used method for controlling excess biomass formation, is so-called backwashing. This method relies on the principle that water addition at high flow rates may be effective in shearing off biomass from the support media. The rate at which the water is pumped through the biofilter as well as the time period of

the flush will thus determine the degree of medium expansion and, subsequently, the amount of biomass to be removed. This method, however, generates large volumes of high BOD wastewater, which must be disposed of. Application of flowing water to organic support media is not advisable because of the probability of compaction, leaching of nutrients, and the enhancement of air channelling effects.

Smith et al. (1996) used this method to control excess biomass formation while maintaining a high toluene removal efficiency of more than 99% in a biotrickling filter. The authors used a specific flow rate of 190 m h^{-1} to allow a bed expansion of 40%. This proved to be successful when repeated twice per week for a period of one hour. The role of backwashing parameters, i.e. frequency, duration and flowrate on the performance on the biofilter system still needs to be established (Smith et al. 1996).

2.9.5.2. Inert salt

Microorganisms vary widely in their requirements with regard to availability of water (water activity, a_w). The addition of inert salts (type and concentration) to media may, therefore, influence the living conditions severely, leading to a shift in the composition and the biological activity of a mixed culture. Microorganisms capable of living under conditions of reduced water availability will, therefore, spend a substantial portion of their energy on establishing and maintaining a gradient of salt concentration between the interior and exterior of the cell. This effect causes a decrease in biological activity (Schönduve et al. 1996).

Diks et al. (1994a) investigated the influence of NaCl on the degradation rate of dichloromethane by a *Hyphomicrobium* sp. The results obtained indicated that microbial growth was strongly inhibited by increased NaCl concentrations (50% reduction in μ_{max} at 200 - 250 mM NaCl). At NaCl concentrations exceeding 600mM a considerable elimination of dichloromethane was still observed, however, the authors concluded that microbial growth inhibition caused by water

activity reduction offers a significant control mechanism against excessive biomass growth in biotrickling filters for waste gas treatment.

2.9.5.3. Sodium hydroxide wash

Weber and Hartmans (1996), as a clogging prevention method, investigated the application of a sodium hydroxide wash to remove excess biomass in a biotrickling filter. The authors added NaOH (end concentration of 0.1 M) to the circulating medium every two weeks. As a result excessive foaming was observed, indicating the release of protein due to the lysis of biomass. The toluene removal rate was restored within a day. Under these conditions an average toluene removal rate of 35 g C $m^{-3}h^{-1}$ was obtained. After about 50 days there was no net increase in the biomass content of the reactor.

2.9.5.4. Nutrient limitation

Nutrient limitation may control biomass effectively in inorganic filter beds. However, maintaining nutrient concentrations at a level that will limit biomass growth with minimum effect on the removal efficiency of the pollutants, is a very difficult balancing act.

Weber and Hartmans (1996) investigated the effect of inorganic nutrient limitation on biomass accumulation in a biotrickling filter. The authors observed, as a consequence of lower nutrient concentration, a decrease in toluene removal rate. However, when a fungal culture was used to inoculate the reactor, the toluene removal rate increased (average of 27 g C m^{-3} h^{-1} over a 375 day period). Although the nutrient limitation did not result in a thin biofilm, a high and stable toluene removal rate could be obtained with the fungal culture. Wübker and Friedrich (1996) also demonstrated the feasibility of limiting the supply of phosphate and potassium ions in order to reduce biomass formation in a bioscrubber treating *n*-butanol. The study reported a significant increase in the

maintenance requirement, thereby, shifting the amount of carbon required for the formation of biomass towards energy generation.

2.9.5.5. Directional switching

Traditionally biofilters have been designed in such a way that the waste gas either enters the system at the top or the bottom of the column, the so-called unidirectional systems. This operational mode cause the support media nearest to the inlet to develop a more active microbial population and an essentially less active population at the outlet of the biofilter (Kinney et al. 1996). When treating high concentrations of a volatile organic compound, this may result in the rapid clogging of the support media and a rise in the pressure drop nearest to the inlet (Sorial et al. 1995).

An alternative strategy is to operate the biofilter in a directional-switching mode where the inlet and outlet of the column are periodically switched. In a directional switching biofilter, the contaminant inlet is continuously cycled back and forth between the top and bottom of the column. The biofilter sections nearest to the inlet consume most of the contaminant feed (i.e. feast) while the remaining section endure carbon-limited conditions (i.e. starve). After a set time, the outlet and the inlet ports are switched and the starving/feasting sections of the biofilter reversed. This alternating feed strategy results in a more uniformly distributed biomass profile across the length of the biofilter. Not only does a uniform distribution reduce clogging, but it also improves the biofilter response to spikes in the inlet concentration (Kinney et al. 1996; Song and Kinney 2001).

2.9.5.6. Inorganic salts addition

Another method often used, is the addition of inorganic salts. This method reduces the overall cell yield by changing the form of the nutrient-nitrogen (N). It has been shown that the biomass yield is lower for an aerobic culture growing on nitrate (NO_3-N) rather than when ammonia (NH_3-N) is used as sole source of

nutrient-N. This reduction in yield may be attributed to the need to expend reducing equivalents to convert nitrate to ammonia for cell synthesis, i.e. proteins (Smith et al. 1996).

Smith et al. (1996) investigated these phenomena by feeding two trickling biofilters treating high toluene loadings with different nutrient-N sources. The authors observed that the trickling filter receiving nitrate (NO_3-N) rather than ammonia (NH_3-N) as nutrient-N source, exhibited superior performance. This was also reported by du Plessis et al. (1998) who suggested that denitrification, together with directional switching of the inlet feed of the biofilter, could be used as a possible biomass control method.

2.9.5.7. Protozoan predation

Cox and Deshusses (1999) investigated the use of protozoan predation as a means of biomass control in a toluene-degrading biotrickling filter. The addition of a mixture of protozoa (*Tetrahymena pyriformis*, *Vorticella microstroma*, as well as an uncharacterized consortium) resulted in the increase of toluene mineralization and a decrease in the biomass accumulation rate. Further stimulation of predation of the biomass immobilized in the reactor required to ensure longterm stability, was, however, suggested. An additional study also suggested that the toxicity of the treated pollutants to the protozoa should also be considered (Cox et al. 1999).

2.10. Conclusions

In recent years, there has been an increased interest in the implementation of biological systems for the treatment of waste gases. These systems certainly pose various advantages compared to traditional systems, the most important being the cost-implications. From this literature review it is, however, evident that although it is considered a relatively simple process, the performances of these systems are governed by various interrelated parameters. A thorough knowledge

of these parameters is thus necessary to ensure successful design, construction and continued operation.

2.11. Aim of this study

Although the primary aim of the literature study was to provide an overview of the currently available technologies and the associated operational difficulties, the various chapters of this thesis focus on additional shortcomings in the existing literature. For each chapter a detailed aim is presented stating the rationale for studying specific aspects where gaps were noticed in the available literature pertaining to either the biofiltration of toluene, as well as BTEX substrate interactions observed when using a toluene acclimatised microbial consortium. A thesis outline map indicating how these shortcomings were addressed and specific chapters overlap is represented in Figure 6.

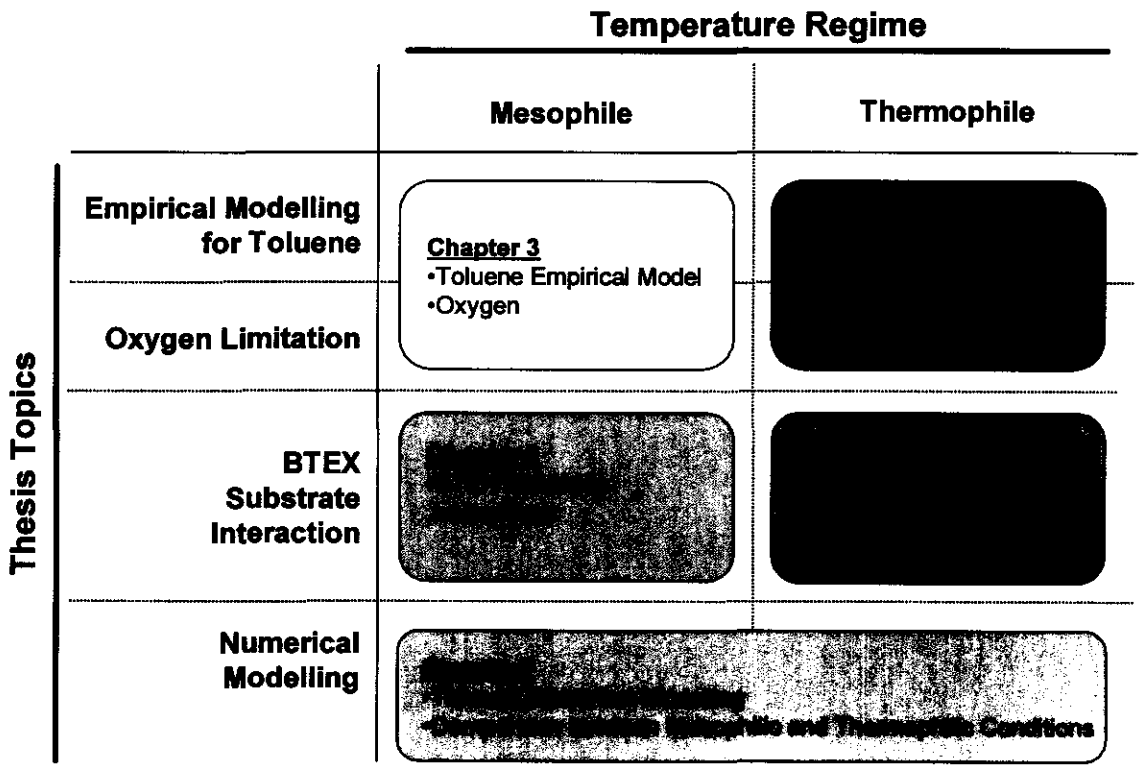

Fig. 6 Thesis map indicating the topics where the individual chapters investigated various gaps in current literature

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3. Empirical model for the biofiltration of toluene

3.1. Abstract

In this study the toluene removal efficiency of a composted pine bark biofilter was determined at loading rates ranging from 9.04 – 54.21 g m^{-3} h^{-1}, retention times of 0.25 – 3.0 minutes, and at various bed heights. Toluene removal efficiencies exceeding 90% were obtained when the biofilter was subjected to a gas retention time in excess of 0.32 minutes (19.2 seconds) and loading rates below 42 g $m^{-3}h^{-1}$. The data obtained was used to develop an empirical model. The empirical model successfully described the overall removal efficiency with an R^2 value of 0.98. The influence of oxygen concentration on the removal efficiency was also evaluated. Reduced biofilter performance was observed at oxygen concentrations below 5 %. A wide range of microorganisms were isolated from the biofilter, which included *Corynebacterium jeikeium A*, *Corynebacterium nitrilophilus*, *Micrococcus luteus*, *Pseudomonas mendocina*, *Sphingobacterium thalphophilum* and *Turicella otitidis*.

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3.2. Introduction

Biological waste gas treatment represents an important development in environmental protection. This is mainly due to increasingly stringent environmental legislation and increasing interest in the cost effective treatment options offered by biological waste gas treatment systems (Cox and Deshusses 1998; Zhu et al. 1998). Biofiltration is particularly suitable in the elimination of high volumes of waste gases contaminated with low concentrations of volatile organic compounds (VOCs) (Kapahi and Gross 1995; Tang and Hwang 1997).

In recent years a large number of studies have been conducted on the microbiological treatment of toluene waste gas. These studies included the use of biofilters, trickling filters and bioscrubbers packed with various types and mixtures of immobilisation materials (Pedersen and Arvin 1997; Matteau and Ramsay 1997; Andreoni et al. 1997; Hwang and Tang 1997). Most of these studies evaluated the performance of bioreactors at single gas retention times and loading rates. The aim of this study was to evaluate biofilter performance as a function of gas retention time, loading rate, and bed height and to develop an empirical model based on these parameters. Furthermore, the influence of oxygen concentration on the removal efficiency was also evaluated.

3.3. Materials and Methods

3.3.1. Reactor Description

The experimental reactor consisted of five PVC sections (Fig. 1), each with an inner diameter of 170 mm and a height of 300 mm. Four of the five sections were packed with support media, with the lower section serving as a liquid reservoir. Each section, separated by a sieve located at the bottom, was packed to 50 mm from the top, forming a plenum to redistribute the gas flow. The total packed bed height was 1 m. Gas sampling points were located in each of the plenums, as well as at each of the inlet and outlet ports of the column. Two separate air streams

entered a mixing chamber having similar dimensions to one of the reactor sections. One air stream, set to a specific flow rate, passed through a humidifier before volatilizing the carbon source of interest. The carbon source was supplied via a syringe pump (Harvard Apparatus), before entering the mixing chamber. The other air stream, also set to a specific flow rate, supplied a nebuliser (Hospitak Upmist) with ambient air to produce a mineral salt medium aerosol (Table 1). This aerosol and toluene (UnivAR 98.8% Saarchem) stream converged in the mixing chamber prior to entering the reactor. The reactor was operated in a directional-switching mode where the flow direction was switched every 3.5 days to ensure uniform distribution of the biomass throughout the reactor (du Plessis et al. 1998). Such uniform biomass distribution and, therefore, toluene degradation capacity were subsequently assumed in the model. Bed height references were related to the inlet position of the reactor.

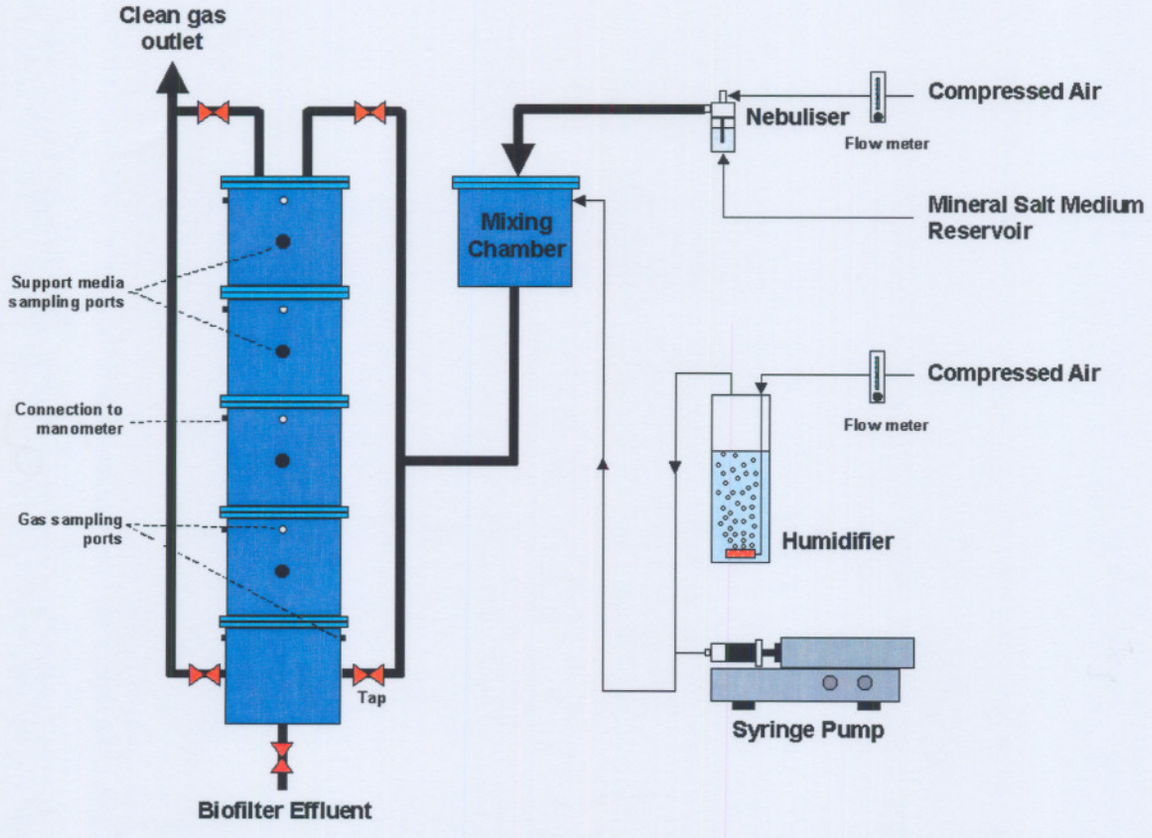

Fig. 1 Schematic presentation illustrating the biofilter system set-up

Table 1 Mineral salt medium composition

Compound	Concentration (g/L)
K_2HPO_4	1.5
KH_2PO_4	0.5
KNO_3	5
$MgSO_4.7H_2O$	0.2
0.5 M EDTA	0.16 mL
Trace mineral solution (Feidieker et al. 1994)	2 mL

3.3.2. Support Media

The reactor was packed with composted pine bark (fraction size 5-12 mm) (Starke Ayres), mixed with one third (v/v) Perlite (Genulite) (fraction size 2-5 mm) (Chemserve Perlite). This resulted in a packed bed volume of 20.26 L and air fill porosity of 13.12 L (35.2 % air fill porosity).

3.3.3. Inoculation

The reactor was inoculated with microbial inoculum from a previous study (du Plessis et al. 1998). The biofilter was filled with this acclimated culture and drained after 12 hours.

3.3.4. Microorganism Identification

Aseptic techniques were used to sample compost via the support media sampling ports after 270 days of continuous operation. These were suspended in a 0.2 % sterile *tetra*-sodium pyrophosphate solution to disassociate the biofilm and to loosen the attached microorganisms from the support media. After performing a dilution series, 1 mL of this solution was plated onto nutrient agar. After purifying the isolates, the bacteria were identified using the Biolog® Identification System (Biolog Inc. Hayward, CA) according to the manufacturer instructions.

3.3.5. Analytical Methods

Gas samples were collected from the biofilter in 5-mL gas-tight sampling syringes (Hamilton Series #1005) equipped with Teflon Mininert® fittings. Samples were analysed using a gas chromatograph (Hewlett-Packard Co.) equipped with a 0.5-mL heated (120°C) gas sample loop and a flame ionisation detector (FID). A HP-5 (Hewlett-Packard Co.) column (15 m x 0.53 mm) was used with N_2 as the carrier gas at a flow rate of 0.6 mL min^{-1}. The make-up gas flow rate to the detector contained H_2 (30 mL min^{-1}) and synthetic air (390 mL min^{-1}). The column temperature was kept constant at 104°C, the injector at 160°C and the detector at 280°C.

3.3.6. Effect of Toluene Loading Rates and Retention Times on Removal Efficiencies

To determine the performance of the biofilter, toluene loading rates ranging from 9.04 to 54.21 g m^{-3} h^{-1} were evaluated at various gas retention times (0.25 to 3.0 minutes). The various loading rates were tested starting at the lowest loading rate and incrementally increased to a maximum loading rate of 54.21 g m^{-3} h^{-1}. At each loading rate different retention times were tested starting at the longest retention time (3.0 minutes). The retention times were incrementally decreased. At each set of parameter conditions, gas chromatograph analyses were done until steady state conditions were reached and the biofilter was acclimatised to the specific conditions. Toluene sampling and analyses were then performed for each reactor section (i.e. different bed heights). The model assumptions were, therefore, based on the prevalence of steady state reactor conditions in the reactor.

3.3.7. Effect of Oxygen Concentrations on Removal Efficiencies

The normal airflow was replaced with various oxygen concentrations to determine the effect of reduced oxygen concentrations on removal efficiency. This was

achieved by adding nitrogen to the air supply at various ratios. Oxygen concentrations were measured using a PCO4 portable carbon dioxide and oxygen analyser (Gas Data Ltd.). The toluene loading rate (32.75 g m^{-3} h^{-1}) and gas retention (0.76 minutes) were kept constant, while the removal efficiencies under various oxygen concentrations were determined.

3.4. Results and Discussion

The toluene removal efficiencies (*RE*) for each of the various heights (*H*) were determined at six different loading rates (*L*) and retention times (*t*) ranging from 0.25 to 3.0 minutes. The removal efficiencies for the outlet (bed height of 1.0 m), at various loading rates, are given in Fig. 2. The parameter values *a* and *b* (Eq. 1) were used to describe the relationship between removal efficiency and retention time at various loading rates and bed heights (Table 2).

$$RE = a(1 - e^{-bt}) \tag{1}$$

Parameters *a* and *b* were then individually fitted to describe their relationship with loading rate at different bed heights (*H*). This relationship was described using Eq. 2 and 3 for parameter *a* and *b*, respectively (Table 2).

$$a = \frac{c}{1 + e^{-\left(\frac{L-d}{f}\right)}} \tag{2}$$

$$b = g + hL \tag{3}$$

Using the above equations, a parameter set (Table 3) for each of the different bed heights was generated. The relationships between each of the parameter values (Table 3) and bed height (*H*), was described using Eq. 4 through 8.

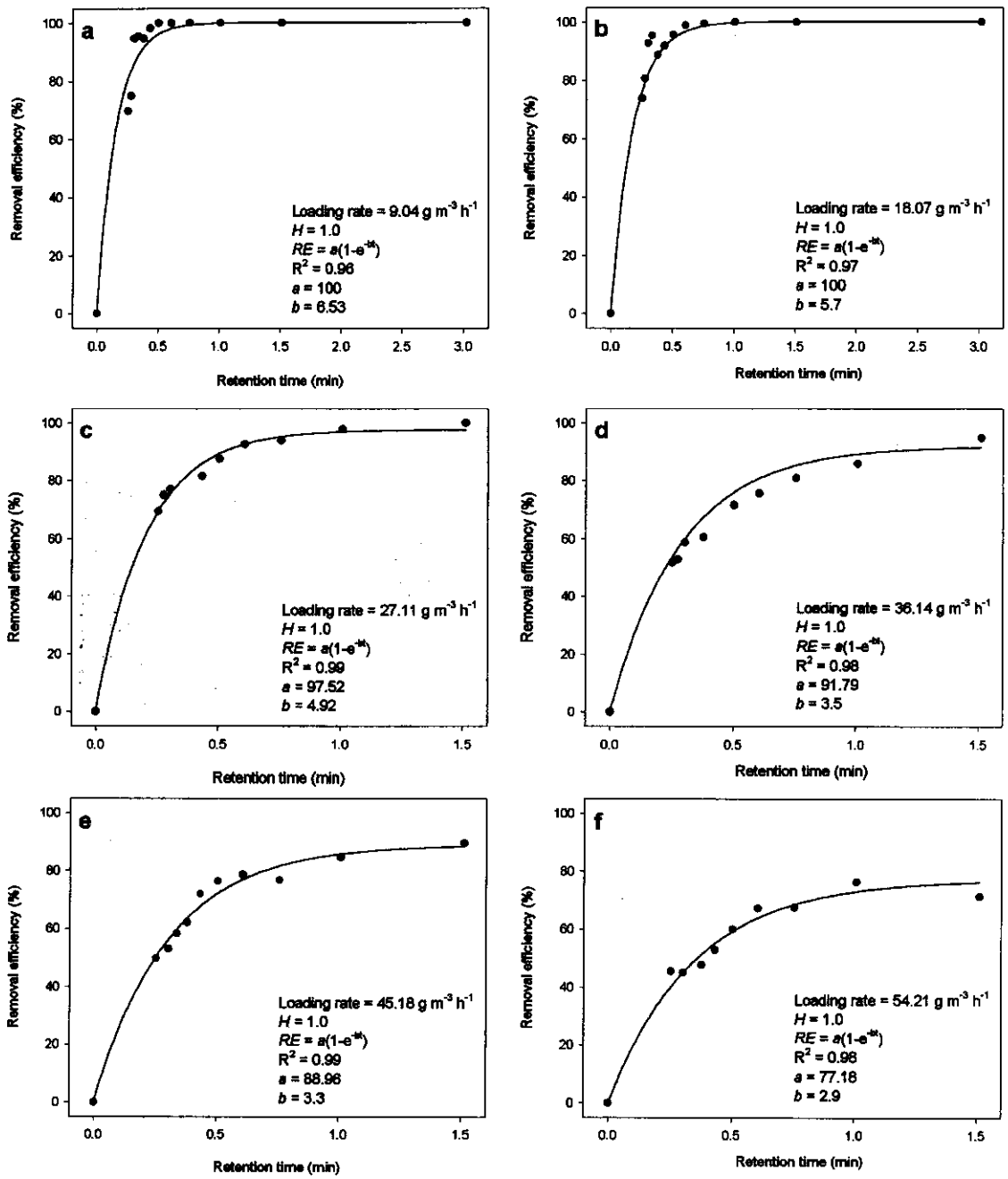

Fig. 2 Effect of retention time on toluene removal efficiency at a loading rate of (**a**) 9.04 g m^{-3} h^{-1}; (**b**) 18.07 g m^{-3} h^{-1}; (**c**) 27.11 g m^{-3} h^{-1}; (**d**) 36.14 g m^{-3} h^{-1}; (**e**) 45.18 g m^{-3} h^{-1}; (**f**) 54.21 g m^{-3} h^{-1} (Data generated at a bed height of 1.0 m)

Table 2 Value parameters *a* and *b* (Eq. 1) for various loading rates and bed heights

	Bed height (m)							
	1.0		0.75		0.5		0.25	
	Parameter		Parameter		Parameter		Parameter	
Loading rate ($g\ m^{-3}\ h^{-1}$)	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*
9.04	100	6.53	100	4.48	99.12	2.6	99.31	1.4
18.07	100	5.7	97.19	4.1	94.81	2.55	86.12	1.59
27.11	97.52	4.92	89.83	3.57	80.16	2.53	60.0	1.91
36.14	91.79	3.5	80.76	3.0	64.5	2.5	33.67	2.3
45.18	88.96	3.3	74.31	2.9	59.47	2.45	33.79	2.76
54.21	77.18	2.9	59.76	2.5	46.89	2.44	24.28	2.9

Table 3 Value parameters *c,d,f* (Eq. 2) and *g,h* (Eq. 3) for various bed heights

	Equation 2			Equation 3	
	Parameter			Parameter	
Bed height (m)	*c*	*d*	*f*	*g*	*h*
1.0	100.95	67.74	-12.24	7.15	-0.08
0.75	108.3	58.88	-19.71	4.86	-0.04
0.5	141.44	34.53	27.84	2.63	-0.0036
0.25	182.45	13.55	-20.91	1.01	0.036

$$c = \frac{218.3 - (362 \times H) + (196.87 \times H^2)}{1 - (1.08 \times H) + (0.61 \times H^3)} \quad (4)$$

$$f = -28.14 \times e^{\left[-0.5\left(\frac{H-0.48}{0.35}\right)^{1.29}\right]} \quad (5)$$

$$d = 14.82 - (74.7 \times H) + (328.86 \times H^2) - (201.24 \times H^3) \quad (6)$$

$$g = -1.26 + (8.27 \times H) \quad (7)$$

$$h = 0.08 - (016 \times H) \quad (8)$$

Substitution of equations 4 through 8 into 2 and 3, and 2 and 3 into 1, provided an empirical model which described the removal efficiency of toluene as a function of gas retention time (EBRT = retention time (L min^{-1}) x 2.84), loading rate and bed height. This empirical equation fitted to the entire data set had and overall R^2 value of 0.98. The reactor performance, as described by the empirical model (for the outlet, i.e. 1.0 m bed height), is shown in Fig. 3. Removal efficiencies greater than 90 % were achieved when the toluene loading rate was lower than 42 g m^{-3} h^{-1} and the retention time greater than 0.32 minutes (19.2 seconds). From the contour plot it is evident that at a retention time of less than 0.32 minutes, the removal efficiency of the reactor decreased significantly. This result is most likely due to a combination of mass transfer limitations and rate limiting toluene degradation capability within the biofilm.

The effects of oxygen concentration on the removal efficiencies at various bed depths were also evaluated (Fig. 4). This effect was evaluated at a single loading rate (32.75 g m^{-3} h^{-1}) and retention time (0.76 minutes). From these results it is evident that oxygen became limiting at concentrations below 5 %.

The relationship between toluene removal efficiency and oxygen concentration at various bed depths, is described by Eq. 9 through 11 with parameter values shown in Table 4.

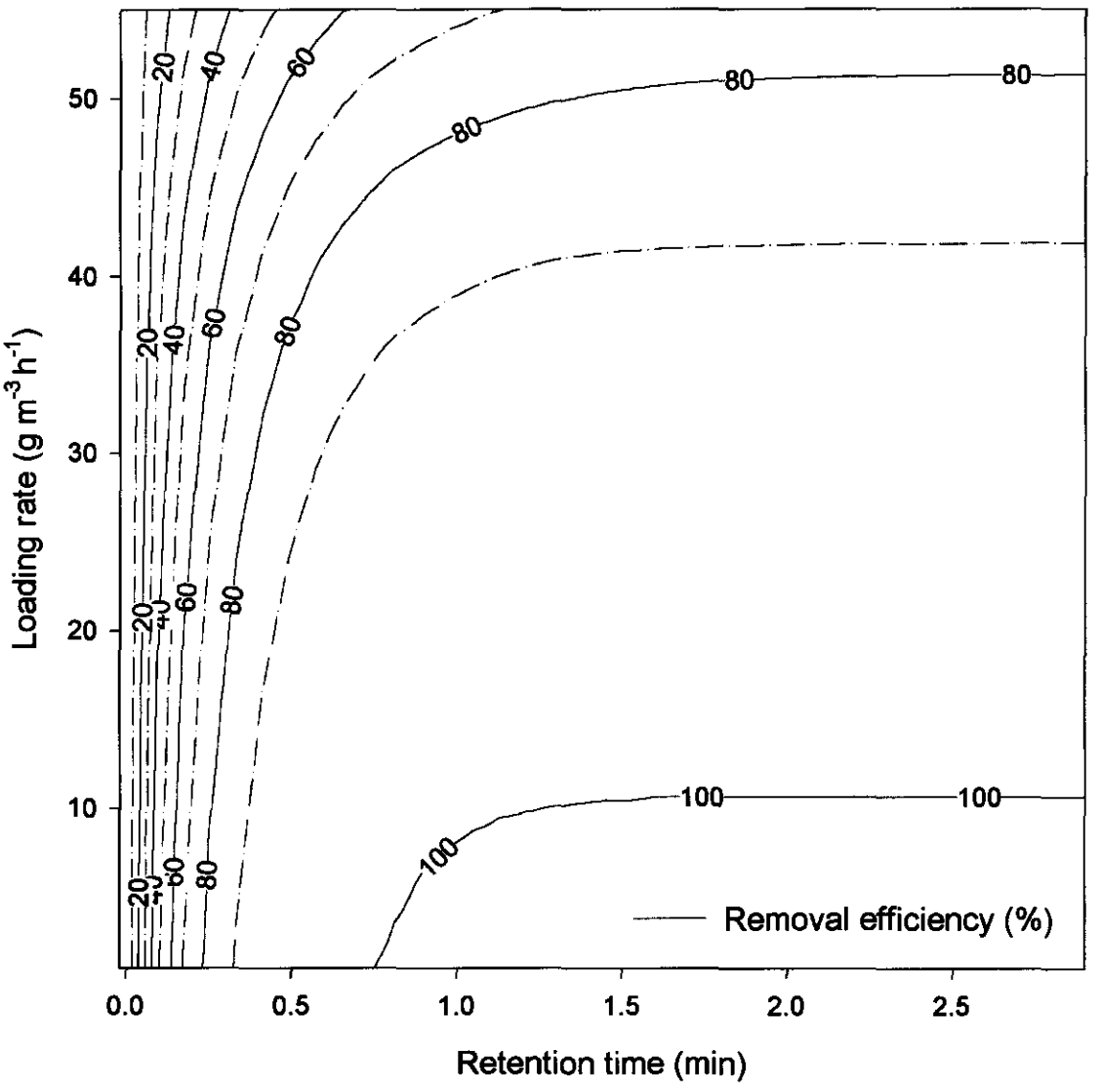

Fig. 3 Contour plot generated using the described empirical model. Data represents removal efficiencies for the outlet at a bed height of 1.0m

$$RE = \frac{m[O_2]}{n + [O_2]} \tag{9}$$

where,

$$m = -180.31 + \frac{283.74}{\left[1 + e^{-\left(\frac{H-0.88}{0.19}\right)}\right]^{59.02}} \tag{10}$$

$$n = 3.54 - (3.08 \times H) \tag{11}$$

Bacterial isolation and identification was done at the end of the experimentation period to give an indication of the bacterial species present at steady state conditions (loading rate of 32.75 g m^{-3} h^{-1} at a retention time of 0.76 minutes). The bacteria isolated were: *Corynebacterium jeikeium A*; *Corynebacterium nitrilophilus*; *Micrococcus luteus*; *Pseudomonas mendocina*; *Sphingobacterium thalphophilum*; and *Turicella otitidis*. Although this information does not provide information as to the relative contribution of each species to toluene degradation and other functions within the reactor, it does provide useful information for comparisons with other studies. *Corynebacterium*, *Micrococcus* and particularly *Pseudomonas* genera have been reported to degrade a wide range of hydrocarbons (Atlas 1981; Andreoni et al. 1997; Kleinheinz and Bagley 1998; Oh and Bartha 1997). Their presence is, therefore, not surprising. No other references could, however, be found which reported the occurrence of *Sphingobacterium* and *Turicella* species in biofiltration or other hydrocarbon degrading systems. It is likely that some of the identified species were responsible for toluene degradation while others were opportunistic bacteria living off the secondary carbon substances produced as a by-product of toluene degradation. The effective role of such species could, therefore, be to limit biomass and biofilm fouling of the reactor.

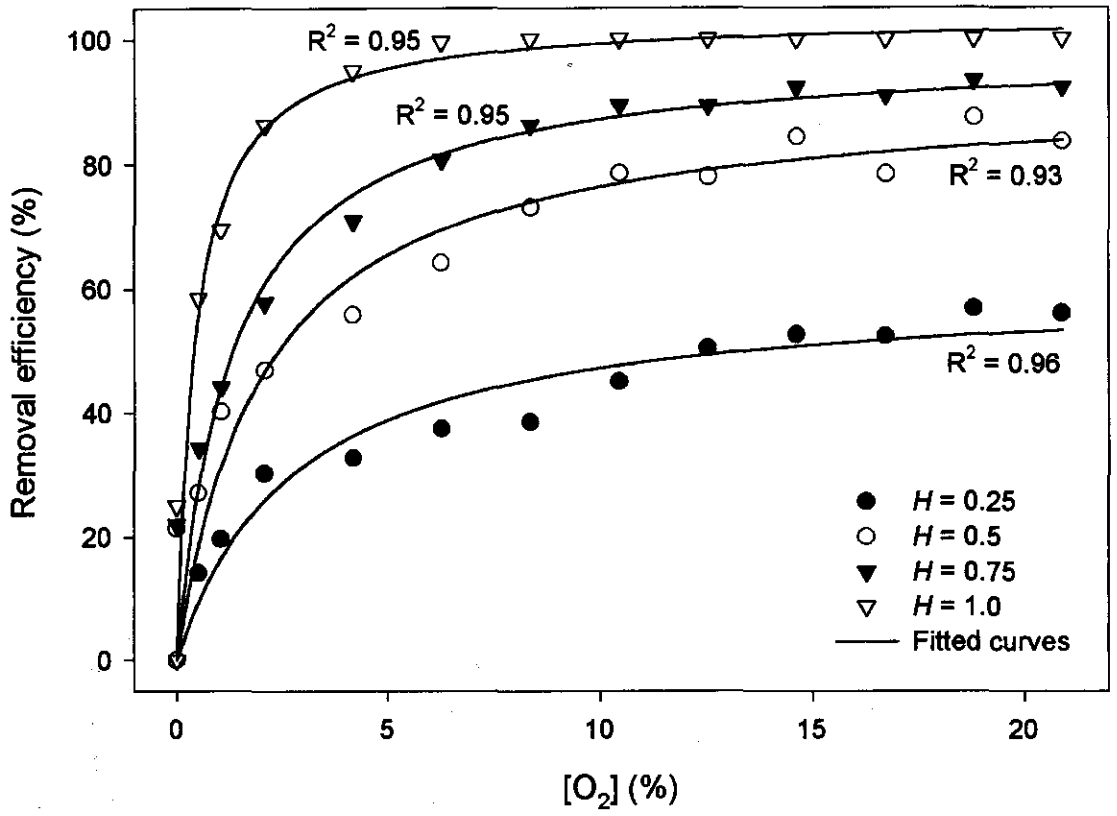

Fig. 4 Effect of oxygen concentration on the toluene removal efficiency

Table 4 Value parameter *m* and *n* (Eq. 9) for various bed heights

	Parameter	
Bed height (m)	***m***	***n***
0.25	60.30	2.76
0.5	91.69	2.0
0.75	98.33	1.28
1.0	103.56	0.43

3.5. Conclusions

Toluene removal efficiencies exceeding 90 %, in the absence of oxygen limitation, were obtained when the biofilter was subjected to a gas retention time in excess of 0.25 minutes (18 seconds) and loading rates below 42 g m^{-3} h^{-1}. These results represented significantly improved biofilter performance than those reported in several other similar studies (Ottengraf 1986; Shareefdeen and Baltzis 1994; Kirchner et al. 1989; Morales et al. 1994; Ottengraf and van den Oeven 1983;

Sorial et al. 1994). The model deduced from this study represents the first comprehensive empirical model to describe toluene removal efficiency in a biofilter as a function of gas retention time, loading and bed height. The experimental data upon which the model is based is, however, specific to the particular set of conditions under which the experiments were conducted. Application of the model to other scenarios might, therefore, not be entirely accurate. Despite these limitations, the model could be useful in estimating potential reactor performance of similar biofilter systems.

The relationship between oxygen concentration and toluene removal efficiency was obtained at a single toluene loading rate and gas retention time. Although this relationship might be somewhat different under other reactor conditions, it does provide a useful estimate of the minimum oxygen requirement for toluene degradation in similar biofilters.

3.6. Acknowledgements

This research was sponsored by Sasol Technology (R&D division) and the National Research Foundation.

3.7. Notation

The following symbols are used:

RE = Removal efficiency (%)

$[O_2]$ = Oxygen concentration

L = Loading rate (g m^{-3} h^{-1})

t = Retention time (minutes)

H = Packed bed height (m)

$a - n$ = Equation fitting parameters

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4. BTEX catabolism interactions in a toluene-acclimatized biofilter

4.1. Abstract

BTEX substrate interactions for a toluene-acclimated biofilter consortium were investigated. Benzene, ethylbenzene, *o*-xylene, *m*-xylene and *p*-xylene removal efficiencies were determined at a loading rate of 18.07 g m^{-3} h^{-1} and retention times of 0.5 - 3.0 minutes. This was also repeated for toluene in a 1:1 (m/m) ratio mixture (toluene: benzene, ethylbenzene, or xylene) with each of the other compounds individually to obtain a final total loading of 18.07 g m^{-3} h^{-1}. The results obtained were modelled using Michaelis-Menten kinetics and an explicit finite difference scheme to generate v_{max} and K_m parameters. The v_{max} / K_m ratio (a measure of the catalytic efficiency, or biodegradation capacity, of the reactor) was used to quantify substrate interactions occurring within the biofilter reactor without the need for free-cell suspended and monoculture experimentation. Toluene was found to enhance the catalytic efficiency of the reactor for *p*-xylene, while catabolism of all the other compounds was inhibited competitively by the presence of toluene. The toluene-acclimatized biofilter was also able to degrade all of the other BTEX compounds, even in the absence of toluene. The catalytic efficiency of the reactor for compounds other than toluene was in the order: ethylbenzene > benzene > *o*-xylene > *m*-xylene > *p*-xylene. The catalytic efficiency for toluene was reduced by the presence of all other tested BTEX compounds, with the greatest inhibitory effect being caused by the presence of benzene, while *o*-xylene and *p*-xylene caused the least inhibitory effect. This work illustrated that substrate interactions can be determined directly from biofilter reactor results without the need for free-cell and monoculture experimentation.

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4.2. Introduction

Biotreatment processes are applied increasingly to waste gases. The advantages offered by these processes are the relatively low operational costs and their environmental friendliness. Several reports have successfully demonstrated the use of biofilters for the treatment of petroleum (gasoline) and BTEX (benzene, toluene, ethylbenzene and xylene) compounds (Oh and Bartha 1997; Wright et al. 1997; Devinny et al. 1999). The use of a combination of volatile organic carbon compounds, such as BTEX, often results in interactions between the various components, which in turn affect the treatment efficiency of each individual compound (Haigler et al. 1992). It is therefore important to understand the substrate interactions of these compounds with respect to their microbial degradation. All of the cited studies investigated the substrate interactions of BTEX compounds with monocultures and microbial associations in homogenous (free-cell) batch reactors. Little research however has been conducted on the effects of transient BTEX compounds and their substrate interactions during *in situ* biofiltration. The aim of this study was therefore to investigate individual BTEX substrate interactions *in situ*, as affected by a toluene-acclimatized biofilter consortium, and to develop a method to evaluate substrate interactions in the reactor. The main focus of this investigation was to elucidate the effects of toluene on the biodegradation of the other BTEX compounds and, in turn, the effects these compounds would have on toluene degradation within a biofilter.

4.3. Materials and Methods

4.3.1. Reactor Description

The experimental reactor (Fig. 1) consisted of five PVC sections, each with an internal diameter of 17 cm and a height of 30 cm. Four of the five sections were packed with support medium, while the lowest section served as a liquid reservoir. Each section, separated by a stainless steel sieve located at the bottom, was

packed to 5 cm from the top, leaving a plenum to allow redistribution of the gas flow. Gas sampling points were located in each of the plenums and at each of the inlet and outlet ports of the column. Two separate air steams entered the mixing chamber, which had dimensions similar to those of each reactor section. One air stream, set to a specific flow rate, passed through a humidifier before volatilizing the carbon source of interest. The carbon source was supplied to the humidified air stream via a syringe pump (Harvard Apparatus). The second air stream, also set to a specific flow rate, supplied a nebuliser (Hospitak) with ambient air to produce a mineral salts solution aerosol (Table 1). This aerosol and carbon source(s) stream converged in the mixing chamber prior to entering the reactor. The reactor was operated in a directional-switching mode with a 3.5 day time interval (Kinney et al. 1996).

Table 1 Mineral salts composition

Compound	Concentration
K_2HPO_4	1.5 g L^{-1}
KH_2PO_4	0.5 g L^{-1}
KNO_3	5 g L^{-1}
$MgSO_4.7H_2O$	0.2 g L^{-1}
0.5 M EDTA	0.16 mL
Trace mineral solution (Feidieker et al. 1994)	2 mL

4.3.2. Support Medium

The reactor was packed with composted pine bark (fraction size 5-12 mm; Starke Ayres) mixed 2:1 with Perlite (Genulite; fraction size 2-5 mm; Chemserve Perlite. This resulted in a total packed bed volume of 20.26 L and air fill porosity of 7.14 L (35.2 % air-fill porosity).

4.3.3. Inoculation and acclimitization

The reactor was inoculated with a microbial consortium from a previous study (du Plessis et al. 1998) by filling the biofilter and draining it after 12 h. The biofilter bed was then acclimatized to toluene biodegradation over a period of 4 months at a loading rate of 32.75 g m^{-3} h^{-1} and retention time of 0.76 minutes. Steady-state

conditions, with toluene removal efficiency >99%, were established before commencing the experiments. The microbial consortium was previously described (Strauss et al. 2000).

4.3.4. Analytical Methods

Gas samples were collected from the biofilter in 5-mL gas-tight syringes (Hamilton Series No. 1005) equipped with Teflon Mininert fittings. The samples were analysed with a gas chromatograph (Hewlett-Packard) equipped with a 0.5-mL heated (120°C) gas sample loop and a flame ionisation detector. A HP-5 column (15 m x 0.53 mm; Hewlett-Packard) was used with N_2 as the carrier gas at a flow rate of 0.6 mL min^{-1}. The make-up gas flow rate to the detector contained H_2 (30 mL min^{-1}) and synthetic air (390 mL min^{-1}). The column temperature programme started at 80°C for an initial period of 1 min and increased at a rate of 3°C min^{-1} to a final temperature of 104°C. The injector and detector temperatures were maintained constant at 160°C and 280°C, respectively. Quantification was by external standards.

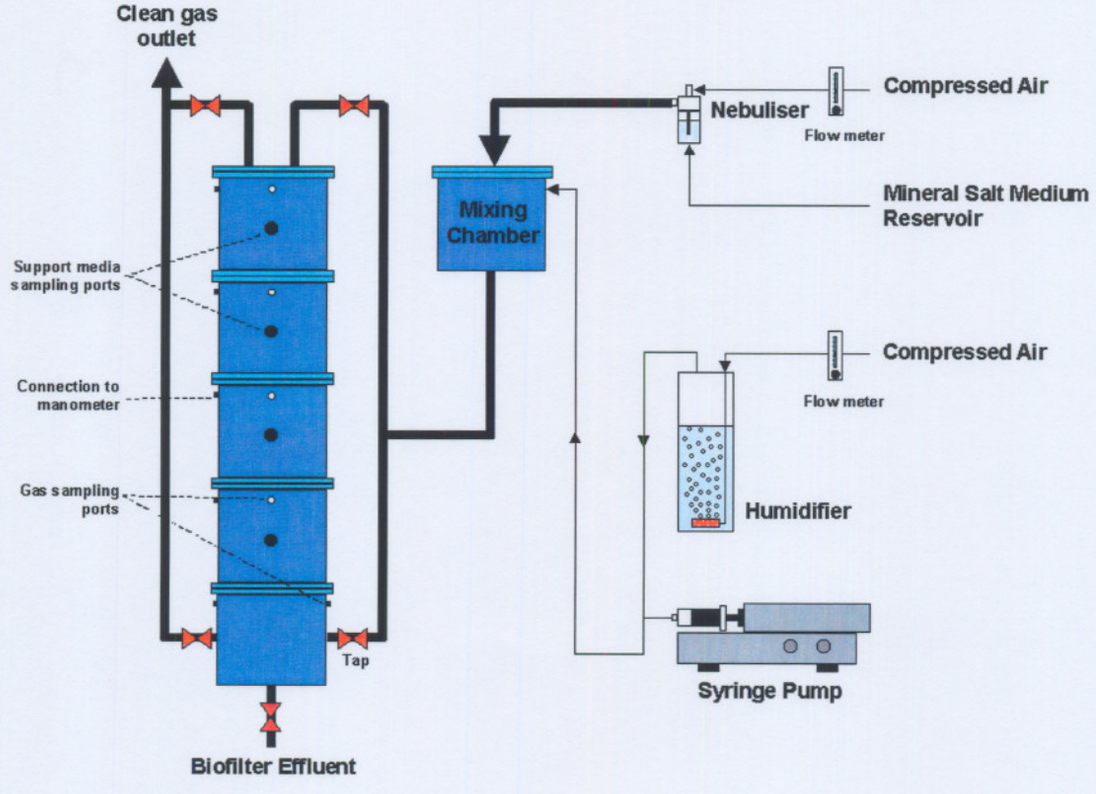

Fig. 1 Schematic diagram of the biofilter

4.3.5. Effect of Carbon Source and Retention Times on Removal Efficiencies

The effects of benzene, ethylbenzene, *o*-xylene, *m*-xylene and *p*-xylene on biofilter efficacy were evaluated at a fixed loading rate (18.07 g m^{-3} h^{-1}) and various gas retention times (0.5 - 3.0 minutes). This protocol was repeated for toluene mixed in a 1:1 (m/m) ratio with each of the other BTEX carbon sources, to obtain a total loading of 18.07 g m^{-3} h^{-1}. The removal efficiencies were determined at each reactor section (bed heights). The duration of each experiment was approximately 48 hours.

4.3.6. Modelling

The biofilter behaviour was modelled with the assumption that the microbial population was uniform and all the reactions occurred throughout the bed. The steady state model (Eq. 1) was used to model the system with boundary conditions $C(x=0) = C_o$. The rate of reaction was described by a Michaelis-Menten function (Eq. 2) where C_o is the inlet gas concentration into the reactor (mg L^{-1}); x the bed position (m), and u the linear gas velocity (m min^{-1}) in the reactor.

$$0 = u \cdot \frac{\partial C}{\partial x} - v(C) \qquad (1)$$

$$v = \frac{v_{max} C}{K_m + C} \qquad (2)$$

The equation was solved numerically using an explicit finite difference scheme. The model was fitted to the experimental data by minimizing the sum of squared errors using an optimization routine to generate values for the parameters v_{max} and K_m. The data did not facilitate the determination of absolute values for v_{max} and K_m because the substrate concentration ranges in all experiments were less than that required to obtain v_{max}. Under such conditions, however, the ratio of v_{max} / K_m can be used as a measure of the catalytic efficiency of the reactor (Smith et al. 1997). For pure enzymatic systems, the v_{max} / K_m rate is considered a fixed parameter in the absence of inhibition kinetics. Applied to a biofilter the v_{max} / K_m ratio provides

a useful parameter where deviations reflect the effects caused by non-Michaelis-Menten biofilm effects (including diffusional and other mass transfer effects).

In the case of gas-phase biofilters, the biofilm thickness is small compared to the diameter of the coated support medium (composted pine bark particles, in this case). Thus the number of mass-transfer units in biofilter beds is generally much higher than in liquid phase filter beds (Ottengraph and van den Oever 1983). The interface resistance in the gas phase can, therefore, generally be neglected and the biofilm concentration at the interface assumed to be in equilibrium with the concentration of the bulk gas. Mass transfer effects, if present, would therefore mainly be diffusion limitations (Ottengraph and van den Oever 1983). The relatively simply model used in this study does not take into account mass transfer interactions (Dehusses et al. 1995). Because the model excludes mass transfer effects, any deviation in v_{max} / K_m ratios, e.g. as a function of retention time, would represent non-Michaelis-Menten (diffusion) effects.

4.4. Results

Benzene, ethylbenzene, *o*-xylene, *m*-xylene and *p*-xylene (BEX compounds, i.e. excluding toluene) were applied individually to the toluene-acclimatized biofilter at a loading rate of 18.07 g m^{-3} h^{-1} and retention times which ranged over 0.5 - 3.0 minutes. A fixed loading rate for all compounds was used in order to facilitate comparisons of catalytic efficiencies of the biofilter for these compounds. The concentration profile throughout the reactor was measured for each component and retention time at regular intervals, until pseudo-steady state was reached after approximately 3 hours. After each test, steady-state toluene conditions (i.e. loading rate of 18.07 g m^{-3} h^{-1}, retention time of 0.76 minutes, 3.5-day directional switching for a total period of 7 days) were reinstated to prevent acclimatisation to BEX molecules. Although the enzymes involved in toluene catabolism are also known to catabolize a wide range of similar hydrocarbon compounds (Sun and Wood 1997), direct acclimatisation to the BEX compounds had to be avoided in order that conclusions could be drawn on the capacity of a toluene-acclimatized biofilter consortium to catabolize BEX molecules. The

application protocol was then repeated with 1:1 (m/m) ratios of benzene, ethylbenzene, *o*-xylene, *m*-xylene and *p*-xylene with toluene. The combined loading rate was again maintained at 18.07 g m^{-3} h^{-1} and retention times ranged from 0.5 - 3.0 minutes. An example of a concentration profile (*p*-xylene/toluene), measured at various bed heights, is illustrated in Fig. 2. The curve represents the fitted Michaelis-Menten model function described earlier. Experimental data obtained for the various bed heights were fitted numerically to generate values for the parameters v_{max} and K_m. This enabled determination of the v_{max} / K_m ratios for each of the compounds individually and in combination with toluene. The ratios obtained for each of the retention times and the various carbon sources (single/dual) are shown in Fig. 3a-e. Each datum point in these figures represents a concentration profile similar to Fig. 2. The relationship between the v_{max} / K_m ratio and retention time for each molecule and mixture was described using Eq. 3. The curve-fitting parameters, *a* and *b* in Eq. 3, which were obtained for each loading (Fig. 3a-e) are summarised in Table 2.

$$\frac{v_{max}}{K_m} = \frac{ab}{b+\tau} \qquad (3)$$

Using the curves in Fig. 3a-e and the parameter values in Table 2, the substrate interactions between toluene and the individual BEX compounds were calculated. A dimensionless substrate interaction value was calculated at each retention time datum point by, e.g. subtracting the v_{max} / K_m ratio value for benzene in the absence of toluene from the v_{max} / K_m ratio value for benzene in the presence of toluene and then dividing the total by the v_{max} / K_m ratio for benzene in the absence of toluene. Such values (Fig. 4) illustrate, in a qualitative manner, the effect of toluene on the catabolism of individual BEX compounds.

Since the presence of toluene affected the catabolism of BEX molecules, these molecules in turn must have affected toluene catabolism (Fig. 5a, b). The curves in these figures were again fitted using Eq. 3, with the parameters detailed in Table 3. Again, the substrate interaction values were calculated (Fig. 6).

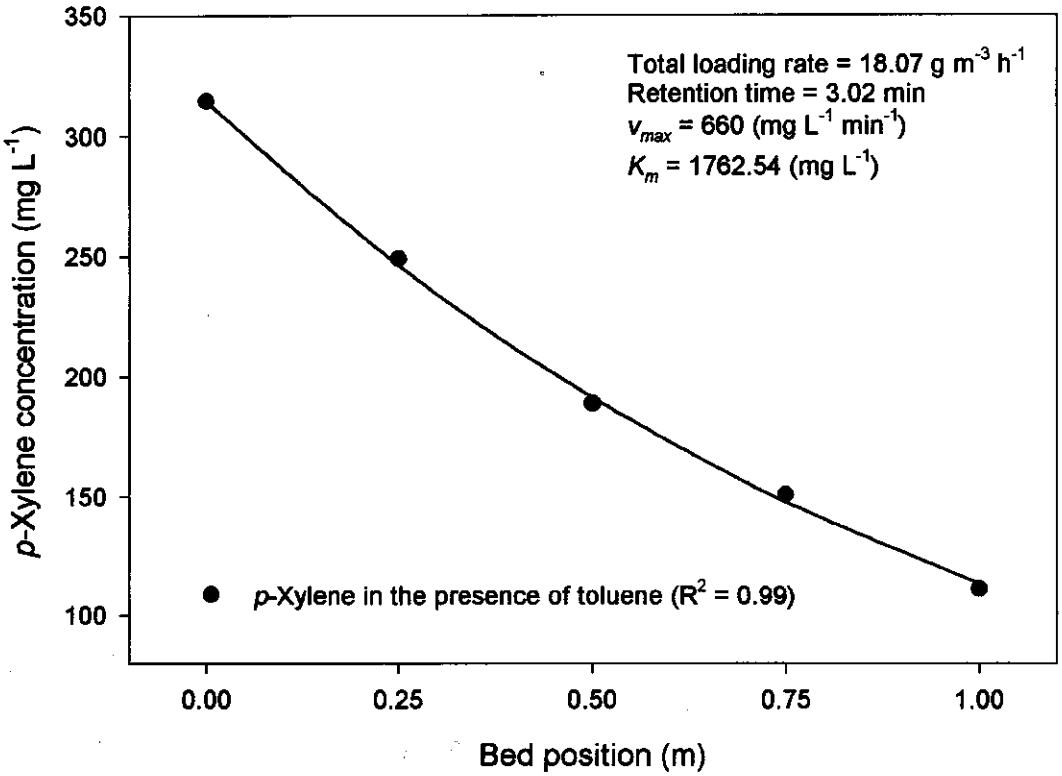

Fig. 2 Removal efficiencies obtained for a 1:1 (m/m) ratio p-xylene/toluene mixture at a final loading of 18.07 g m^{-3} h^{-1} and a retention time of 3.02 minutes. The data were fitted numerically to determine v_{max}/K_m ratios for the two carbon sources

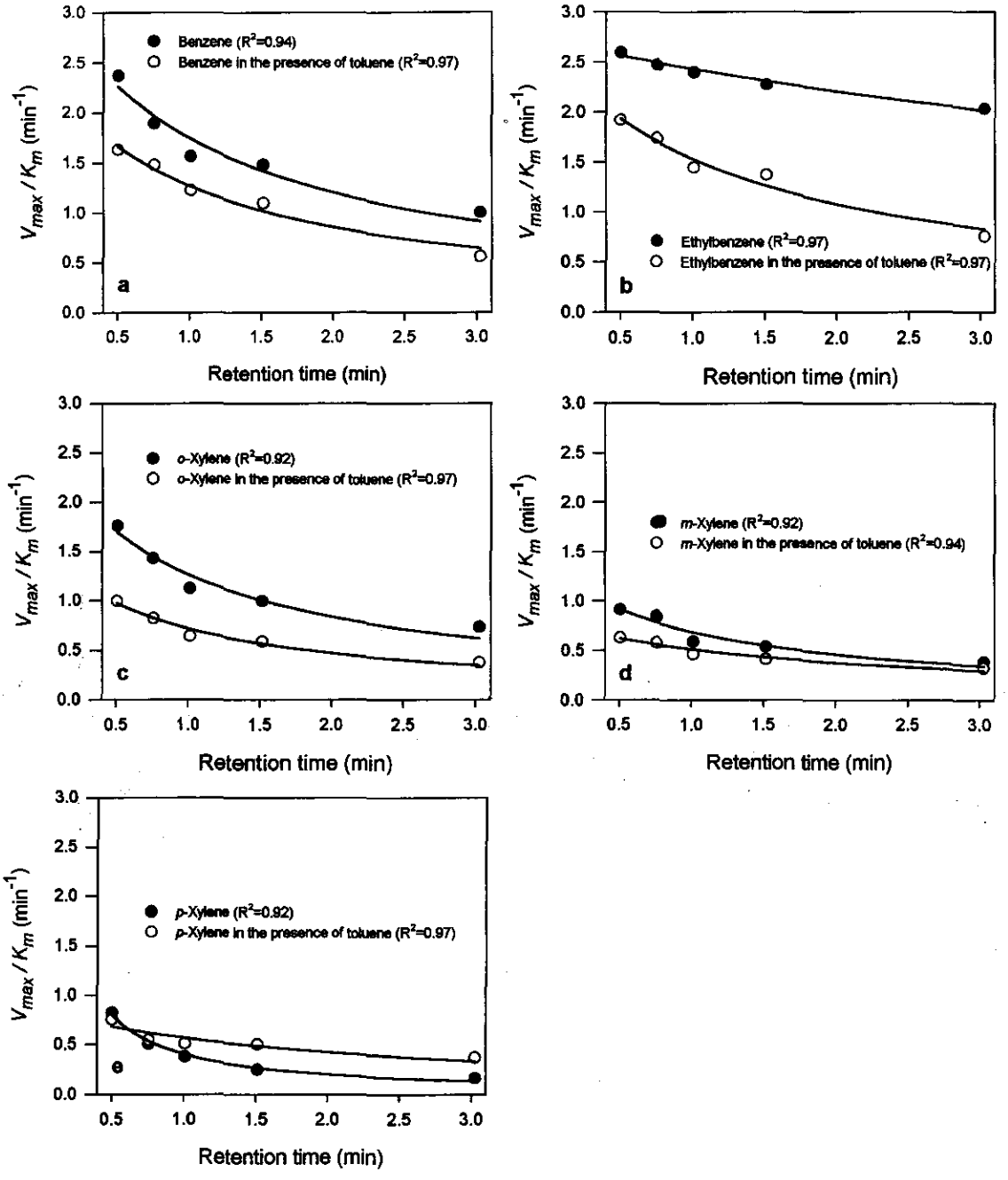

Fig. 3 The effect of toluene, as illustrated by the v_{max}/K_m ratio as a function of retention time, on benzene (**a**), ethylbenzene (**b**), *o*-xylene (**c**), *m*-xylene (**d**), and *p*-xylene (**e**)

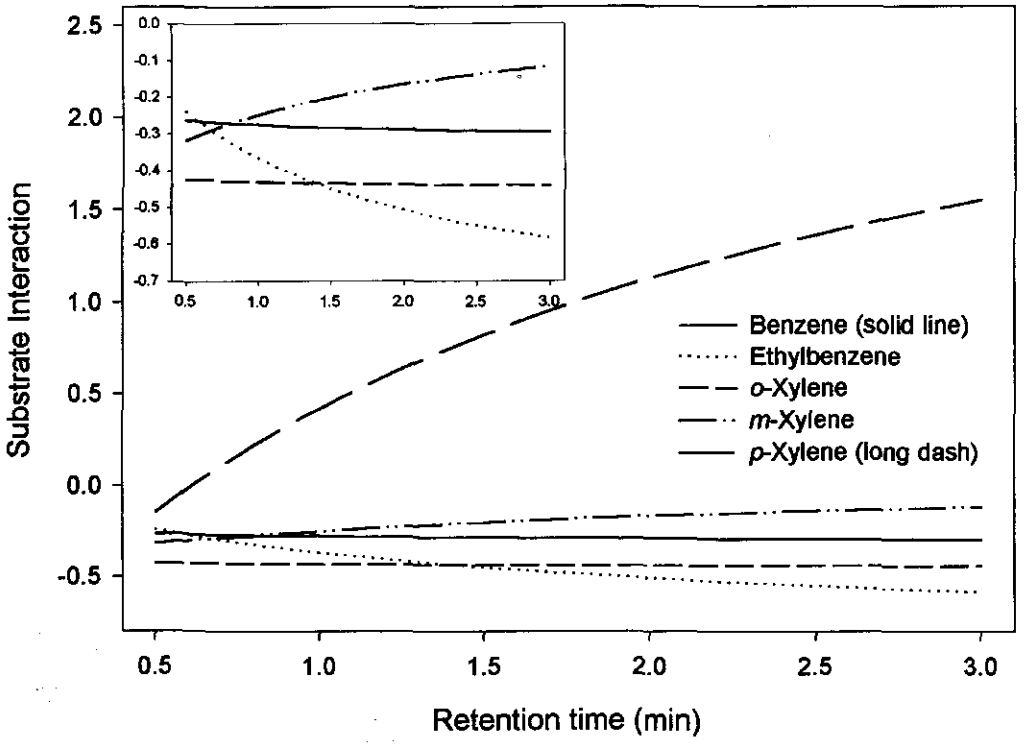

Fig. 4 The effects of toluene on BEX compounds, as illustrated by the substrate interaction values, for y-axis ranges from –0.5 to 2.5 and from –0.7 to 0.0 (*insert*)

Table 2 Fitting parameter values for Fig. 3a-e

	Parameter	Benzene	Ethylbenzene	*o*-Xylene	*m*-Xylene	*p*-Xylene
Carbon source in the absence of toluene	***a***	3.224	2.691	2.595	1.364	55.200
	b	1.180	8.828	0.949	1.015	0.007
Carbon source in the presence of toluene	***a***	2.458	2.647	1.528	0.793	0.858
	b	1.056	1.365	0.885	1.807	1.958

Table 3 Fitting parameter values for Fig. 5b

Parameters	Benzene	Ethylbenzene	*o*-Xylene	*m*-Xylene	*p*-Xylene
a	1.57	0.94	3.13	1.63	0.88
b	2.83	4.53	3.60	3.36	5.66

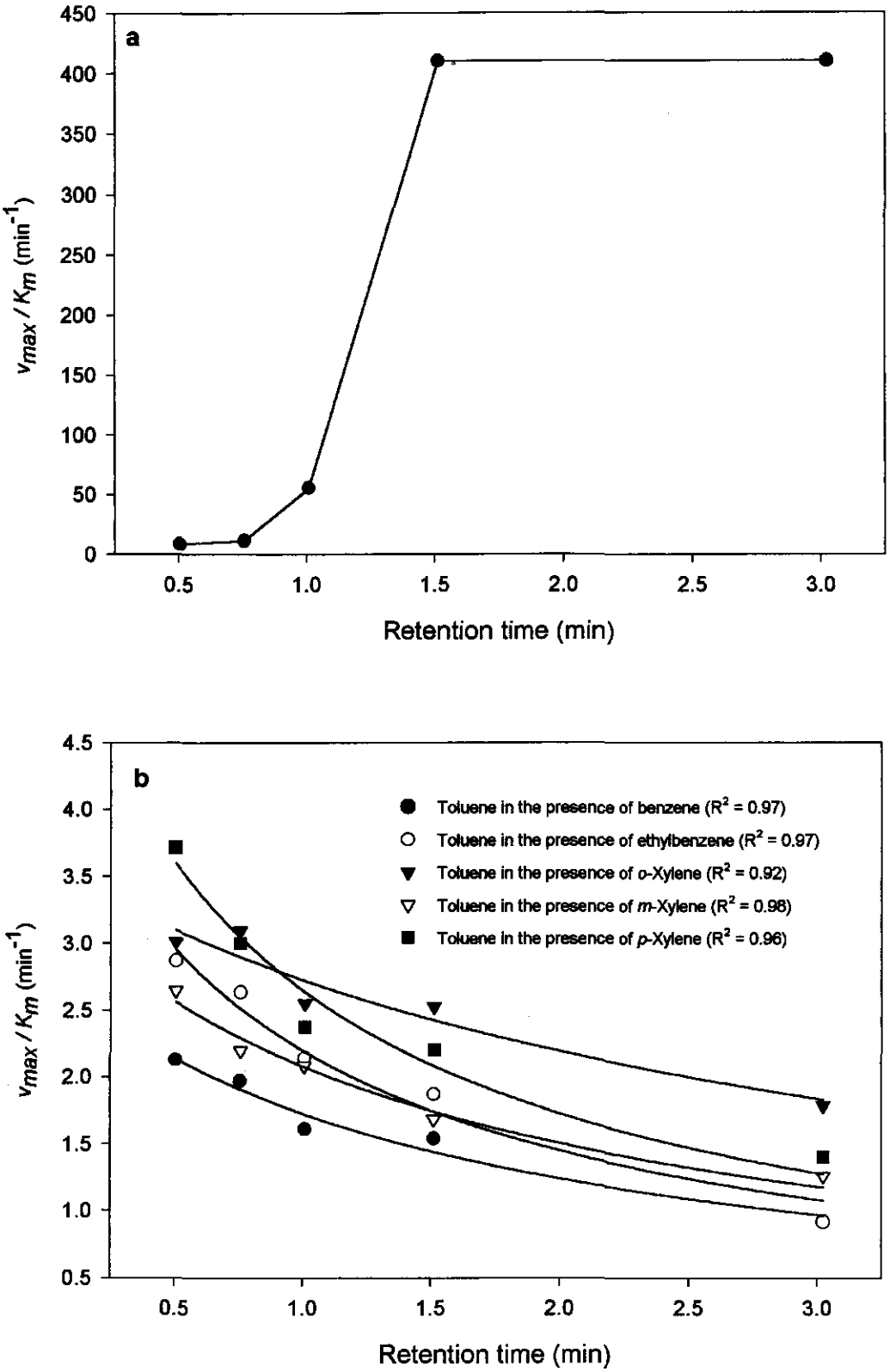

Fig. 5 v_{max}/K_m ratios, as a function of time, for toluene in the absence (**a**) and presence (**b**) of BEX molecules

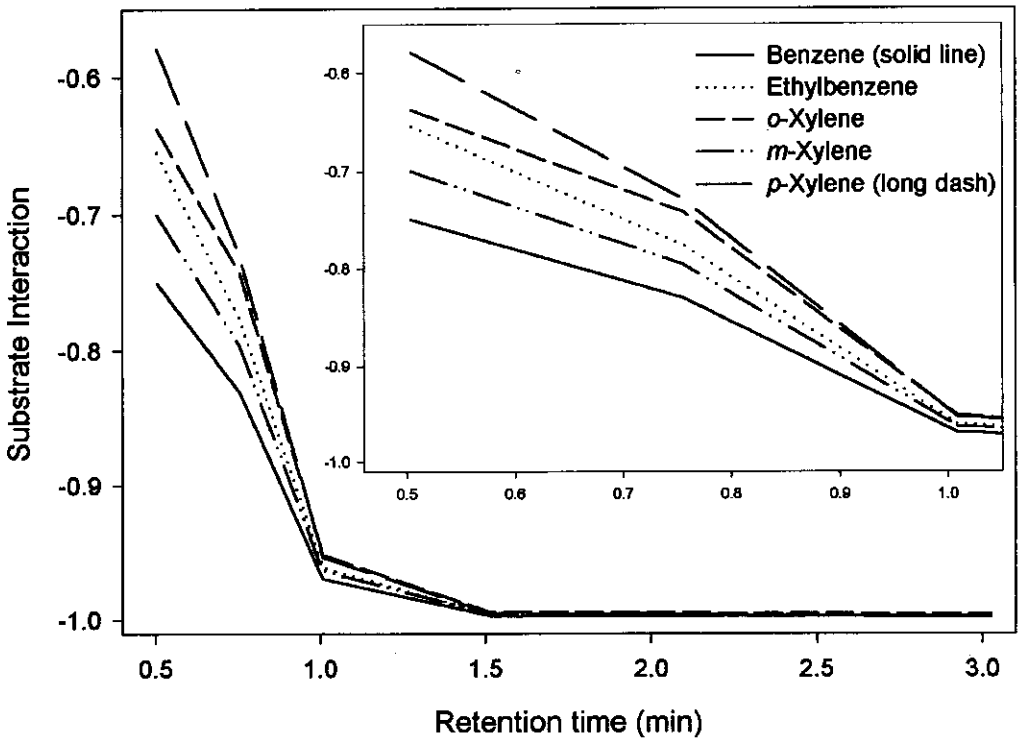

Fig. 6 The effects of the BEX compounds on toluene, as illustrated by the substrate interaction values, for x-axis ranges 0.5-3.0 and 0.5-1.0 (*insert*)

4.5. Discussion

4.5.1. The effects of toluene on the biodegradation of BEX molecules

High (positive) v_{max} / K_m ratios represent high catalytic / biodegradation efficiencies for a particular compound. For BEX molecules biofilter efficacy was in general greater in the absence of toluene (Fig. 3a-d). Thus, toluene competed for biodegradation capacity within the biofilter to the detriment of BEX molecule catabolism (Chang et al. 1993; Oh et al.1994; Yerushalni and Guiot 1998). The one exception was *p*-xylene (Fig. 3e), where greater catabolic activity was attributed to a co-metabolic effect (Alvarez and Vogel 1991; Arcangeli and Arvin 1995; Tsao et al. 1998; Deeb and Alvares-Cohen 1999).

In the absence of toluene, catabolic activity was ranked ethylbenzene > benzene > *o*-xylene > *m*-xylene > *p*-xylene. The ability of the toluene-acclimatized microbial

association to catabolize BEX compounds was attributed to similar catabolic pathways (Di Lecce et al. 1997). The biodegradation pathways for *o*-xylene and *m*-xylene have been found to be similar to each other, but different from the catabolic pathway for *p*-xylene (Smith 1990). The biodegradation of *m*- and *p*-xylenes result in two different methylcatechols (3-methylcatechol from *m*-xylene and 4-methylcatechol from *p*-xylene). The comparatively low efficiency of *p*-xylene catabolism and the requirement for co-metabolism could be ascribed to: (1) the fact that the ring-fission products of these two different methylcatechols are catabolized by different enzyme systems (Duggleby and Williams 1986) and (2) the possible accumulation and polymerization of intermediates such as 3,6-dimethylcatechol (Chang et al. 1993; Oh et al. 1994; Yerushalmi and Guiot 1998).

Substrate interaction values > 0, reflect a positive influence of toluene on the biodegradation of the second carbon source, while a negative value indicates competition or inhibition (Fig. 4). Thus, only *p*-xylene catabolism was enhanced by the presence of toluene. Inhibitory or competitive effects of toluene were most prominent for *o*-xylene (retention time ≤ 1.5 minutes) and ethylbenzene (retention times > 1.5 minutes). For all molecules, toluene-BEX interactions were dependent on the gas retention time probably due to mass transfer effects within the reactor bed.

4.5.2. The effects of BEX molecules on toluene catabolism

The addition of each of the BEX compounds, particularly benzene, in a 1:1 (m/m) mixture with toluene, had a detrimental effect on toluene degradation (Fig. 5). Substrate interaction value calculations (Fig. 6) showed that differentiation between the inhibitory effects of different molecules was impossible with retention times > 1 minute, due to toluene mineralization in the first sections of the reactor bed and, thus, no assayable concentrations at the reactor outlet. All the BEX molecules competed for biodegradation capacity within the reactor thereby reducing the toluene biodegradation capacity. This competition is ascribed to similarities in catabolic pathways and enzymatic systems of these structurally related molecules (Schraa et al. 1987; Smith 1990). The observed competition

increased with the retention time (Fig. 6), probably due to non-Michaelis-Menten (i.e., biofilm diffusion) effects. A comparison of Fig. 6 with Fig. 4 shows that toluene catabolism was more limited (more negative substrate interaction values) by the presence of BEX compounds than the reverse situation.

The results of this study exemplified that substrate interactions in biofilters can be determined directly without the need for homogenous- and monoculture experimentation. Also, the results correlate with results obtained with homogenous cultures.

4.6. Acknowledgements

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5. Empirical Model for the Thermophilic Biofiltration of Toluene and Comparison with Mesophilic Conditions

5.1. Abstract

In this study the toluene removal efficiencies of a biofilter packed with mature composted pine bark operated at a thermophilic temperature (50°C), were determined at loading rates ranging from 9.04 to 54.21 g m^{-3} h^{-1}, retention times of 0.32 to 3.86 minutes, and various bed heights. Toluene removal efficiencies exceeding 90% were obtained when the biofilter was subjected to retention times in excess of 0.6 minutes (36 seconds) and loading rates below 54 g m^{3} h^{-1}. The data obtained were used to develop an empirical model and successfully described the removal efficiencies evaluated overall with an R^2 value of 0.93. The influence of oxygen concentration on the thermophilic removal efficiency for a single loading rate and retention time was also evaluated. Determined Michaelis-Menten constant (K_m) values (for the outlet) indicated an overall stronger affinity for oxygen at reduced temperatures (0.36 and 1.06 [O_2] (%) (v/v) for mesophilic and thermophilic conditions, respectively). Comparison of the model deduced in this study with a previous mesophilic (25°C) investigation (Strauss et al. 2000) indicated that higher removal efficiencies could be obtained at higher loading rates under thermophilic conditions, although a slightly longer retention time was required to obtain the same removal efficiency.

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5.2. Introduction

The biological treatment of gaseous emissions, compared to conventional treatment options, has proved to be a cost effective, environmentally friendly alternative. Biofiltration is particularly suitable for the elimination of high volumes of waste gases contaminated with low concentrations of volatile organic compounds (VOCs) (Kapahi and Gross 1995; Tang and Hwang 1997, Devinny et al. 1999) and is, therefore, applicable to a wide range of industries. In biofiltration, emissions are passed through a porous packed bed onto which microorganisms are naturally immobilised. The immobilized microorganisms biodegrade the pollutants to primarily carbon dioxide (CO_2) and water (H_2O). To ensure a viable biofilter with optimum performance, the support media moisture content, pH, temperature and oxygen should be carefully controlled (Devinny et al. 1999). The maintenance of moisture content is particularly important in the case of thermophilic biofiltration.

Biofiltration of mesophilic gaseous emissions (15-40°C) for a wide range of compounds have been studied extensively (van Lith et al. 1997). Various industrial operations, however, emit waste gas emissions at elevated temperatures. The use of thermophilic microorganisms for the biological treatment of these gases would reduce the necessity and treatment cost involved in cooling. Relatively few studies have, however, been reported on biological treatment of high temperature gaseous emissions (Karamanev et al. 1999; Matteau and Ramsay 1997, 1999; Cox et al. 2001; Dhamwichukorn et al. 2001; Kong et al. 2001). Increased temperatures may also have important effects on treatment rate efficiencies due to direct microbial effects and secondary factors related to solubility of the contaminant gases and oxygen.

The aim of this study was to evaluate biofilter performance under thermophilic conditions (50°C), using mature composted pine bark as support medium, as a function of gas retention time, loading rate, and bed height and to develop an empirical model based on these parameters. Furthermore, the influence of oxygen concentration on the removal efficiency was also evaluated. Finally, this study aimed to compare biofilter reactor performance under thermophilic and

mesophilic conditions, using data obtained in a previous study (Strauss et al. 2000).

5.3. Materials And Methods

5.3.1. Reactor Description

The experimental reactor used during this study consisted of five PVC sections (Fig. 1), each with an inner diameter of 170 mm and a height of 300 mm. Two U-form thermostated elements were installed throughout the length of the biofilter and controlled by a thermocouple mounted in the centre of the column (Bartec, Johannesburg, South Africa). This enabled continuous temperature control at 50°C. Four of the five sections were packed with support media, with the lower section serving as a liquid reservoir. Each section, separated by a sieve located at the bottom, was packed to 50 mm from the top, forming a plenum to allow gas flow redistribution. The total packed bed height was 1 m. Gas sampling points were located in each of the plenums, as well as at each of the inlet and outlet ports of the column. Two separate air streams entered a mixing chamber having similar dimensions to one of the reactor sections. One air stream, set to a specific flow rate, passed through a humidifier before volatilising the toluene. Toluene was supplied via a syringe pump (Harvard Apparatus, Holliston, Mass.), before entering the mixing chamber. The other air stream, also set to a specific flow rate, supplied a nebuliser (Hospitak Upmist, Lindenhurt, N.Y.) with compressed air to produce a mineral salt medium aerosol. This aerosol and toluene (UnivAR 98.8% Saarchem, Johannesburg, South Africa) stream converged in the mixing chamber prior to entering the reactor. High humidity levels inside the reactor were maintained by irrigating the support media on a regular basis with mineral salt medium (100mL once every hour). The reactor was operated in a directional-switching mode where the flow direction was switched every 3.5 days to ensure uniform distribution of the biomass throughout the reactor (du Plessis et al. 1998).

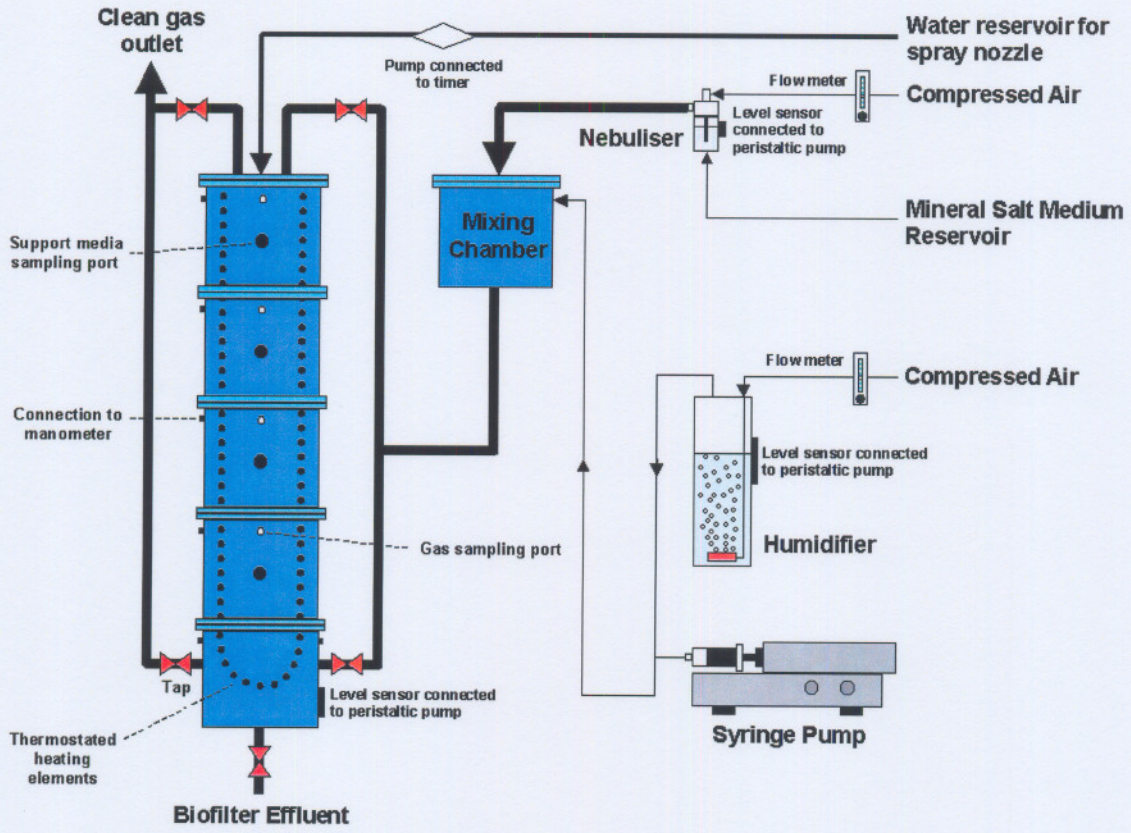

Fig. 1 Schematic presentation illustrating the thermophilic biofilter system set-up

5.3.2. Mineral salt medium composition

The mineral salt medium used in the study had the following composition: K_2HPO_4, 1.5 g L^{-1}; KH_2PO_4, 0.5 g L^{-1}; KNO_3, 5 g L^{-1}; $MgSO_4.7H_2O$, 0.2 g L^{-1}; 0.5 M EDTA, 0.16 mL L^{-1}; trace mineral solution (Freidieker et al. 1994), 2 mL L^{-1}.

5.3.3. Support Media

The reactor was packed with mature composted pine bark (fraction size 5-12 mm) (Culterra, Muldersdrif, South Africa), mixed with one third (v/v) Perlite (Genulite) (fraction size 2-5 mm) (Chemserve Perlite, Parklands, South Africa). This resulted in a porosity of 0.45.

5.3.4. Inoculation

The reactor was inoculated with an enrichment culture obtained by sub culturing mineral salt medium inoculated with mature composted pine bark (Culterra, Muldersdrif, South Africa) in an incubator at 50°C. During the acclimatization period of the biofilter, enrichment culture was periodically added to the biofilter support media in order to ensure uniform distribution of the biomass. Uniform biomass distribution and, therefore, toluene degradation capacity were subsequently assumed in the model.

5.3.5. Analytical Methods

Gas samples were collected from the biofilter in 5-mL gas-tight sampling syringes (Hamilton Series No. 1005, Reno, Nev.) equipped with Teflon Mininert fittings. Samples were analyzed by gas-liquid chromatography using a HP 6850 gas chromatograph (Agilent Technologies) equipped with a 0.5-mL heated (120°C) gas sample loop and a flame ionization detector (FID). A non-polar cross-linked methyl silicone capillary column (30 m x 0.25 mm x 0.25µm, Agilent Technologies) was used with N_2 as the carrier gas at a flow rate of 0.8 mL min^{-1}. The make-up gas flow rate to the detector contained H_2 (40 mL min^{-1}) and synthetic air (450 mL min^{-1}). The column temperature was kept constant at 104°C, the injector at 160°C and the detector at 280°C.

5.3.6. Effect of Toluene Loading Rates and Retention Times on Removal Efficiencies

The effects of toluene loading rates in the range 9.04 to 54.21 g m^{-3} h^{-1} on biofilter removal efficiencies were evaluated at various actual gas retention times ranging from 0.32 to 3.86 minutes. Loading rates, starting at the lowest, and incrementally increasing to the maximum loading rate were evaluated. At each loading rate different retention times were tested starting at the longest (3.86 minutes), and incrementally decreasing the retention time to 0.32 minutes. Gas chromatograph

analyses (for outlet and different bed heights) were performed until steady state conditions were reached at each set of parameter conditions. The model assumptions were, therefore, based on the prevalence of steady state, or pseudo-steady state conditions within the reactor. Toluene removal efficiencies were determined by comparison of the inlet with outlet concentrations, as well as the concentrations obtained at various bed heights.

5.3.7. Effect of Oxygen Concentrations on Removal Efficiencies

Various oxygen concentrations were obtained by the addition of nitrogen to the normal air supply in various ratios in order to determine the effect of reduced oxygen concentrations on toluene removal efficiencies. Oxygen concentrations were measured using a PCO4 portable carbon dioxide and oxygen analyser (Gas Data Ltd.). The toluene loading rate (32.75 g m^{-3} h^{-1}) and gas retention time (0.76 minutes) were kept constant, while the removal efficiencies under various oxygen concentrations were determined.

5.4. Results and Discussion

Toluene removal efficiencies (*RE*) for each of the various bed heights (*H*) were determined at five different loading rates (*L*) and retention times (*t*) ranging from 0.32 to 3.86 minutes. The removal efficiencies for the outlet (bed height of 1.0 m) as a function of retention time, at various loading rates, are illustrated in Fig. 2. The curve fitting parameter values *a* and *b* (Eq. 1) used to describe the relationships between the toluene removal efficiencies and retention times, at various loading rates and bed heights, are given in Table 1.

$$RE = \frac{at}{b+t} \qquad (1)$$

Parameters *a* and *b* were then individually fitted to describe their relationship with the loading rate at different bed heights (*H*). This relationship was described using Eq. 2 and 3 for parameters *a* and *b* respectively.

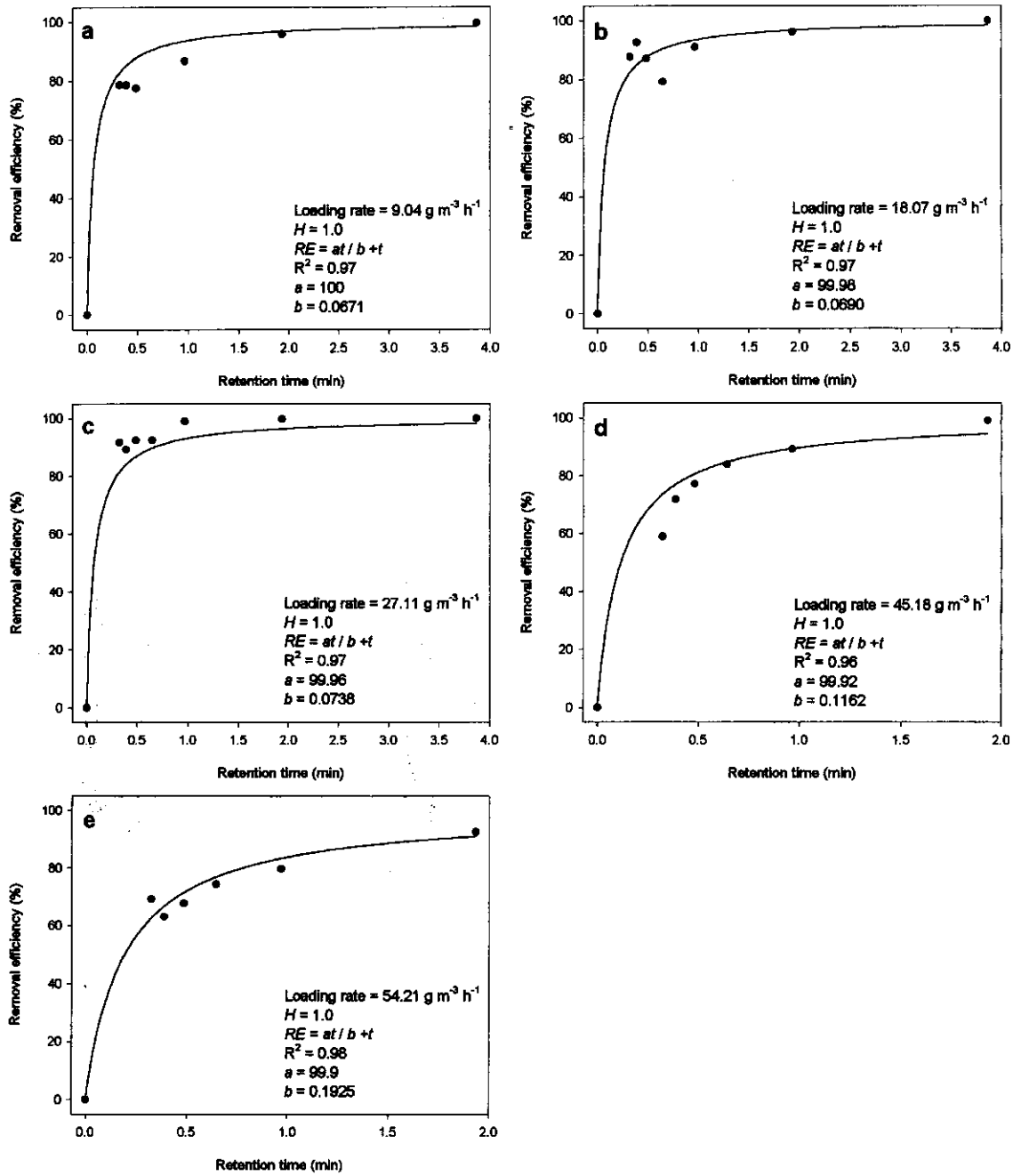

Fig. 2 Effect of retention time on toluene removal efficiency at a loading rate of (**a**) 9.04 g m^{-3} h^{-1}; (**b**) 18.07 g m^{-3} h^{-1}; (**c**) 27.11 g m^{-3} h^{-1}; (**d**) 45.18 g m^{-3} h^{-1}; (**e**) 54.21 g m^{-3} h^{-1}. (Data generated at a bed height of 1.0 m)

$$a = d + cL \tag{2}$$

$$b = f + ge^{hL} \tag{3}$$

Using the above equations, a parameter set (Table 2) for each of the different bed heights was generated. The relationships between each of the parameter values (Table 2) and bed heights (*H*), was described using Eq. 4 to 8.

Table 1 Value parameters *a* and *b* (Eq. 1) for various loading rates and bed heights

Loading rate ($g\ m^{-3}\ h^{-1}$)	1.0 m		0.75 m		0.5 m		0.25 m	
	a	***b***	***a***	***b***	***a***	***b***	***a***	***b***
9.04	100.00	0.067	99.99	0.134	99.85	0.194	96.50	0.268
18.07	99.98	0.069	99.79	0.136	99.18	0.195	92.24	0.268
27.11	99.96	0.074	99.59	0.139	98.51	0.198	87.98	0.270
45.18	99.92	0.116	99.20	0.175	97.17	0.228	79.46	0.293
54.21	99.90	0.193	99.00	0.242	96.50	0.291	75.20	0.369

Table 2 Value parameters *c,d* (Eq. 2) and *f,g,h* (Eq. 3) for various bed heights

Bed height (m)	*c*	*d*	*f*	*g*	*h*
1.0	-0.002	100.02	0.066	5.00e-4	0.102
0.75	-0.022	100.19	0.133	3.28e-4	0.107
0.5	-0.074	100.52	0.193	2.03e-4	0.114
0.25	-0.472	100.76	0.268	2.35e-5	0.154

$$c = -3.0913 + 3.0861\left(1 - e^{-7.5601H}\right) \quad (4)$$

$$d = 101.013 - 1.0243H \quad (5)$$

$$f = 0.3316 - 0.2665H \quad (6)$$

$$g = -0.000125 + 0.0006218H \quad (7)$$

$$h = 0.1027 + 0.2254e^{-5.8928H} \quad (8)$$

Substitution of Eq. 4 to 8 into Eq. 2 and 3, and Eq. 2 and 3 into Eq. 1 provided an overall empirical model that described the removal efficiency of toluene as a function of actual gas retention time (for this reactor, actual retention time (minutes) = empty bed residence time (minutes) / 2.22), loading rate, and bed height under thermophilic conditions. The empirical equation fitted to the entire data set had an overall R^2 value of 0.93. The reactor performance as a function of toluene loading rate ($g\ m^{-3}\ h^{-1}$) and retention time (minutes), as described by the thermophilic empirical model for the outlet (1.0-m bed height), is illustrated in a contour plot (Fig. 3a). Removal efficiencies of >90% were achieved when the toluene loading rate was <54 $g\ m^{-3}\ h^{-1}$ and the retention time >0.6 minutes (36 seconds). Results obtained by a similar study (Strauss et al. 2000) for the development of an empirical mesophilic model (25°C), indicated a >90% removal efficiency when the toluene loading rate was <42 $g\ m^{-3}\ h^{-1}$ and the retention time >0.32 minutes (19.2 seconds) (Fig. 3b). Comparison of biofilter reactor performance at 50°C and 25°C indicated that higher removal efficiencies

could be obtained at higher loading rates under thermophilic conditions, although a slightly longer retention time was required to obtain the same removal efficiency. From the contour plots it is also evident that at retention times <0.1 minutes (60% removal efficiency), the removal efficiency for thermophilic conditions decreased more significantly compared to mesophilic conditions. This result is most likely due to a mass transfer limitation of toluene into the biofilm rather than microbial catalytic limitations at higher temperatures. The solubility effects and thus mass transfer differences are evident from the dimensionless Henry's constants, which are 0.263 and 0.642 at 25°C and 50°C respectively (Leighton and Calo 1981).

The effects of oxygen concentration on the removal efficiencies at various bed depths were also evaluated and compared at 50°C and 25°C (Fig. 4). This effect was evaluated at a single loading rate (32.75 g m^{-3} h^{-1}) and retention time (0.76 minutes). Determination of the Michaelis-Menten constant (K_m) (for the outlet) indicated a K_m value of 0.36 [O_2] (%) (v/v) and 1.06 [O_2] (%) (v/v) for the mesophilic and thermophilic data, respectively. The lower K_m value observed for the mesophilic data represents an overall stronger affinity for oxygen at a reduced temperature. The overall reduction in removal efficiency under thermophilic conditions is, therefore, expected due to an increase in the Henry's constant with temperature, and the subsequent decrease of toluene and oxygen in the biofilm. The relationship between toluene removal efficiencies and oxygen concentrations at various bed depths is described by Eq. 9 to 11, with parameter values shown in Table 3

$$RE = m\left(1 - e^{(-n[O_2])}\right) \tag{9}$$

where,

$$m = -378.29 + \frac{471.88}{\left[1 + e^{-\left(\frac{H+1.73}{0.30}\right)}\right]^{87.83}} \tag{10}$$

$$n = 0.29 - (0.34 \times H) \tag{11}$$

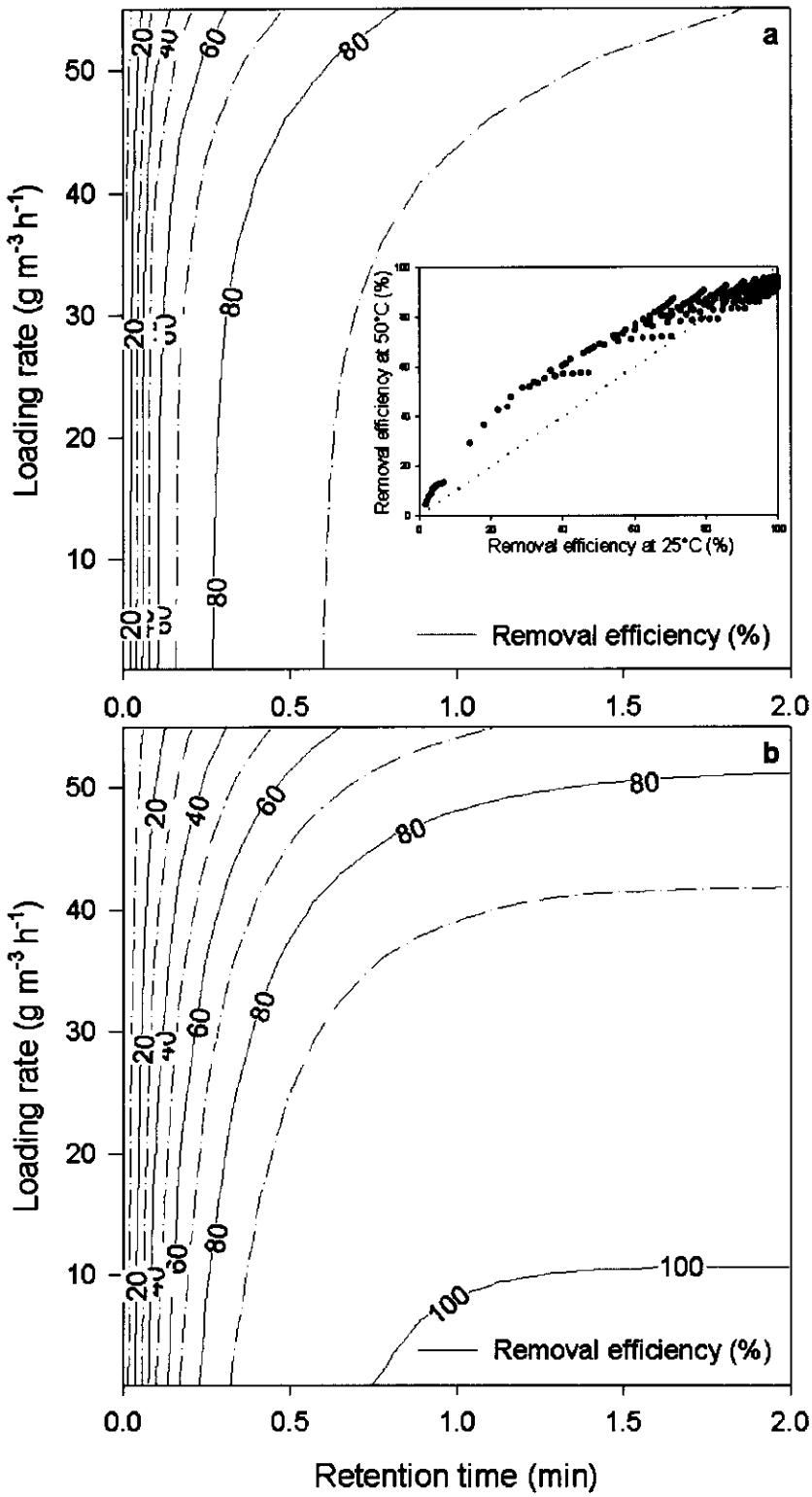

Fig. 3 Contour plot generated using the described thermophilic empirical model (**a**) and the previously published mesophilic empirical model (**b**) (Strauss et al. 2000). Comparative removal efficiency for thermophilic and mesophilic conditions shown in insert. (Data represents removal efficiencies for the outlet at a bed height of 1.0 m and retention times of 0 - 2 minutes)

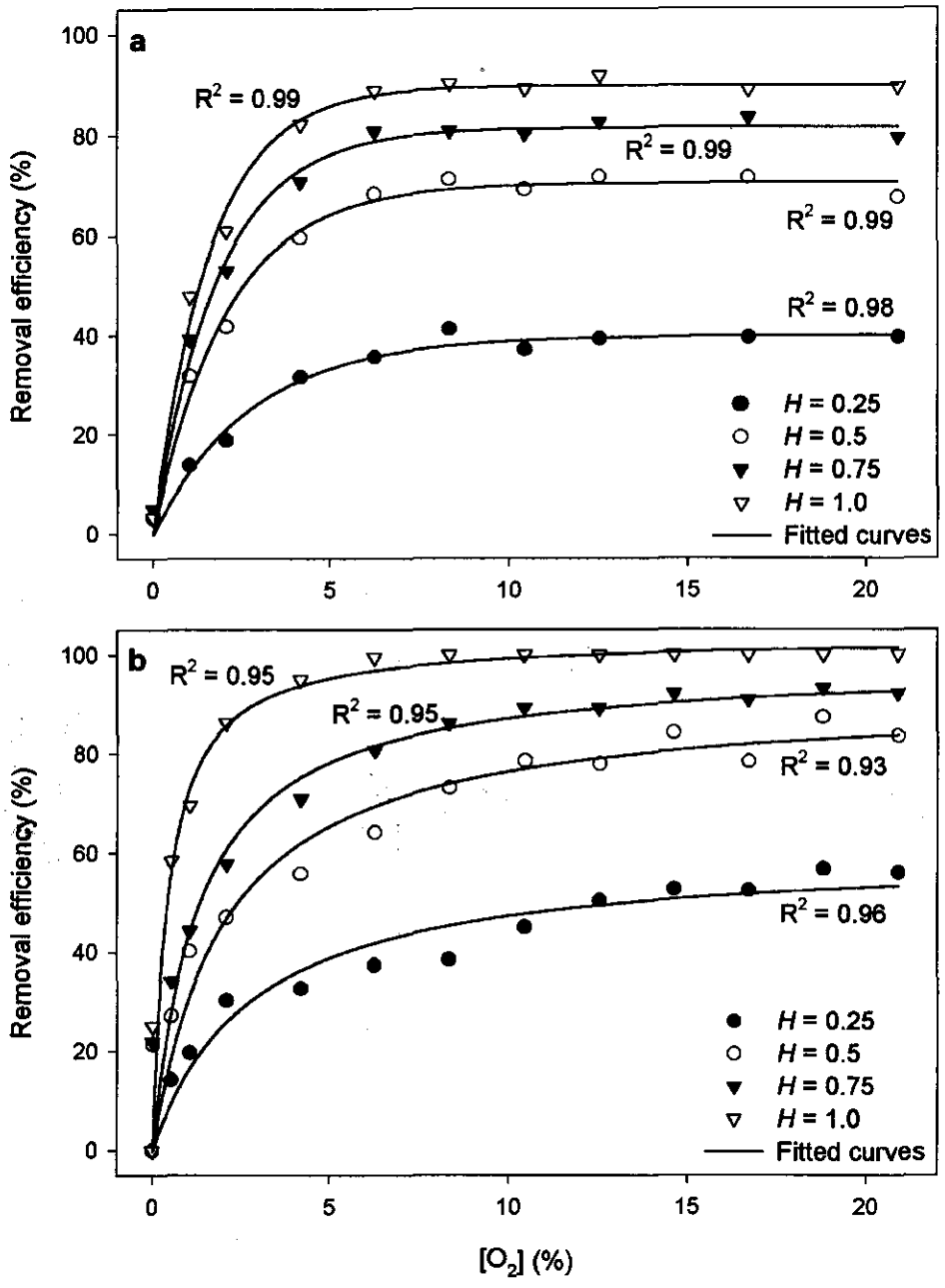

Fig. 4 Effect of oxygen concentration on the toluene removal efficiency during thermophilic conditions (**a**) and mesophilic conditions (**b**) (Strauss et al. 2000)

Table 3 Value parameter *m* and *n* (Eq. 9) for various bed heights

Bed height (m)	*m*	*n*
0.25	89.78	0.623
0.5	81.47	0.546
0.75	70.46	0.483
1.0	39.91	0.359

5.5. Conclusions

Toluene removal efficiencies exceeding 90% were obtained when the biofilter was subjected to toluene loading rates below 54 g m^{-3} h^{-1} and retention times in excess of 0.6 minutes (36 seconds). The results obtained and the model deduced in this study represents the first comprehensive empirical model that describes toluene removal efficiency in a thermophilic (50°C) biofilter, packed with mature composted pine bark, as a function of gas retention time, loading rate, and bed height. Comparison with a previous mesophilic (25°C) study indicated that higher removal efficiencies could be obtained at higher loading rates under thermophilic conditions, although a slightly longer retention time were required to overcome mass transfer limitations at higher temperatures, and thus to obtain the same removal efficiency. The results, therefore, successfully illustrated that thermophilic biofiltration could be successfully applied to waste gas streams released at 50°C. Gas streams that previously were not considered biologically treatable due to cooling cost considerations could now be more comparable with conventional treatment systems, broadening the application of biofiltration. Thermophilic biofiltration does, however, require additional control systems in order to maintain optimum humidity to prevent drying of the support media when treating an unsaturated waste gas stream.

It should be noted that the obtained data were related to the specific set of prevailing experimental conditions described in these two studies and the models, therefore, are empirical analytical models. Despite these limitations, these models could be useful in estimating potential reactor performance and minimum oxygen requirements of similar biofilter systems.

5.6. Acknowledgements

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5.7. Notation

The following symbols are used in this paper:

RE = Removal efficiency (%)

$[O_2]$ = Oxygen concentration

L = Loading rate (g m^{-3} h^{-1})

t = Retention time (minutes)

H = Packed bed height (m)

$a - n$ = Equation fitting parameters

5.8. References

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6. Mesophilic and Thermophilic BTEX Substrate Interactions for a toluene-acclimatized biofilter

6.1. Abstract

BTEX substrate interactions for a mesophilic (25°C) and thermophilic (50°C) toluene acclimatized composted pine bark biofilter were investigated. Toluene, benzene, ethylbenzene, *o*-xylene, *m*-xylene and *p*-xylene removal efficiencies, both individually and in paired mixtures with toluene (1:1 ratio (m/m)), were determined at a total loading rate of 18.1 g m^{-3} h^{-1} and retention time ranges of 0.5 - 3.0 minutes and 0.6 - 3.8 minutes for mesophilic and thermophilic biofilters, respectively. Overall toluene degradation rates under mesophilic conditions were superior to degradation rates of individual BEX compounds. With the exception of *p*-xylene, higher removal efficiencies were achieved for individual BEX compounds compared to toluene under thermophilic conditions. Overall BEX compound degradation under mesophilic conditions was ranked as ethylbenzene > benzene > *o*-xylene > *m*-xylene > *p*-xylene. Under thermophilic conditions overall BEX compound degradation was ranked as benzene > *o*-xylene > ethylbenzene > *m*-xylene > *p*-xylene. With the exception of *o*-xylene, the presence of toluene in paired mixtures with BEX compounds resulted in enhanced removal efficiencies of BEX compounds, both under mesophilic and thermophilic conditions. A substrate interaction index was calculated to compare removal efficiencies at a retention time of 0.8 minutes (50 seconds). A reduction in toluene removal efficiencies (negative interaction) in the presence of individual BEX compounds was observed under mesophilic conditions, while enhanced toluene removal efficiency was achieved in the presence of other BEX compounds, with the exception of *p*-xylene under thermophilic conditions.

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6.2. Introduction

Biotreatment processes are increasingly being applied in the treatment of mesophilic waste gases. Low capital and operational costs and the fact that biofiltration technology is considered an environmentally friendly process make this an attractive alternative treatment option. Various industrial operations, however, also emit waste gases at elevated temperatures and the biological treatment of elevated gas emissions without significant cooling could therefore broaden the application of biofiltration processes (Matteau and Ramsay 1999).

Numerous studies have successfully demonstrated the use of biofilters for the treatment of petroleum (gasoline) and BTEX (benzene, toluene, ethylbenzene and xylene) compounds (Oh and Bartha 1997; Wright et al. 1997; Devinny et al. 1999). BTEX compounds often occur together and interact with each other with respect to their degradation and removal efficiencies in a biofilter environment. The presence of one specific BTEX compound could either stimulate (co-metabolize) or inhibit (competitive inhibition, diauxy, catabolic repression) the biodegradation of another BTEX compound (Alvarez and Vogel 1991; Haigler et al. 1992). Furthermore, the influence of temperature on specific mass transfer could have definite influences on reactor performance and superimpose conditions that may cause overall biofiltration removal efficiencies to deviate from catabolism-predicted literature results (Alvarez and Vogel 1991; Chang et al. 1993; Oh et al. 1994; Deeb and Alvarez-Cohen 1999).

Due to the condition-specific and sometimes conflicting nature of BTEX substrate interactions found in literature, such interactions cannot definitively be anticipated when considering the use of biofiltration systems for the treatment of BTEX vapors. The aim of this study was, therefore, to investigate individual and paired BTEX substrate interactions on a toluene acclimatized biofilter consortium under both mesophilic and thermophilic conditions and to develop a method to compare these observed interactions.

6.3. Materials and Methods

6.3.1. Reactor Description

The general construction and operation of the reactors used in this study has been described previously (du Plessis et al. 2001). Changes made to enable thermophilic operation at 50°C, were the installation of two U-form thermostated elements throughout the length of the biofilter that enabled continuous heating control by a thermocouple mounted in the centre of the column (Bartec, South Africa). A temperature of 50°C was selected as it was easier to maintain homogeneity of humidity as well as a mainly bacterial consortium (Matteau and Ramsay 1999). A relative humidity of 100% was furthermore ensured by irrigating the support media with 100 mL mineral salt medium (du Plessis et al. 2001) once every hour. Additional liquid level controls were installed for the reactor reservoir, humidifier and nebulizer and connected to peristaltic pumps in order to remove excess biofilter effluent or supply liquid (Fig. 1).

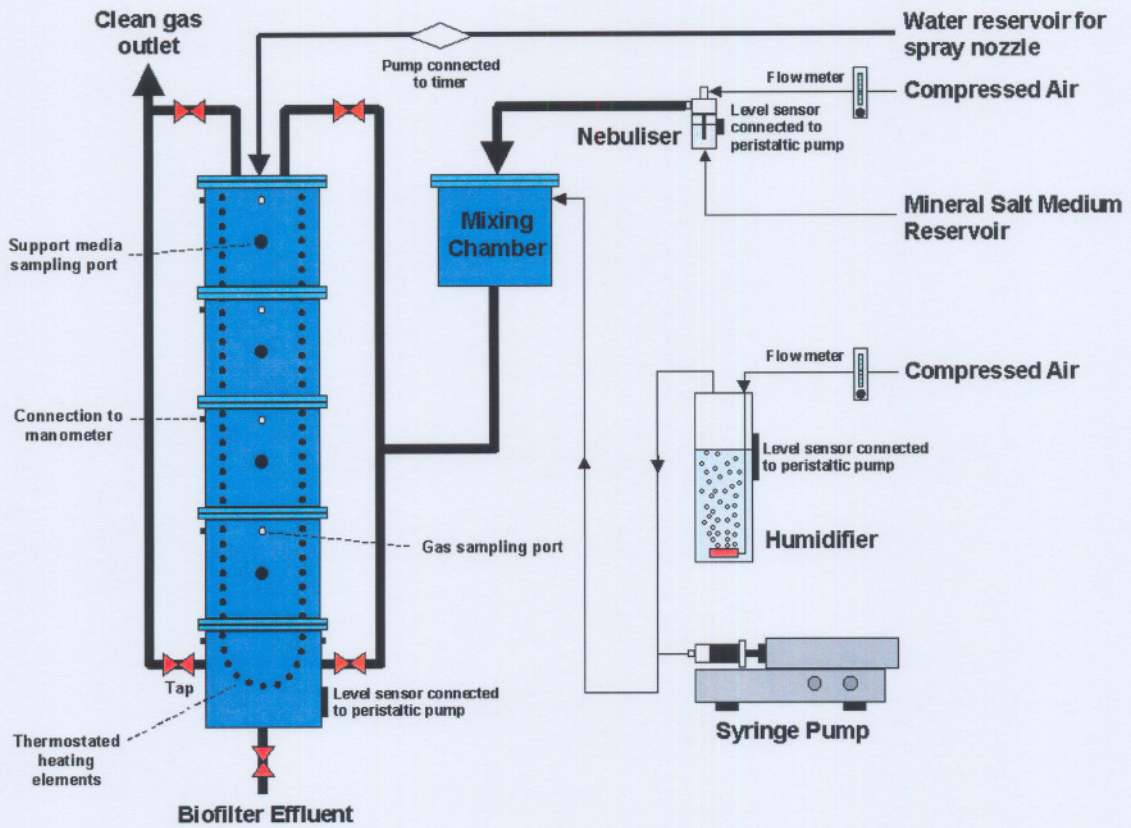

Fig. 1 Schematic diagram of the thermophilic biofilter

6.3.2. Support Media

The mesophilic and thermophilic reactors were packed with mature composted pine bark (fraction size 5-12 mm) obtained from Starke Ayres (South Africa) and Culterra (South Africa), respectively. Composted pine bark was selected based on its diverse microbial consortia, long term durability and integrity due to mainly lignin-type molecules, and non-liable carbon compound composition that is not readily decomposed (du Plessis et al. 2003). The composted pine bark was mixed with one third (v/v) Perlite (Genulite) (fraction size 2-5 mm) (Chemserve Perlite, South Africa). This resulted in a porosity of 0.35 for the mesophilic biofilter and 0.45 for the thermophilic biofilter.

6.3.3. Inoculation and acclimatization

The mesophilic biofilter was inoculated by filling the reactor with inoculum obtained from a previous acclimated culture (du Plessis et al. 1998) and drained after 12h. The biofilter bed was then acclimatized to toluene biodegradation over a 4 month period at a loading rate of 32 g $m^{-3} h^{-1}$ and retention time of 0.8 minutes. Steady-state conditions, with toluene removal efficiencies >99%, were established before commencing the experiments. For the thermophilic biofilter, the reactor was initially inoculated and periodically thereafter with an enrichment culture obtained by sub-culturing mineral salt medium inoculated with mature composted pine bark (Culterra, South Africa) in an incubator at 50°C. The biofilter bed was then acclimatized to toluene biodegradation at a loading rate of 32 g $m^{-3} h^{-1}$ and retention time of 0.8 minutes. Experiments were only performed when steady state conditions were reached and toluene removal efficiencies exceeded 93%. Both biofilters were operated in a directional switching mode (du Plessis et al. 1998) to ensure uniform distribution of the biomass (confirmed with top and bottom flow degradation profiles).

6.3.4. Analytical Methods

Gas samples were collected from the biofilter in 5-mL gas-tight sampling syringes (Hamilton Series #1005) equipped with Teflon Mininert® fittings. Samples were analyzed by gas-liquid chromatography using a HP 6850 gas chromatograph (Agilent) equipped with a 0.5-mL heated (120°C) gas sample loop and a flame ionization detector (FID). A non-polar cross-linked methyl silicone capillary column (30 m x 0.25 mm x 0.25µm, Agilent) was used with N_2 as the carrier gas at a flow rate of 0.8 mL min^{-1}. The make-up gas flow rate to the detector contained H_2 (40 mL min^{-1}) and synthetic air (450 mL min^{-1}). The column temperature was kept constant at 104°C, the injector at 160°C and the detector at 280°C.

6.3.5. Effect of carbon source and retention times on removal efficiencies

The effects of benzene, ethylbenzene, toluene, *o*-xylene, *m*-xylene and *p*-xylene on biofilter efficacy were determined at a fixed loading rate (18.1g m^{-3} h^{-1}) and various gas retention times (0.5 – 3.0 minutes and 0.6 – 3.8 minutes for the mesophilic and thermophilic study, respectively). This protocol was repeated for toluene mixed in a 1:1 (m/m) ratio with each of the other BEX carbon compounds to obtain a total loading of 18.1 g m^{-3} h^{-1}. The removal efficiencies were determined at each reactor section (bed heights). Abiotic removal of BTEX compounds was ruled out by GC analyses of the biofiltration effluent and nitrogen gas pulse experiments prior to the study. This entailed the pulse replacement of oxygen in the normal air flow with nitrogen and comparative monitoring of toluene removal during both aerobic and anoxic conditions.

6.4. Results

Benzene, ethylbenzene, toluene, *o*-xylene, *m*-xylene and *p*-xylene were applied individually to a toluene-acclimatized biofilter under both mesophilic and thermophilic conditions. Removal efficiencies were monitored at a fixed loading rate of 18.1 g m^{-3} h^{-1} and retention times ranging from 0.5 - 3.0 minutes and 0.6 - 3.8 minutes for mesophilic and thermophilic biofilters, respectively. The paired

BTEX application protocol was then repeated with a 1:1 (m/m) ratio of benzene, ethylbenzene, *o*-xylene, *m*-xylene and *p*-xylene paired with toluene, to achieve and maintain a total loading rate of 18.1 g m^{-3} h^{-1}. The concentration profile was measured for each component and retention time at regular intervals, until changes of less than 1% per hour were observed (pseudo-steady state conditions, approximately after 3h). The reactor was allowed to reach toluene-degrading steady state conditions after each BEX compound analyses (i.e., loading rate of 18.1 g m^{-3} h^{-1}, retention time of 0.8 minutes and 3.5-day directional switching for a total period of 7 days) as enzymes involved in toluene catabolism are known to catabolise a wide range of similar hydrocarbon compounds (Sun and Wood 1997). The outlet removal efficiencies for toluene (T), toluene in the presence of a BEX compound (e.g. T_B), BEX compound in the presence of toluene (e.g. B_T) and individual BEX compounds (i.e., benzene (B), ethylbenzene (E), *o*-xylene (*o*X), *m*-xylene (*m*X), *p*-xylene (*p*X)) under mesophilic and thermophilic conditions, are illustrated in Fig. 2 and 3 respectively. All data in Figures 2 and 3 were fitted using Eq. 1

$$RE = a\left(1 - e^{-bt}\right) \tag{1}$$

where, *RE* represents the removal efficiency (%), *a* and *b* the curve-fitting parameters (Table 1) and *t* the retention time (minutes).

In order to simplify the evaluation and comparison of removal efficiency and substrate interaction data at both mesophilic and thermophilic conditions, comparisons were made at a retention time of 0.8 minutes (50 seconds) (indicated by dotted line in Fig. 2 and 3). Selection of 0.8 minutes (50 seconds) retention time point was a judgement call based on the available data and relevance to commercial and industrial full-scale applications (Leson and Winer 1991). A substrate interaction index (Fig. 4) was determined based on these removal efficiency values and used as an indication of positive or negative interactions on the effect of BEX compound addition on toluene degradation (Eq. 2) and toluene addition on BEX compound degradation (Eq. 3).

$$\text{Substrate interaction index} = \frac{\left(T_{\text{BEX compound}} - T\right)}{T} \tag{2}$$

$$\text{Substrate interaction index} = \frac{\left(\text{BEX compound}_T - \text{BEX compound}\right)}{\text{BEX compound}} \tag{3}$$

Table 1 Fitting value parameters for Fig. 2 and 3

Parameter	Mesophilic biofilter				Thermophilic biofilter			
	T	T_B	B_T	B	T	T_B	B_T	B
a	100.11	99.96	100.24	92.89	98.58	99.53	99.62	100.09
b	6.28	2.94	2.48	1.86	2.55	3.16	4.49	3.54
	T	T_E	E_T	E	T	T_E	E_T	E
a	100.11	99.89	98.29	98.73	98.58	99.29	96.28	124.33
b	6.28	4.65	2.82	2.45	2.55	3.75	1.50	0.28
	T	T_{oX}	oX_T	oX	T	T_{oX}	oX_T	oX
a	100.11	99.75	95.80	80.60	98.58	99.58	100.51	100.06
b	6.28	4.02	1.36	1.77	2.55	4.64	1.56	1.57
	T	T_{mX}	mX_T	mX	T	T_{mX}	mX_T	mX
a	100.11	99.64	86.47	59.64	98.58	99.38	64.94	22.97
b	6.28	4.34	0.98	1.51	2.55	3.55	0.59	3.08
	T	T_{pX}	pX_T	pX	T	T_{pX}	pX_T	pX
a	100.11	99.04	77.04	32.54	98.58	95.23	40.30	13.25
b	6.28	3.87	0.80	4.64	2.55	2.39	0.82	2.70

6.5. Discussion

The biodegradation of toluene in the absence of BEX compounds (i.e., T) by the toluene enriched consortium indicated higher removal efficacy under mesophilic conditions when compared to when BEX compounds were introduced individually (i.e., BEX compound) (Fig. 2). The opposite occurred for thermophilic conditions, with the exception of *p*-xylene, where improved removal efficiencies were obtained for individual benzene, ethylbenzene, *o*-xylene and *m*-xylene compounds (Fig. 3). Comparison of the data obtained revealed that toluene degradation was enhanced at shorter retention times under mesophilic conditions (Fig 2 and 3) and is most likely due to mass transfer limitation of toluene into the biofilm rather than microbial catalytic limitations at elevated temperatures. The solubility effects, and thus mass transfer differences, are evident from the dimensionless toluene Henry's constants, which are 0.263 and 0.642 at 25°C and 50°C, respectively (Leighton and Calo 1981). Mesophilic toluene removal efficiencies reached values of > 95% after retention times > 0.48 minutes, while the same removal efficiencies were only achieved after 1.3 minutes under thermophilic conditions. Maximum removal efficiencies (100%) for toluene under mesophilic conditions was reached after 2.3 minutes, while a maximum removal efficiency of 98.6% under

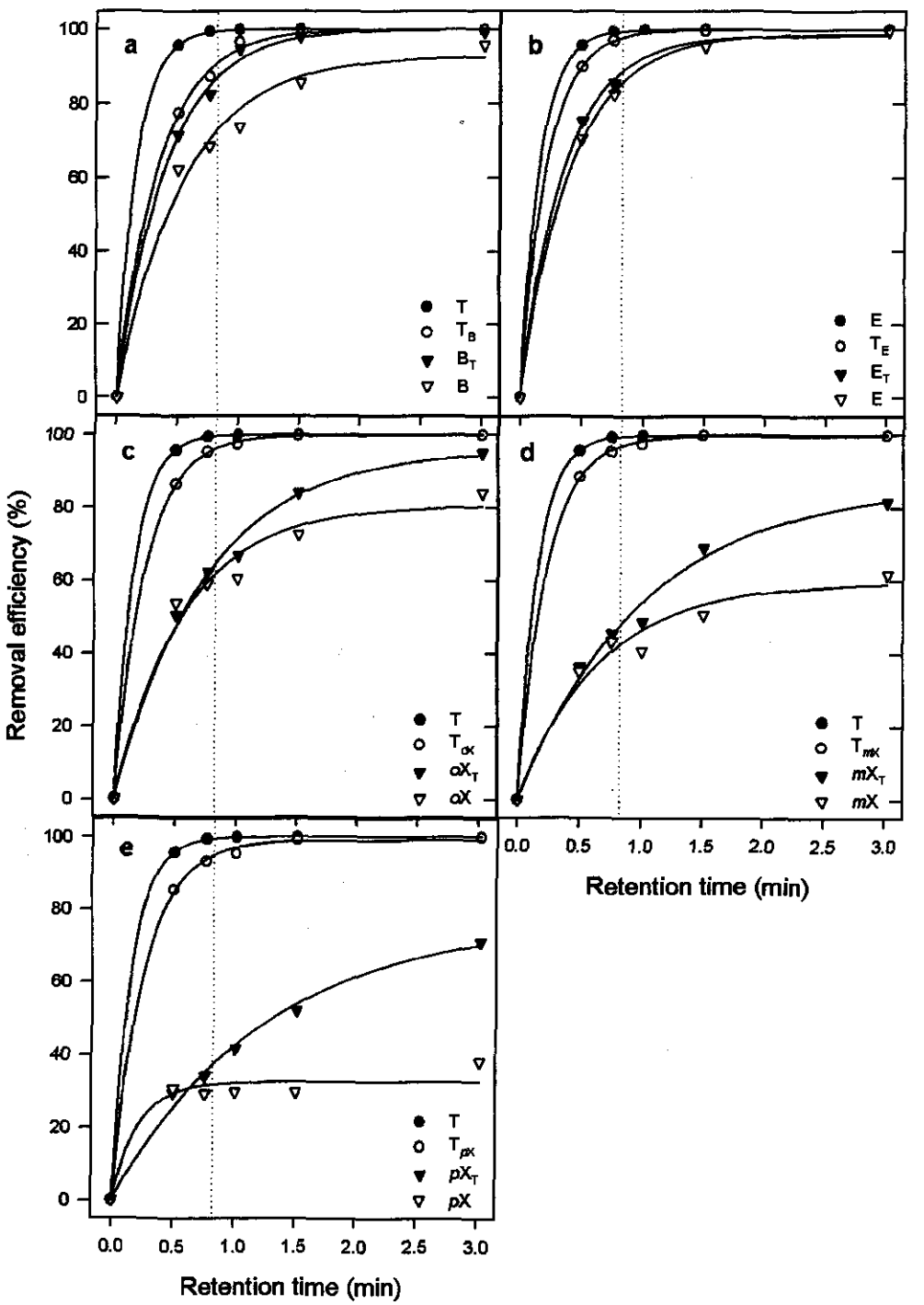

Fig. 2 Effect of retention time on outlet removal efficiencies for toluene (• T), toluene in the presence of a BEX compound (i.e., ○ $T_{BEX\ compound}$), BEX compound in the presence of toluene (i.e., ▼ BEX $compound_T$) and individual BEX compounds (i.e., (**a**) benzene (▽ B), (**b**) ethylbenzene (▽ E), (**c**) o-xylene (▽ *o*X), (**d**) *m*-xylene (▽ *m*X), (**e**) *p*-xylene (▽ *p*X)) under mesophilic conditions. The individual compound loading was 18.1 g m^{-3} h^{-1}, while the paired toluene/BEX compound mixture (1:1 ratio (m/m)) had a total loading of 18.1 g m^{-3} h^{-1}

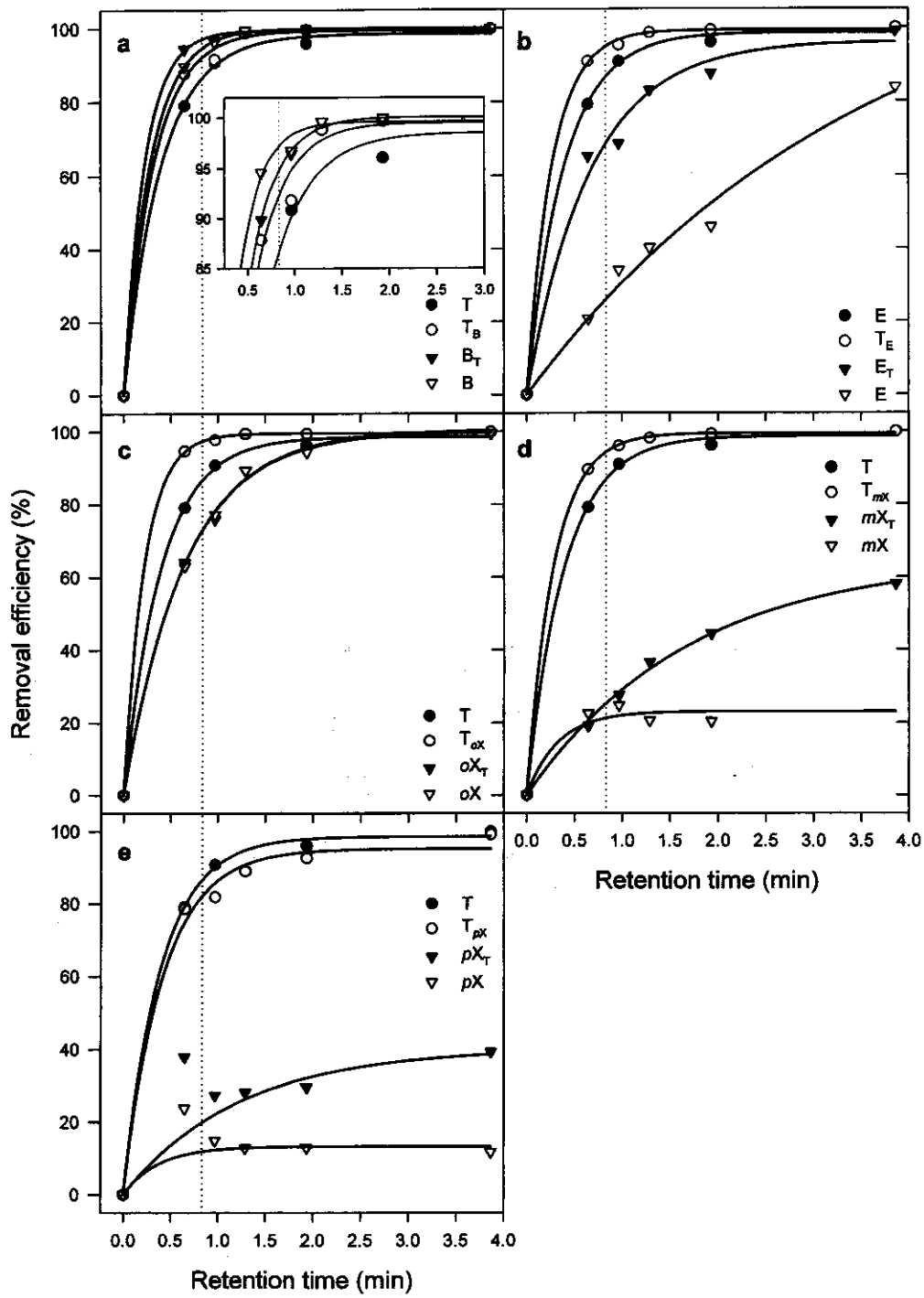

Fig. 3 Effect of retention time on outlet removal efficiencies for toluene (• T), toluene in the presence of a BEX compound (e.g. ○ $T_{BEX\ compound}$), BEX compound in the presence of toluene (i.e., ▼ BEX $compound_T$) and individual BEX compounds (i.e., (**a**) benzene (▽ B), (**b**) ethylbenzene (▽ E), (**c**) *o*-xylene (▽ *o*X), (**d**) *m*-xylene (▽ *m*X), (**e**) *p*-xylene (▽ *p*X)) under thermophilic conditions. The individual compound loading was 18.1 g m^{-3} h^{-1}, while the paired toluene/BEX compound mixture (1:1 ratio (m/m)) had a total loading of 18.1 g m^{-3} h^{-1}

thermophilic conditions could only be achieved at the longest retention time evaluated (3.9 minutes). Comparison of removal efficiencies obtained at the selected retention time (0.8 minutes) indicated 99.6% and 86.7% degradation under mesophilic and thermophilic conditions, respectively.

The ranking of removal efficiencies for BEX compounds in the absence of toluene (i.e., BEX compound) also differed at the evaluated temperatures, with the relative position of ethylbenzene in the ranking being the most prominent. Under mesophilic conditions the removal efficiency was ranked ethylbenzene > benzene > *o*-xylene > *m*-xylene > *p*-xylene and under thermophilic conditions benzene > *o*-xylene > ethylbenzene > *m*-xylene > *p*-xylene. The ability of the toluene-acclimatized consortium to catabolise individual BEX compounds is not surprising and could be attributed to their similar chemical structures and biochemical enzyme pathways (Chen and Taylor 1995; Di Lecce et al. 1997).

Under mesophilic conditions toluene removal efficiency was inhibited by the presence of other BEX compounds (i.e., $T_{BEX\ compound}$) while toluene, in turn, had an enhancing effect on the removal efficiency of other BEX compounds when paired with them (i.e., BEX $compound_T$) (Fig. 2 and 4). Under these conditions, improved removal efficiency of BEX compounds, when paired with toluene, occurred at the expense of toluene removal efficiency mainly due to the similarities in the catabolic pathways and enzymatic systems of these structurally related molecules (Schraa et al. 1987; Smith 1990). In contrast, under thermophilic conditions both toluene removal efficiency and that of the other BEX compounds were improved under paired conditions when compared to removal efficiencies achieved for individual compounds (Fig. 3 and 4). The presence of paired compounds thus resulted in the mutual enhancement of the removal efficiencies of both compounds. Increased removal efficiency of one compound did, therefore, not occur at the expense of the paired compound under thermophilic conditions, except in the case of the toluene – *p*-xylene pair, where improved toluene removal (i.e T_{pX}) was observed to be at the expense of *p*-xylene removal efficiency (i.e., pX_T) (Fig. 4). A possible explanation for this phenomenon is based on the higher enzymatic reaction times at elevated temperatures. At thermophilic temperatures

the biofilm would rapidly be depleted of residual BTEX compounds, thus avoiding negating competitive effects found at mesophilic temperatures.

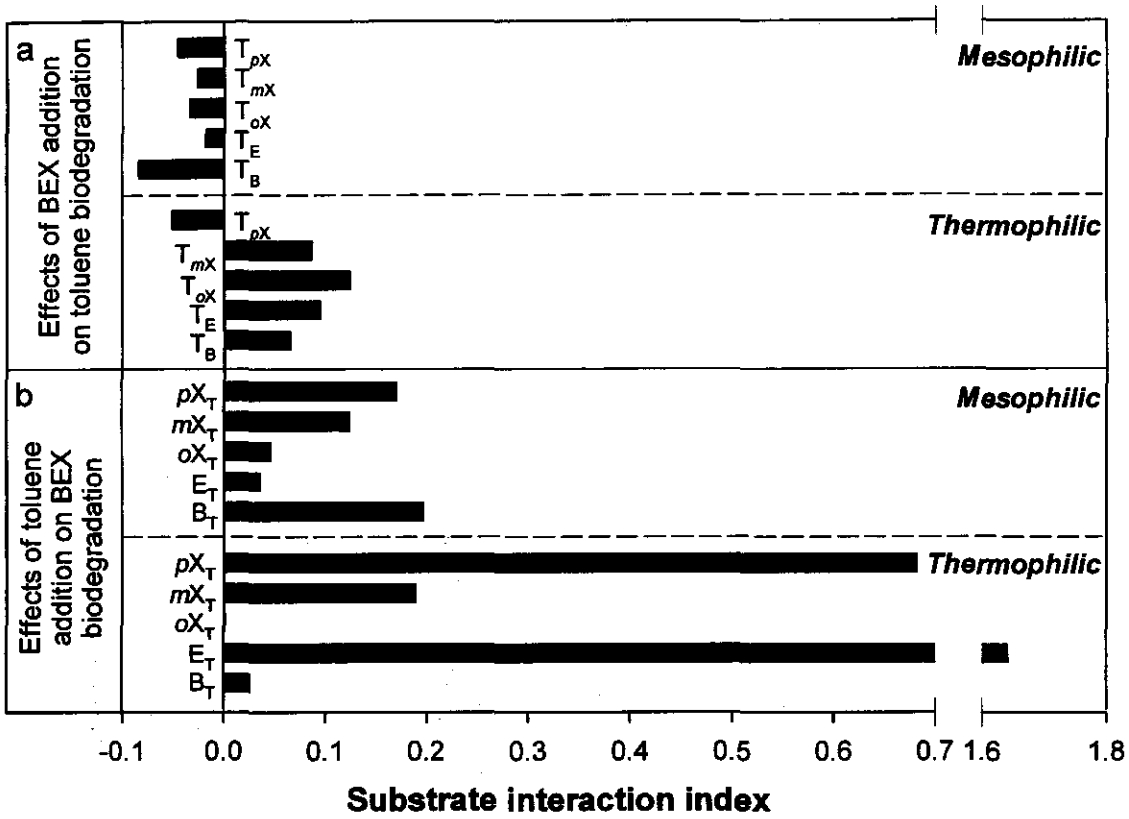

Fig. 4 Substrate interaction indices indicating the effects of BEX addition on toluene biodegradation ($T_{BEX\ compound}$) (**a**) and the effects of toluene addition on BEX biodegradation (BEX $compound_T$) (**b**) for both mesophilic and thermophilic conditions

In general xylene was less amenable to treatment than other BTEX compounds (Fig. 2c-e; Fig. 3c-e). The position of the functional group was an important factor in the removal efficiency ranking of the different xylene isomers (Alvarez and Vogel 1991; Deeb and Alvarez-Cohen 1999, Jorio et al. 1998). The ranking in this study was, however, in contrast with previous studies where *o*-xylene was indicated to be the most recalcitrant of the xylene isomers (Alvarez and Vogel 1991; Bibeau et al. 2000; Jorio et al. 1998). No attempt was made in this study to determine the catabolic pathways for different compounds. No plausible biochemical reason for the discrepancy in removal ranking achieved in this study, compared to other literature, can therefore be put forward. The discrepancy in the

ranking of *o*-xylene degradation is, however, not too surprising given the variable nature of the suite of catabolic capabilities associated with different consortia.

In conclusion, both positive and negative effects of toluene, individual BEX compounds and BEX compounds in paired mixtures with toluene have been identified using a mesophilic and thermophilic toluene-acclimatized microbial consortium. The removal efficiency results presented in this study represent a comprehensive comparative study undertaken in order to compare mesophilic and thermophilic data obtained using a toluene acclimatized biofilter consortium and could provide a better understanding of substrate interactions under similar conditions. It is well known that complicated substrate interactions are likely to occur when investigating the biodegradation of monoaromatic compounds in mixtures. This is even despite similarities in the chemical properties and structures of these compounds (Deeb and Alvarez 1999) or microbial consortia being acclimatized for specific hydrocarbon biodegradation (Yerushalmi and Guiot 1998). These interactions could, therefore, have a significant effect on biofiltration efficacy and should be considered when a complex BTEX waste gas stream is being treated.

6.6. Acknowledgements

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7. Model application and evaluation for the mesophilic and thermophilic biofiltration of toluene

7.1. Abstract

In this study, the application of a model previously developed by Deshusses et al. (1995a) to a comprehensive dataset that included height differentiation is described for a mesophilic and thermophilic operated composted pine bark biofilter. The model and experimental data were used to perform model parameter optimization and parametric sensitivity analyses. The model considered the height of the biofilter to be divided in 8 layers, while the gas phase and biofilm, which was considered as 8 subdivisions, were used to describe the concentrations of toluene in the gas phase and biofilm during steady state conditions. The model simulated the experimental results with good agreement. Comparison between the mesophilic and thermophilic data indicated that higher elimination capacities could be obtained at thermophilic temperatures. Experimental results further indicated that the maximum elimination capacity for thermophilic conditions was not reached (for all loading rates and gas flow rates evaluated), thereby emphasizing the future applicability of biofiltration applications at elevated temperatures.

This chapter was written in collaboration with Prof Marc A Deshusses of the Department of Chemical and Environmental engineering, University of California Riverside, California, USA and will be submitted for publication in the journal Environmental Progress

7.2. Introduction

The application of biofiltration for the cost-effective treatment of a wide range of pollutants generated by various industries has played an important role worldwide in environmental protection. Biofiltration is particularly suitable for the elimination of high volumes of waste gases contaminated with low concentrations of pollutants, and is therefore more widely applied where conventional treatment techniques would be lesser cost-effective (Devinny et al. 1999; Lim and Lee 2003). Biofiltration is based on a process that occurs naturally in soils and water and thus represents a safe, environmentally friendly technology.

In biofilter reactors, a humid polluted waste gas stream is passed through a porous biologically active bed. The pollutants are converted into harmless by-products that are primarily carbon dioxide and water. To ensure a viable biofilter with optimum performance, the support media moisture content, pH, temperature and oxygen should be carefully controlled (Devinny et al. 1999). Currently most biofiltration reactors used in industry only treat gaseous emissions being emitted at mesophilic temperatures (15-40°C), with limited studies available in literature (Matteau and Ramsay 1997, 1999; Devinny et al. 1999; Karamanev et al. 1999; Cox et al. 2001; Dhamwichukorn et al. 2001; Kong et al. 2001) reporting the biological treatment at elevated temperatures (>45°C). Various industries, however, emit gaseous pollutants at higher temperature and the use of thermophilic microorganisms would reduce the necessity and treatment cost involved in cooling, thereby broadening the application range for biofiltration systems. The use of increased temperatures may also have important effects on the treatment rate efficiencies due to direct microbial effects related to the solubility of pollutants and oxygen. However, in order to fully understand the process better and subsequently develop it into an optimized technology, effective modelling of the process and correlation with experimental results is required.

Various chemical, physical and biological phenomena are involved in biofiltration and due to the increased interest in biofiltration and the aim to optimize and better understand the inherent processes, an increased number of studies investigated

this complexity through mathematical modelling. Several biofiltration models have been proposed, with various steady state and unsteady state models describing model components incorporating various components and characteristics of the gas phase, biofilm, sorption volume and adsorption (Ottengraf 1986; Hirai et al. 1990; Shareefdeen et al. 1993; Deshusses et al. 1995a; Hodge and Devinny 1994a,b; Zarook et al. 1997; Amanullah et al. 1999; Karamenev et al. 1999).

In this study, the application of a previously developed dynamic model by Deshusses et al (1995a) is described with regards to model parameter optimization, parameter sensitivity analyses and evaluation for a mesophilic and thermophilic operated toluene composted pine bark biofilter. The analyses is based on a comprehensive dataset obtained for various toluene loading and gas flow rates and allows a direct comparison between the data.

7.3. Materials and Methods

7.3.1. Biofilter description

The general construction and operation of the reactors used in this study has been described previously (du Plessis et al. 2001). Changes made to enable thermophilic operation at 50°C, were the installation of two U-form thermostated elements throughout the length of the biofilter that enabled continuous heating control by a thermocouple mounted in the centre of the column (Bartec, South Africa). A relative humidity of 100% was ensured by irrigating the support media with 100 mL mineral salt medium (du Plessis et al. 2001) once every hour. Additional liquid level controls were installed for the reactor reservoir, humidifier and nebulizer and connected to peristaltic pumps in order to remove excess biofilter effluent or supply liquid (Fig 1).

before commencement of the experiments. For the thermophilic biofilter, the reactor was initially inoculated and periodically thereafter with an enrichment culture obtained by sub-culturing mineral salt medium inoculated with mature composted pine bark (Culterra, South Africa) in an incubator at 50°C. The biofilter bed was then acclimatized at similar toluene loading and gas flow rates. Experiments were only performed when steady state conditions were reached and toluene removal efficiencies exceeded 93%. Both biofilters were operated in a directional switching mode (du Plessis et al. 1998) to ensure uniform distribution of the biomass (confirmed with top and bottom flow degradation profiles).

7.3.4. Operating conditions

To determine the performance of the mesophilic and thermophilic biofilters, toluene loading concentrations ranging from 0.10 to 3.58 g m^{-3} were evaluated at various gas flow rates (0.14 to 1.70 m^3 h^{-1}). Loading concentrations, starting at the lowest, and incrementally increasing to the maximum were evaluated. At each concentration, different gas flow rates were tested starting at the fastest (1.70 m^3 h^{-1}), and incrementally decreasing to a gas flow rate of 0.14 m^3 h^{-1} (longest retention time). Gas chromatographic analyses (for outlet and different bed heights) were performed until steady state conditions were reached at each set of parameter conditions. The model assumptions were, therefore, based on the prevalence of steady state, or pseudo-steady state conditions within the reactor.

7.3.5. Analytical methods

Gas samples were collected in 5-mL gas-tight sampling syringes (Hamilton Series #1005) equipped with Teflon Mininert® fittings. Samples were analyzed by gas-liquid chromatography using a HP 6850 gas chromatograph (Agilent) equipped with a 0.5-mL heated (120°C) gas sample loop and a flame ionization detector (FID). A non-polar cross-linked methyl silicone capillary column (30 m x 0.25 mm x 0.25µm, Agilent) was used with N_2 as the carrier gas at a flow rate of 0.8 mL min

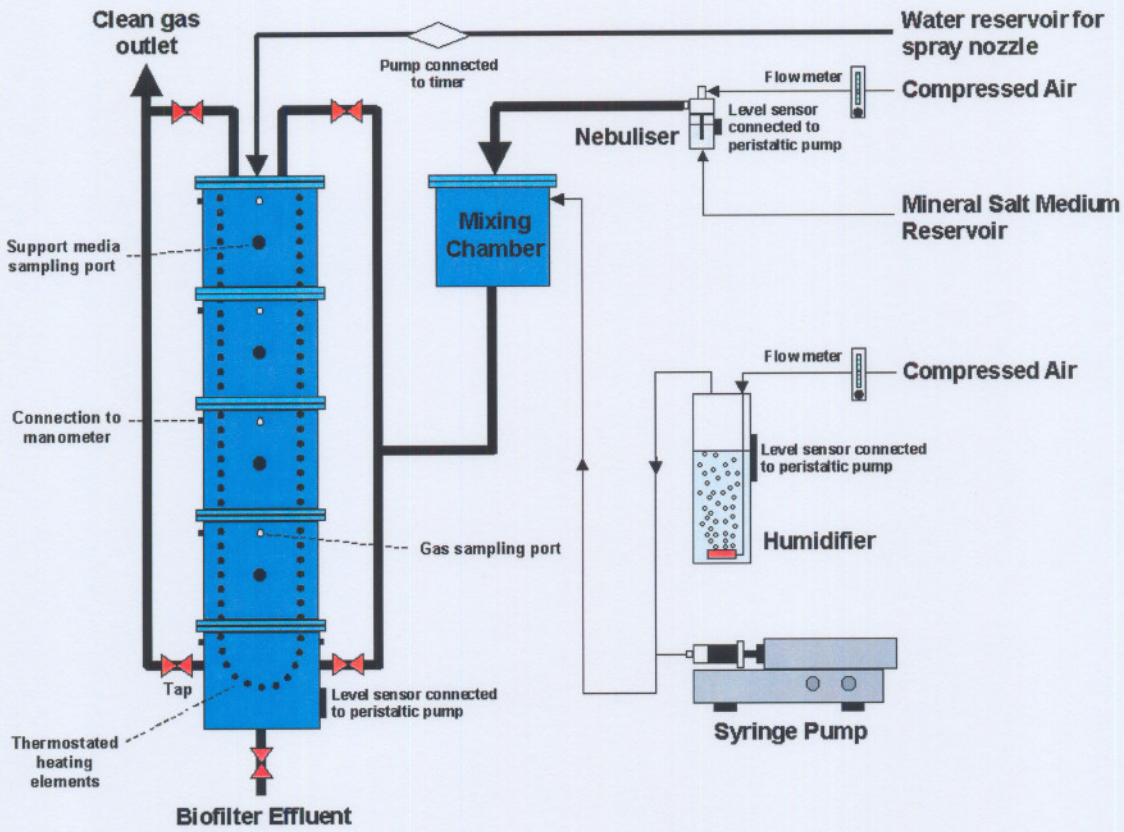

Fig. 1 Schematic presentation illustrating the thermophilic biofilter system set-up

7.3.2. Packing material

The mesophilic and thermophilic reactors were packed with mature composted pine bark (fraction size 5-12 mm) obtained from Starke Ayres (South Africa) and Culterra (South Africa), respectively. The composted pine bark was mixed with one third (v/v) Perlite (Genulite) (fraction size 2-5 mm) (Chemserve Perlite, South Africa) and resulted in a porosity of 0.45.

7.3.3. Inoculation and acclimatization

The mesophilic biofilter was inoculated by filling the reactor with inoculum obtained from a previous acclimated culture (du Plessis et al. 1998) and drained after 12h. The biofilter bed was then acclimatized to toluene biodegradation over a 4 month period at a toluene loading rate of 32 g m^{-3} h^{-1} and a 0.6 m^3 h^{-1} gas flow rate. Steady-state conditions, with toluene removal efficiencies >99%, were established

^{1}. The make-up gas flow rate to the detector contained H_2 (40 mL min^{-1}) and zero air (450 mL min^{-1}). The column temperature was kept constant at 104°C, the injector at 160°C and the detector at 280°C.

7.3.6. Model development

The model used in this study is based on a previous model development by Deshusses et al. (1995a) with the exception that sorption volume was not considered. This is due to the fact that all experiments were performed at steady-state or pseudo-steady state conditions. For modeling purposes, the overall structure of the biofilter is considered with the bed height being divided into layers and the fate of the pollutants in any section described based on the mass balances for individual sections (Fig. 2). The modeling details for individual sections are indicated in Fig. 2c, with the gas phase and biofilm being considered as the main mass transfer matrix. In the present model, the biofilter height and the subdivision of the biofilm was considered to comprise of 8 layers each. The polluted air is considered to flow downwards and therefore a vector of pollutant transfer in the gaseous phase. At the gas-biofilm interface, equilibrium is assumed to occur and relates the gaseous and interfacial liquid concentrations governed by Henry's law. In the biofilm, the pollutants simultaneously diffuse and are degraded by the microorganisms.

For modeling purposes, similar assumptions to those described by Deshusses et al. (1995) were made:

1. Each subdivision, as defined in Fig. 2, is ideally mixed and the pollutant concentration is homogenous.
2. The gas phase interfacial resistance is negligible.
3. The gas and the liquid (biofilm) phases are in equilibrium at the interface.
4. The biofilm is treated as a planar structure, with the microorganisms homogenously distributed throughout.
5. Substrate transport between the liquid subdivisions (biofilm) is by diffusion and can be described by an effective diffusion coefficient.
6. Oxygen limitation does not occur.

7. In the biofilm, no net growth of biomass is assumed and would allow for the kinetic constants to remain constant over the time considered.

For each layer and subdivision a mass balance equation was written and solved by finite differences (Rosenbrock (stiff) algorithm) using Berkeley Madonna™, a general-purpose differential equation solver. In the following equations, *C* refers to gaseous concentrations and *S* to liquid concentrations.

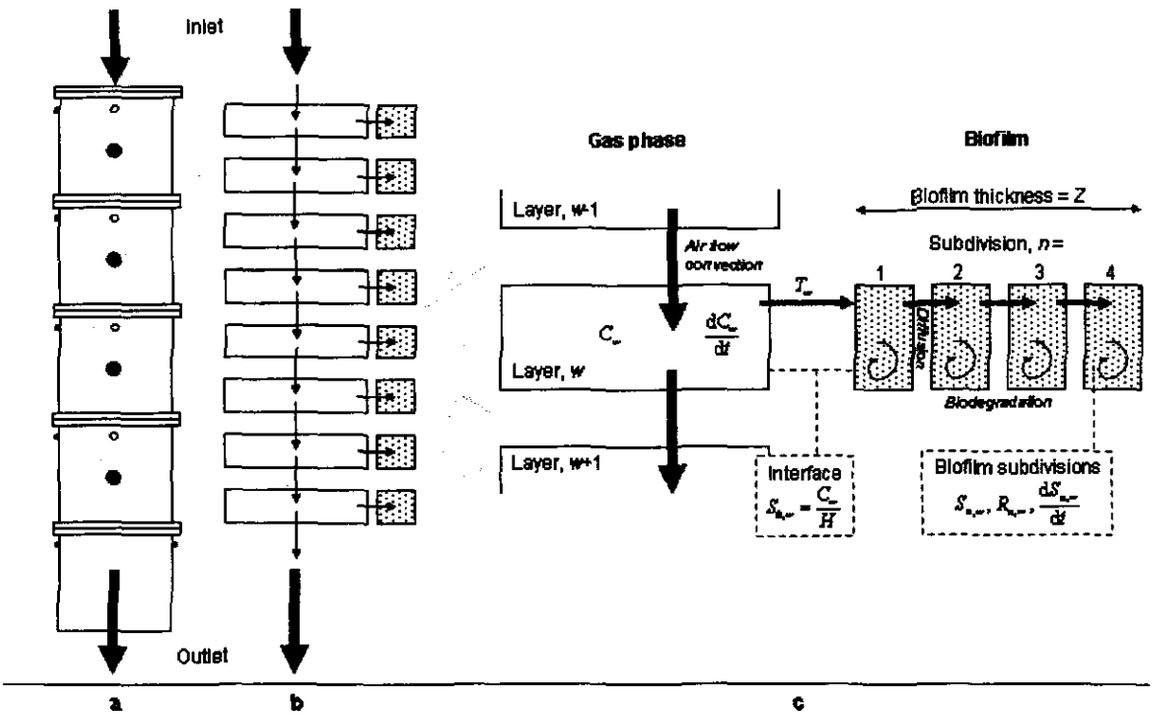

Fig. 2 Overall structure of biofilter considered for stage-wise model using finite difference calculations (**a**, **b**). The mass transfer matrix for one section is illustrated (**c**) with the gas phase and biofilm being considered. The polluted air flows through the gaseous section, where gas-biofilm equilibrium is assumed, and simultaneous diffusion and biodegradation occurs in the biofilm subdivisions.

Mass Balance over the Gas Phase. For the gas phase in the layer *w*, the balance for the gaseous concentration C_w can be written as

$$\frac{V\varepsilon}{W}\frac{dC_w}{dt} = G(C_{w-1} - C_w) - T_w \frac{aV}{W} \qquad (1)$$

where ($V\varepsilon/W$) is the volume of each gaseous subdivision, (aV/W) is its interfacial area, G the total gas flow, W is the total number of layers, and index w refers to the layer considered.

The diffusion flux for toluene (T) into the biofilm is evaluated by finite differentiation:

$$T_W = D\left(\frac{dS_w}{dz}\right)_{z=0} = D\frac{S_{0,w} - S_{1,w}}{\frac{Z}{N}} \tag{2}$$

Gaseous concentrations (C_w), and interfacial concentrations ($S_{0,w}$) are linked by the interfacial equilibrium hypothesis:

$$S_{0,w} = \frac{C_w}{H} \tag{3}$$

Mass balances over the Biofilm. In the biofilm, the mass balance over a subdivision n is described as

$$\frac{aV}{W}\frac{Z}{N}\frac{dS_{n,w}}{dt} = D\frac{aV}{W}\left(\frac{S_{n-1,w} - S_{n,w}}{\frac{Z}{N}} - \frac{S_{n,w} - S_{n+1,w}}{\frac{Z}{N}}\right) - R_{n,w}\frac{aV}{W}\frac{Z}{N} \tag{4}$$

where (aV/W)(Z/N) is the volume of one biofilm subdivision and (aV/W) is its cross section. R is the biodegradation rate, and N is the total number of biofilm subdivisions. Indices n and w refer to the number of biofilm subdivisions and biofilter stages, respectively. In Equation 4, the term in parenthesis associated with D represents the incoming and outgoing pollutant diffusion fluxes in the subdivision, as given by the finite-difference gradients.

Considering a non-growth biofilm, the degradation rate R is given for each subdivision in the biofilm by Michaelis-Menten type kinetics and described by Equation 5.

$$R_{n,w} = \frac{V_m S_{n,w}}{K_m + S_{n,w}} \tag{5}$$

7.3.7. Model parameter determination

For model parameter determination, steady state or pseudo-steady state conditions were assumed. The mesophilic model parameters were determined by a trial and error process whereby first previously published interfacial area and biofilm thickness data (Deshusses et al. 1995b) were used to determine the maximum degradation rate based on experimental data, and then using low loading experimental results to optimize the Michaelis-Menten constant. More weight (5x) was given to the outlet concentrations in relation to the other height sections. A random subset over the full loading range was then selected and enabled the further optimization of the interfacial area and biofilm thickness parameters. The thermophilic model parameters were determined based on the assumption that the compost used for both the mesophilic and thermophilic studies were similar, thereby assuming similar interfacial areas and biofilm thickness. The Michaelis-Menten constant for the thermophilic range was determined in a similar way and allowed the optimization of the maximum degradation rate. The specific optimized model parameters are listed in Table 1.

Table 1 Model parameters for the simulation of toluene in mesophilic and thermophilic operated biofilters

Biofilter characteristics	**Symbol**	**Values**	**Unit**	**Source**
Interfacial area per volume unit	A	184	$m^2\ m^{-3}$	model fitting to random data set
Biofilm thickness	Z	88	µm	model fitting to random data set
Porosity of the filter bed	ε	0.45	-	experimentally determined

		Values			
Pollutant characteristics	**Symbol**	**Mesophilic**	**Thermophilic**	**Unit**	**Source**
Effective diffusion coefficient	D	3.11×10^{-6}	3.37×10^{-6}	$m^2\ h^{-1}$	(Lide 2000)
Maximum degradation rate	V_m	2580	19970	$g\ m^{-3}\ h^{-1}$	model fitting
Michaelis-Menten constant	K_m	7.75×10^{-4}	1.87×10^{-4}	$g\ m^{-3}$	model fitting to low loading experimental data
Henry coefficient	H	0.263	0.642		(Leighton and Calo 1981)

The results presented in this study are in units that would allow easy comparison between different studies, with the equations used for the various comparisons indicated below.

Removal efficiency (RE) is defined as the percentage of pollutant being converted and can be applied for various height sections (Equation 6). For this study the removal efficiency was determined for height sections with 0.25 m increments up to a maximum biofilter height of 1 m. The loading rate (Equation 7) represents the mass of pollutant entering the biofilter per volume unit biofilter packing and time, and similarly the elimination capacity (EC) (Equation 8) the mass of pollutant being degraded per volume unit biofilter packing and time.

$$RE = \frac{C_{in} - C_h}{C_{in}} \times 100 \quad (\%) \quad (6)$$

$$\text{Loading rate} = \frac{G \times C_{in}}{V} \quad (g\ m^{-3}\ h^{-1}) \quad (7)$$

$$EC = \frac{(C_{in} - C_{out})G}{V} \quad (g\ m^{-3}\ h^{-1}) \quad (8)$$

where C_{in} = inlet concentration (g m^{-3}), C_h = the concentration at various height sections (g m^{-3}), C_{out} = outlet concentration (g m^{-3}), G = gas flow rate (m^3 h^{-1}) and V = biofilter bed volume (m^3)

7.4. Results and discussion

In the present study, the model is applied using the model parameters outlined in Table 1 and compared with experimental results under steady state or pseudo-steady state conditions. Fig. 3 compares the mesophilic and thermophilic experimentally determined outlet elimination capacities at various empty bed residence times to the model simulated values. From the results it can be observed that for both the mesophilic and thermophilic data the model simulated with good agreement at the longer empty bed residence times, while with the shorter empty bed residence times an underestimation of the simulated elimination capacities can be observed at the lower loading rates. This is especially the case for the mesophilic data (loading rate of 20 – 40 g m^{-3} h^{-1} range). The thermophilic

model also fitted the experimental data well, with almost complete elimination of toluene being observed for long empty bed residence time (258 seconds). A comparison between the simulated and experimentally determined outlet elimination capacity values indicated a good distribution of the data over the full toluene loading and gas flow rate (in essence the empty bed residence time) ranges investigated (Fig. 4). This is further exemplified by a full comparison of the removal efficiencies obtained at the various bed heights investigated (Fig. 5). More scattering of the removal efficiencies at the first height sections can be observed, especially for the thermophilic data set (where h = 0.25 m and h = 0.50 m). This could be explained mainly due to more weight that was given to the outlet concentrations during the model parameter determination, high removal rates especially in the first height section as well as more complex mass transfer phenomena that occur with thermophilic biodegradation. Despite this impediment, the model simulates with satisfactory agreement over a comprehensive data set range and gives a good estimate of various removal efficiencies over the full length of the biofilter.

7.4.1. Parameter sensitivity of the model

The parametric sensitivity of the model was determined for mesophilic and thermophilic conditions at both high inlet concentrations (2.28 g m^{-3} h^{-1}) with a low gas flow rate (0.4 m^3 h^{-1}) (case A) and low inlet concentrations (0.11 g m^{-3} h^{-1}) with a high gas flow rate (1.62 m^3 h^{-1}) (case B). Two different scenarios were considered in order to investigate the general trends with respect to parameter sensitivity and to make a sensible comparison between mesophilic and thermophilic conditions. Additional inlet concentrations and gas flow rates were also considered and provided valuable information that enabled comparison of these results. From these investigations, as well as through the trial and error model optimization process, the influence of K_m was determined to be insignificant and therefore not included in these parameter sensitivity analyses.

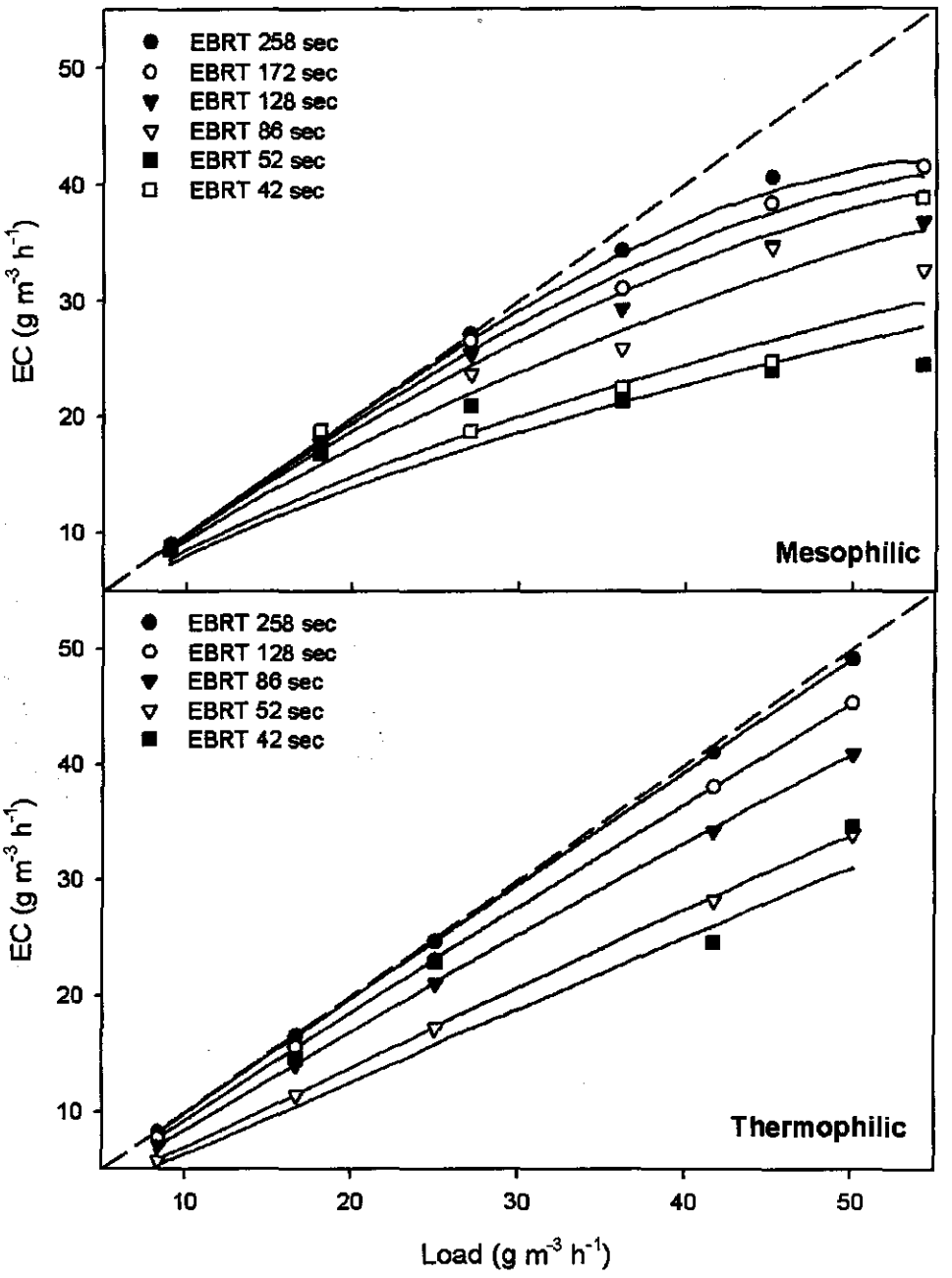

Fig. 3 Comparison of the simulated outlet elimination capacity (EC)/loading characteristics (lines) and experimental data evaluated for various empty bed residence times (EBRT) at mesophilic and thermophilic conditions. The dashed line represents 100% removal of toluene

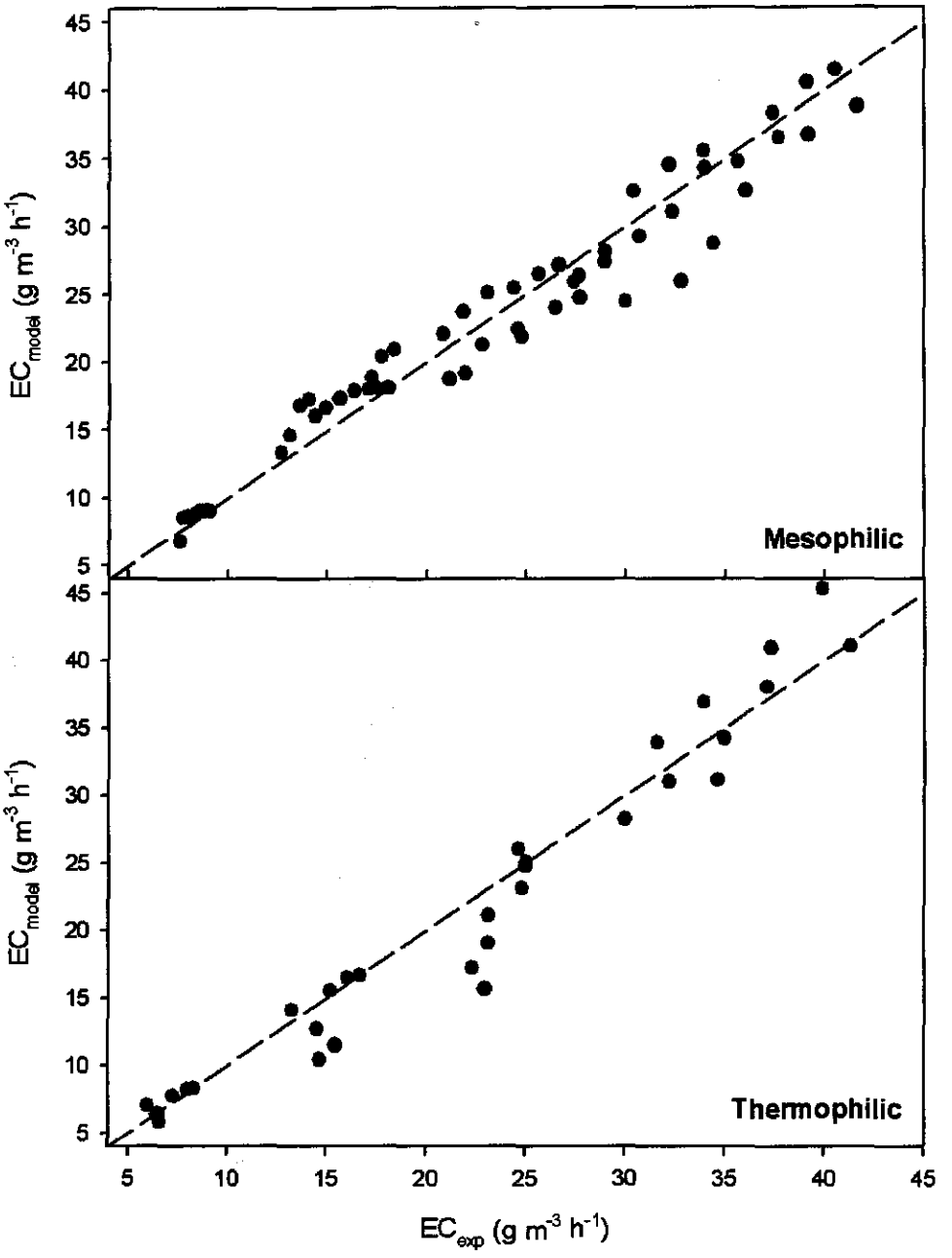

Fig. 4 Comparison of the simulated and experimental outlet elimination capacities (EC) obtained for mesophilic and thermophilic conditions

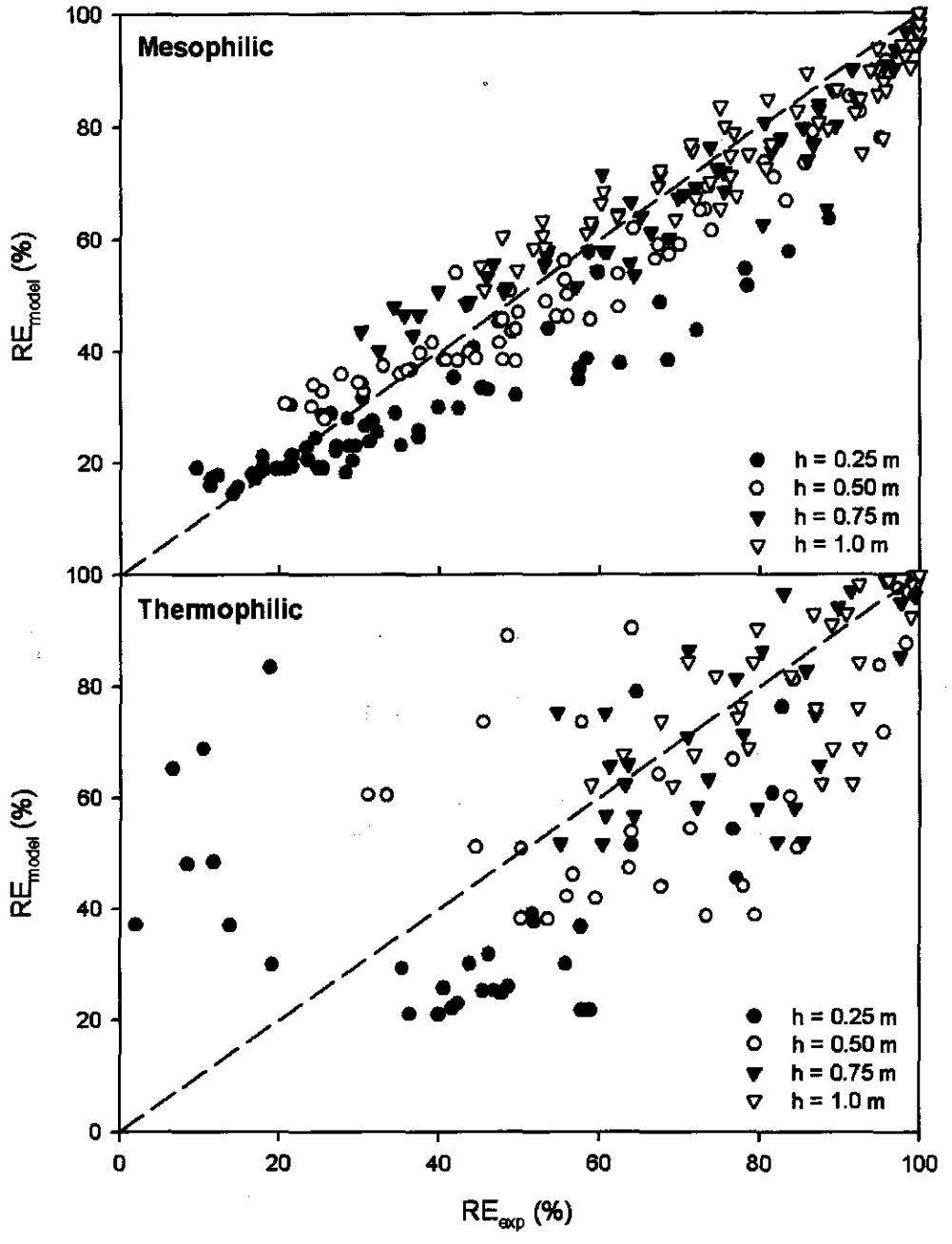

Fig. 5 Comparison of the simulated and experimental removal efficiencies (RE) obtained for mesophilic and thermophilic conditions at various bed heights (h)

The influence of the biofilm thickness (Z) and the interfacial area (A) on the toluene removal efficiency was investigated (Fig. 6). Comparison of the results obtained indicated that only during mesophilic case A conditions, the biofilm thickness made a significant difference (Fig. 6 a). A biofilm thickness of 44 µm indicated a linear relationship, while 88 µm, 176 µm and 352 µm indicated an exponential rise to maximum relationship and only reaching removal efficiencies of

>90% when the interfacial area was greater than 225 m^2 m^{-3}. A biofilm thickness of 176 µm and 352 µm also indicated similar model predictions. For similar thermophilic conditions (case A), the biofilm thickness made no difference in the model prediction of the removal efficiency and a similar exponential rise to maximum trend could be observed. Higher removal efficiencies could, however, be reached with a smaller interfacial area (Fig. 6 b). The other scenario (case B) indicated that a similar trend with an experimental rise to maximum prediction, irrespective of the biofilm thickness, applied for both the mesophilic and thermophilic conditions. Higher removal efficiencies were, however, simulated for the mesophilic model with a higher rise to maximum at an increased interfacial area.

The influence of the degradation rate (R_m) and the diffusion coefficient (D) on the toluene removal efficiency were also investigated for similar case scenarios (Fig. 7). These parameters are of particular importance mainly due to the fact that they dictate the elimination rate (Deshusses et al. 1995a). For mesophilic case scenario A in Fig. 7a, a region of reaction rate limitation can be identified when the diffusion coefficient increases to larger than $3x10^{-6}$ m^2 h^{-1}, and especially at the lower degradation rate values (R_m < 2180 g m^{-3} h^{-1}). An area with diffusion limitation can also be identified at the smaller diffusion coefficients (<$1.5x10^{-6}$ m^2 h^{-1}). Similar diffusion limitations can also be observed for mesophilic case scenario B, but to a greater degree (Fig. 7b). Furthermore, the influence of the reaction rate on the removal efficiency has a lesser effect at lower inlet concentrations (case B). For thermophilic conditions it became apparent that the reaction rates do not really have an effect on the removal efficiency in both case scenarios (Fig. 7c). The degradation rate was varied with 5000 g m^{-3} h^{-1} for both, but only minor changes could be observed for case A, while similar removal efficiencies was observed for case B. For case A, however, an area where the removal efficiency is also governed by the diffusion coefficient has been identified (D < $1.5x10^{-6}$ m^2 h^{-1}). Furthermore, from these results it became apparent that higher thermophilic removal of toluene could be obtained with higher inlet concentrations (Case A) compared to lower inlet concentrations (Case B). This is also the case when compared to similar high inlet concentrations during mesophilic operation (Fig. 7a,c).

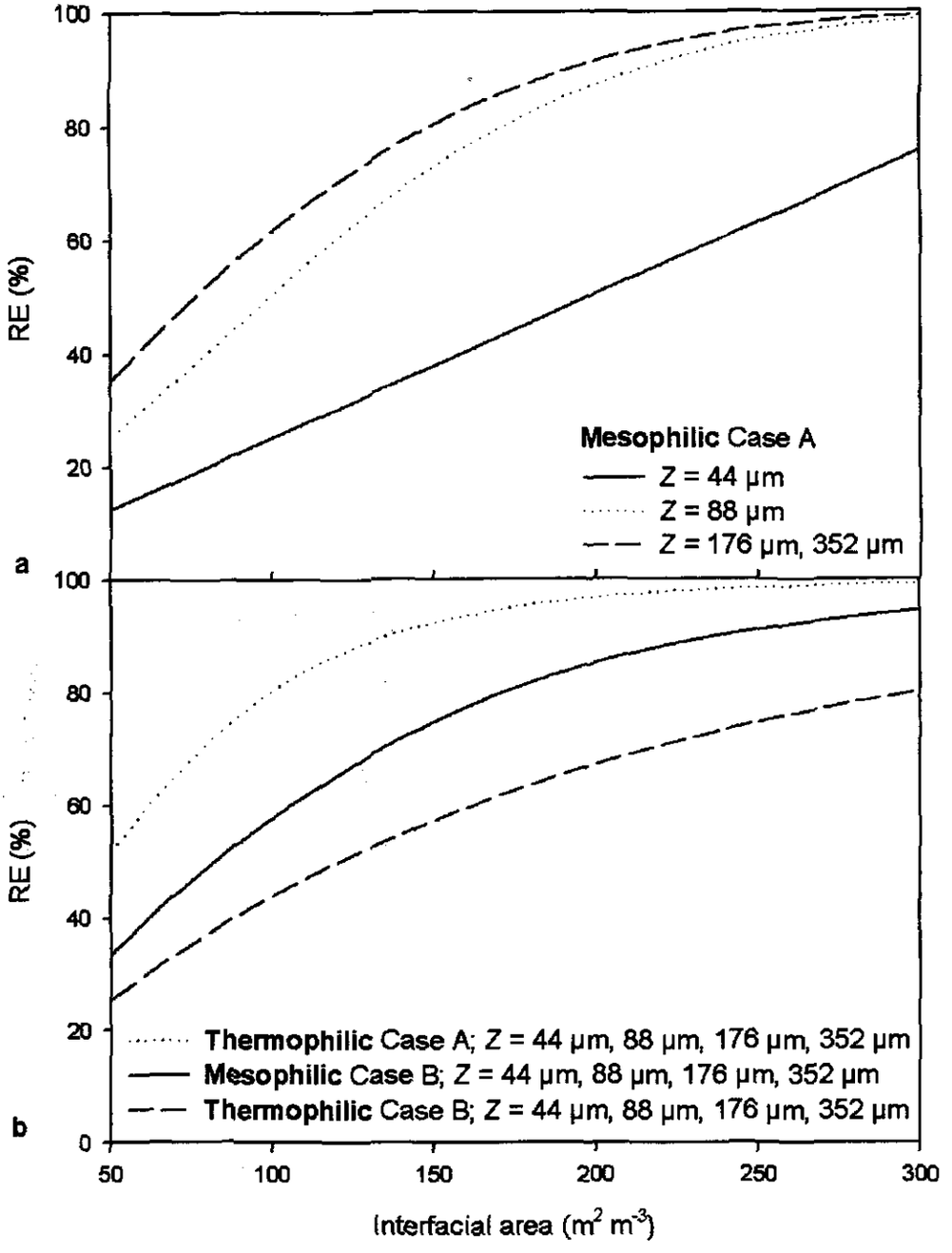

Fig. 6 Parametric sensitivity for mesophilic and thermophilic conditions indicating the effect of the number of biofilm sections *n* and the interfacial area *A* on the toluene removal efficiency at both high inlet concentration (2.28 g m^{-3} h^{-1}) with a low gas flow rate (0.4 m^3 h^{-1}) (Case A) and low inlet concentration (0.11 g m^{-3} h^{-1}) at a high gas flow rate (1.62 m^3 h^{-1}) (case B). Mesophilic graphs for case scenario A are indicted in (**a**), and all other in (**b**).

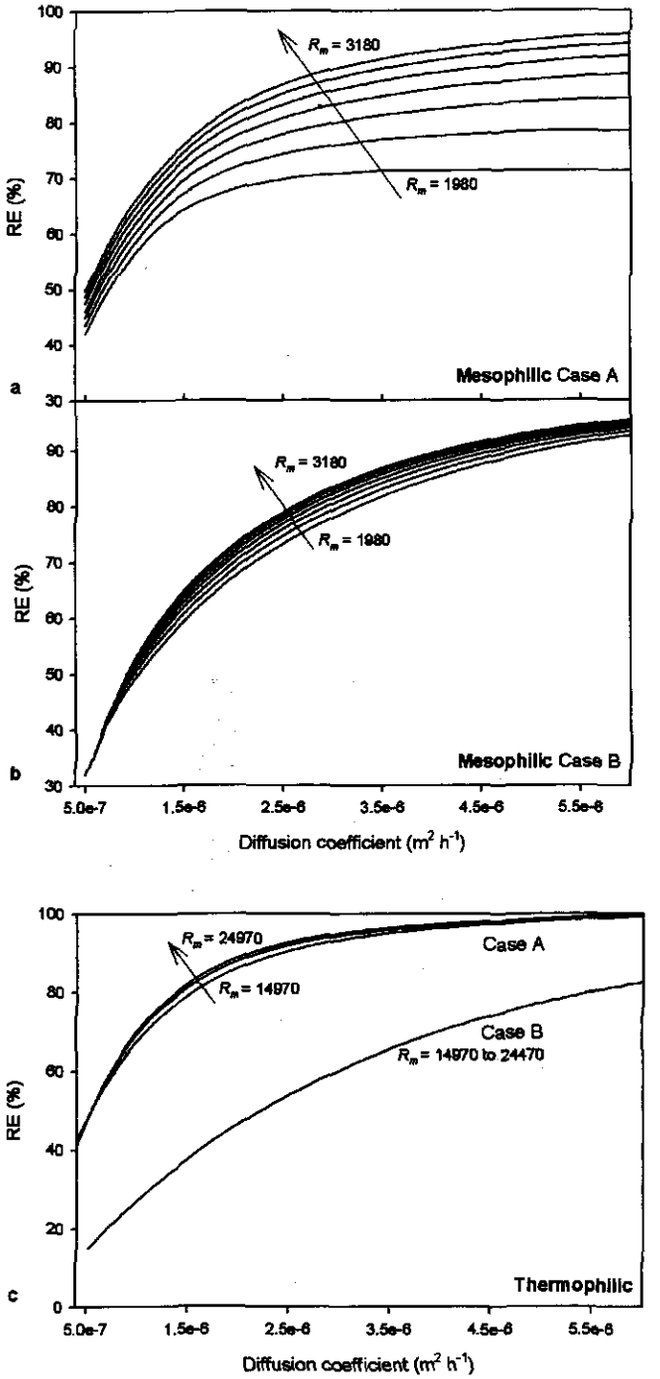

Fig. 7 Parametric sensitivity for mesophilic (**a, b**) and thermophilic (**c**) conditions indicating the effect of the degradation rate R_m (g m^{-3} h^{-1}) and diffusion coefficient D (m^2 h^{-1}) on the toluene removal efficiency at a high inlet concentration (2.28 g m^{-3} h^{-1}) with a low gas flow rate (0.4 m^3 h^{-1}) (Case A) and low inlet concentration (0.11 g m^{-3} h^{-1}) with a high gas flow rate (1.62 m^3 h^{-1}) (Case B). (Mesophilic and thermophilic graphs indicates increments in the degradation rates of 200 g m^{-3} h^{-1} and 5000 g m^{-3} h^{-1}, respectively)

7.5. Conclusions

The application of a model, with model optimization and parametric sensitivity analyses is described and verified using a comprehensive dataset obtained for a mesophilic and thermophilic operated composted pine bark biofilter. The model considered the height of the biofilter to be divided in 8 layers, while the gas phase and biofilm, which was considered as 8 subdivisions, were used to describe the concentrations of toluene in the gas phase and biofilm during steady state conditions.

In general the simulated model results correlated with high accuracy to the experimental results for both the mesophilic and thermophilic experiments. Results indicated that much higher elimination capacities could be obtained using a biofilter operating at thermophilic temperatures. For the mesophilic biofilter, although very long empty bed residence times were considered (258 seconds), indicated that the maximum degradation capacity for the reactor could be reached. This was, however, not the case for the thermophilic reactor where signs of maximum removal could not be observed for the loading rates experimentally evaluated in this study. Similar observations were made by Matteau and Ramsay (1999) using an active compost toluene degrading biofilter. This is further evident when considering the maximum degradation rate determined in this study, i.e., 2580 g m^{-3} h^{-1} vs 19970 g m^{-3} h^{-1} for mesophilic conditions and thermophilic conditions, respectively. Although the validity of this optimized parameter for thermophilic conditions might be questioned, it must be considered that the solubility and mass transfer differences at elevated temperatures using totally different consortia of microorganisms and subsequently metabolic processes, is not fully understood. Furthermore, although similar parameters (i.e., interfacial area and biofilm thickness) were considered for the thermophilic reactor as optimized for the mesophilic reactor, these might be totally different. The model does, however, indicate that thermophilic biofiltration definitely holds potential and should be explored with future industrial application for the treatment of gaseous emissions at elevated temperatures.

7.6. Acknowledgements

This research was sponsored by Sasol Technology (Research and Development Division), South Africa and the Technology and Human Resources for Industry Programme (THRIP), South Africa.

7.7. Notation and units

Unless specified otherwise, the units used in all equations are as follows:

C (g m^{-3}) gaseous concentration of toluene

D (m^2 h^{-1}) effective diffusion coefficient of toluene

G (m^3 h^{-1}) airflow rate

H Henry's coefficient for toluene

K_m (g m^{-3}) Michaelis-Menten constant for toluene

N number of biofilm subdivisions in each layer

n biofilm subdivisions ($1 \leq n \leq N$)

R (g m^{-3} h^{-1}) degradation rate for toluene

$S_{n,w}$ (g m^{-3}) liquid concentration of toluene, subdivision *n*, layer *w*

T (g m^{-2} h^{-1}) diffusion flux of toluene into the biofilm

t (s,h) time

V_m (g m^{-3} h^{-1}) maximum degradation rate

V (m^3) total reactor bed volume

W number of layer subdivisions

w biofilter layer subdivisions ($1 \leq w \leq W$)

Z (m, μm) biofilm thickness

z biofilm depth coordinate

Greek Symbols

ε filter bed porosity

7.8. References

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8. General Discussion and Conclusions

Biofiltration is without doubt emerging as a technology for the future. It has been seen as a simple process with the understanding that contaminated air enters the reactor and clean air exits, thereby often being described as a "black boxe". The true understanding of the processes that govern and the full potential of these systems is, however, slowly starting to be explored with more and more publications investigating this technology. Current research efforts are primarily targeted at improving the control of the essential operating parameters and increasing the biodegradation rates for, in particular, recalcitrant compounds. As the demand for biofilters are growing, basic biofilter design and its scale-up becomes necessary, with the need for industrial operators of biofilters to understand the process conceptually.

In this particular study the application of a toluene degrading mesophilic and thermophilic operated biofilter was investigated. The reactors were packed with composted pine bark and the mainly naturally occurring bacterial consortia acclimatized for optimal removal of toluene. Both reactors' performance were evaluated over an extended loading range, as well as at different gas flow rates, thereby allowing the development of empirical and numerical diffusion models. These models were developed with the aim to better understand the overall process and allowing the successful comparison between the performances that could be expected at the different temperatures. Operation at thermophilic conditions would further give an indication of the differences in treatment rate efficiencies due to direct microbial effects and secondary factors related to the solubility of toluene and oxygen.

Comparison of the performance using empirical models indicated that higher removal efficiencies could be obtained under thermophilic conditions, although a slightly longer retention time was required to obtain the same efficiency. Toluene removal efficiencies exceeding 90% were obtained when the reactor was subjected to retention times in excess of 0.6 minutes (36 seconds) and loading rates below 54 g m^{-3} h^{-1}. For the mesophilic conditions similar efficiencies could

be obtained with retention times longer than 0.32 minutes (19 seconds) and loading rates below 42 g m^{-3} h^{-1}. Areas where the thermophilic degradation rate decreased more rapidly compared to mesophilic conditions were identified indicating that possible mass transfer limitations of toluene into the biofilm might be occurring. Investigations into the effect of oxygen on the removal efficiencies at these different operating temperatures indicated in general a lower removal at higher temperatures for the same loading rate and retention time, which is as expected due to the increase of the Henry's constant with temperature, and the subsequent decrease of toluene and oxygen diffusion in the biofilm. The higher removal efficiency at thermophilic conditions was further reflected by the simulated model results. Optimized model degradation rates for thermophilic conditions were several times higher than that obtained for the mesophilic conditions using the extensive experimental data range. One can possibly speculate regarding the validity of the modelled degradation rate, but as mentioned, very little research have been conducted for biofiltration systems at elevated temperatures. The difference in solubility and mass transfer of toluene, and also the totally different microbial consortia with subsequently different metabolic processes, is not fully understood. The model simulated the experimental results very well, and indicated that the maximum elimination capacity for the thermophilic conditions was not reached for this investigation.

The study successfully illustrated that thermophilic biofiltration could effectively be applied to waste gas emissions being emitted at elevated temperatures. Gas streams that were previously not considered biologically treatable due to cooling considerations could now be more comparable with conventional treatment systems, broadening the application of biofiltration. Thermophilic biofiltration, does, however, require additional control systems in order to maintain optimal humidity to prevent drying of the support when treating unsaturated waste gas streams.

BTEX substrate interactions using this toluene acclimatized biofilter consortium were further investigated at a single loading rate of 18 g m^{-3} h^{-1} and retention times ranging from 0.5 to 3 minutes. The mesophilic results obtained were modelled using Michaelis-Menten kinetics and an explicit finite difference scheme to

generate V_m and K_m parameters, of which the ratio can be used as an indication of the catalytic efficiency in order to quantify substrate interactions occurring within the biofilter. Toluene was found to enhance the catalytic efficiency for *p*-xylene, while catabolism of all other compounds was inhibited competitively by the presence of toluene. All BTEX compounds could be degraded by the microbial consortium even in the absence of toluene. The catalytic efficiency of the reactor for the compounds was in the order: ethylbenzene > benzene > *o*-xylene > *m*-xylene > *p*-xylene. The catalytic efficiency of toluene was reduced by the presence of all other BTEX compounds, with the greatest inhibitory effect caused by the presence of benzene, while o-xylene and p-xylene caused the least inhibitory effect.

The effect of BTEX on the microbial consortium was further extended to include the thermophilic conditions at a similar loading and the degradation results compared overall comparatively. Overall toluene degradation rates under mesophilic conditions were found to be superior to degradation rates of individual BEX compounds. With the exception of *p*-xylene, higher removal efficiencies were achieved for individual BEX compounds compared to toluene under thermophilic conditions. Overall BEX compound degradation under mesophilic conditions was ranked as ethylbenzene > benzene > *o*-xylene > *m*-xylene > *p*-xylene. Under thermophilic conditions overall BEX compound degradation was ranked as benzene > *o*-xylene > ethylbenzene > *m*-xylene > *p*-xylene. With the exception of *o*-xylene, the presence of toluene in paired mixtures with BEX compounds resulted in enhanced removal efficiencies of BEX compounds, both under mesophilic and thermophilic conditions. A substrate interaction index was calculated to compare removal efficiencies at a retention time of 0.83 minutes (50 seconds). A reduction in toluene removal efficiencies (negative interaction) in the presence of individual BEX compounds were observed under mesophilic conditions, while enhanced toluene removal efficiency was achieved in the presence of other BEX compounds, with the exception of *p*-xylene under thermophilic conditions.

This study not only illustrated the potential of biofiltration as an emerging technology, especially at elevated temperatures, but emphasized the complexity of interactions that might occur between individual compounds that could influence

the performance of the reactors when treating mixed pollutant gas streams. Biofiltration, although at first glance seems simple, is complex and the complexity in future modeling is not easily avoidable. Extension of models for the biofiltration of pollutant mixtures is not direct and simple as it involves, in addition to some of the processes mentioned above, interactions between pollutants and oxygen as well as multi component adsorption.

At present various companies are developing novel biofilter designs with better operational control and packing in an aim to enhance biofilter performance. In addition, research is now directed towards understanding pollutant biodegradation pathways, transient behavior, nutrient limitation, inhibitors, biomass overgrowth suppression, and process modeling. It is only through such research that biofiltration can move forward to a more predictable engineering approach. As the technology advances, further research in the field will transform it from an empirical practice to one more deeply rooted in concrete theory and scientific principles. Biofiltration is "simple" and inexpensive when it is done right, but the knowledge to "do it right" is at the frontier of science and engineering.

9. Appendix I: Photographs of experimental set-up

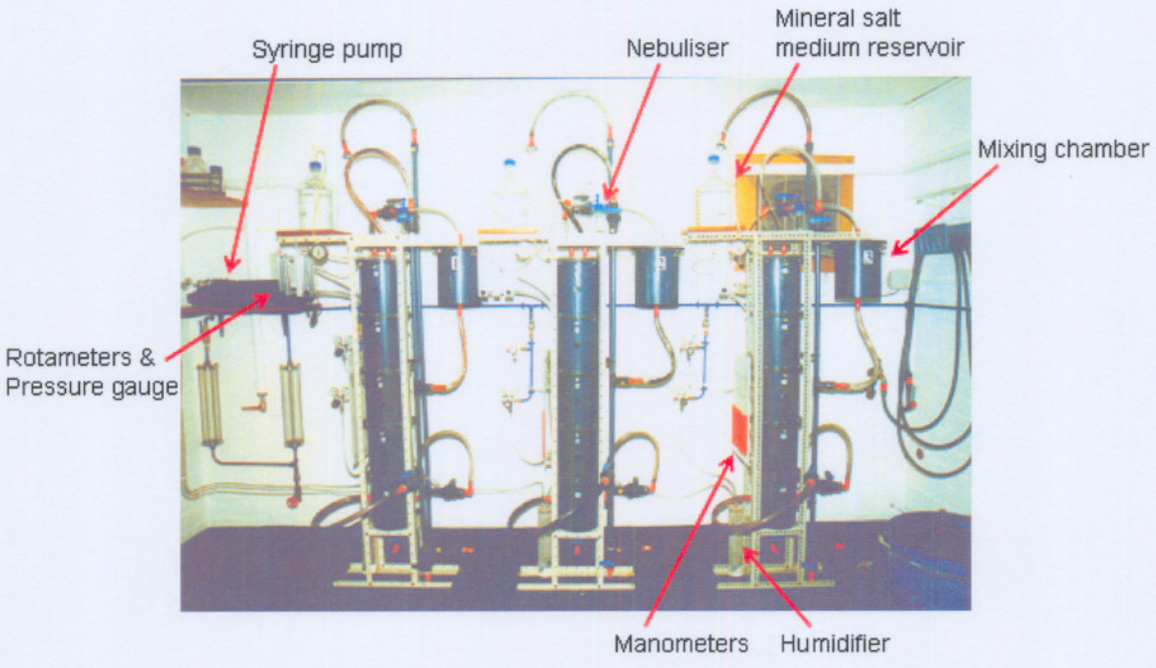

Fig 1. General set-up of three mesophilic biofilters. The biofilter on the right were used for the mesophilic experimentation.

Fig 2. Composted pine bark / Perlite support media used during experiments

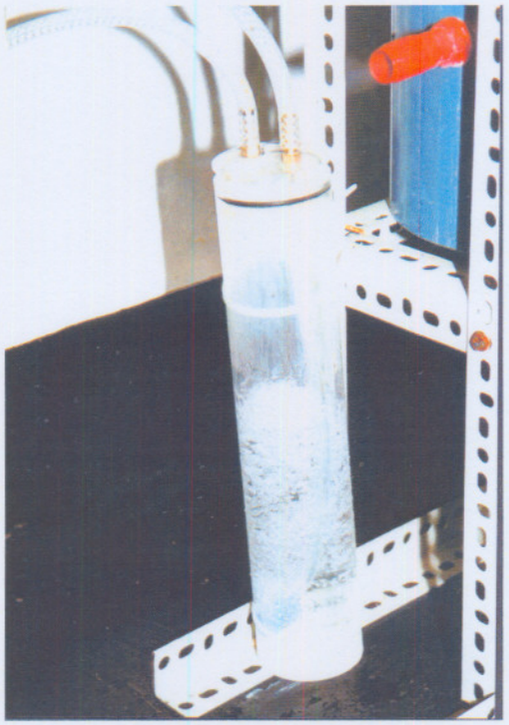

Fig 3. Humidifier used for mesophilic experiments. The mineral salt medium mist generated by the nebuliser can be observed from the biofilter reservoir section (red fitting, top right)

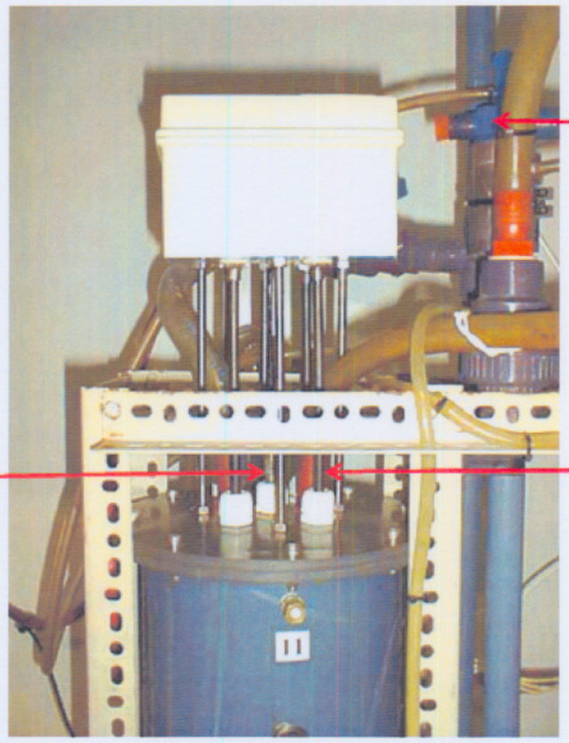

Fig. 4 Heating element and thermocouple used for thermophilic experiment.

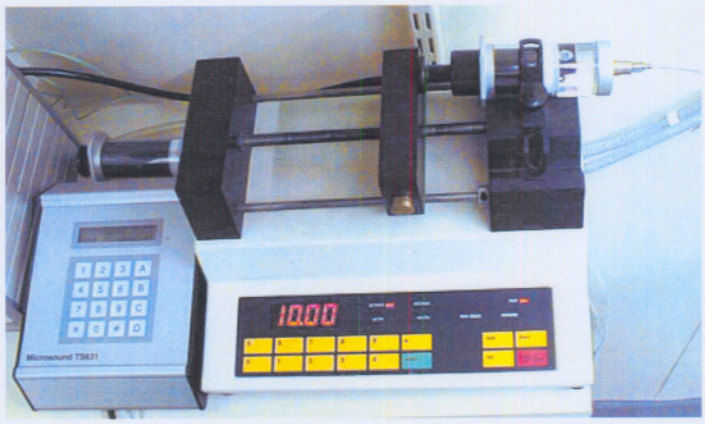

Fig. 5 Irrigation timer (left) and syringe pump (right) used for thermophilic biofiltration studies

Fig. 6 Additional irrigation were installed in order to keep high humidity levels inside the thermophilic biofilter bed

Fig. 7 Nebuliser with mineral salt medium level control used for thermophilic experiments

Fig. 8 Humidifier with water level control used for thermophilic experiment