BIODEGRADATION OF MONO-CHLOROBENZENE IN A TRICKLE BED AIR BIOFILTER

A DISSERTATION

Submitted in partial fulfilment of the requirements for the award of the degree of

MASTER OF TECHNOLOGY

in

CHEMICAL ENGINEERING

(With Specialization in Industrial Pollution Abatement)

By

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Candidate's Declaration

I here by declare that the work which is being presented in this dissertation entitled **"Biodegradation of Mono-Chlorobenzene in a Trickle bed air biofilter"** in partial fulfillment of the requirements for the award of degree of Master of Technology in Chemical Engineering with specialization in Industrial Pollution Abatement(IPA), and submitted in the Department of Chemical Engineering, Indian Institute of Technology Roorkee, is an authentic record of my work under the supervision of Dr. C.Balomajumder, Associate Professor, Department of Chemical Engineering, Indian Institute of Technology Roorkee.

The matter presented in this dissertation has not been submitted by me for the award of any other degree of this/or any other institute/industry.

Date: June 30, 2005

Place: IIT Roorkee

(J.SUNDARAMURTHY)

Certificate

This is to certify that the above statements made by the candidate are correct to the best of my knowledge and belief.

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Abstract

Volatile organic compounds (VOCs) are among the new class of air pollutants generated from a variety of industrial sources. The presence of VOCs in the atmosphere creates a number of problems for human health as well as environmental quality. Many technologies are available for treating the VOCs. Among them biofiltration is the one which has attracted wide attention in the recent years. Biofiltration is based on biological destruction where VOCs present in the air streams are treated, without producing further more pollutants. Biofiltration is a cost effective air pollution control technology for volatile organic compounds. Biofiltration involves contacting of VOCs with microbial biofilms which are immobilized on porous support materials. Then the microorganisms in the biofilm degrade VOC into CO_2, water and biomass.

Biofiltration of Mono-Chlorobenzene (MCB) vapor from the air stream was evaluated using a biotrickling filter packed with coal. Mixed consortium of activated sludge was used as inoculum. The continuous performance of biotrickling filter for the Mono-Chlorobenzene removal was monitored at different gas concentrations, gas flow rates, and EBRT's. A maximum removal efficiency of 95.20 % was achieved for the inlet MCB concentration of 1.069 g/m^3 and EBRT of 94.26 s. The effect of temperature and pH on the degradation of MCB in biotrickling filter was studied. The optimum temperature and pH were found to be 22^0C-30^0C and pH 7-7.7. The effect of starvation on the biotrickling filter was studied. After starvation, the biotrickling filter lost its ability to degrade MCB initially, but recovered very quickly within a short period of time. The kinetic constants such as half saturation constant and maximum reaction rate were determined for the degradation of MCB. A mathematical model was developed and the experimental results were compared with the theoretical values. The model showed that the degradation of MCB followed first order kinetics.

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Date: June, 30, 2005

Place: IIT Roorkee

(J.SUNDARAMURTHY)

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Nomenclature

A	Cross-sectional area of the biotrickling filter, m^2
A_s	Specific surface area packing material, m^{-1}
C_{in}	Inlet VOC concentration in the gas phase, g/m^3
C_{out}	Outlet VOC concentration in the gas phase, g/m^3
C_g	MCB concentration in the gas phase, g/m^3
d_p	Diameter of the coal particle, m
D_e	Effective diffusion coefficient, m^2/s
h	Height of the packing material, m
K	Overall mass transfer coefficient, $g/m^3/s$
k_f	Rate constant, s^{-1}
K_m	Half saturation constant, g/m^3
m	Henry's dimensionless coefficient,
N_s	Mass flux, biofilm, $g/m^2/s$
Q	Volumetric gas flow rate, m^3/h
r	Overall reaction rate, $g/m^3/s$
r_{max}	Maximum reaction rate, $g/m^3/s$
t	Time, s
U_g	Superficial velocity of the gas, m/s
V	Volume of the biotrickling filter, m^3
x	Distance in biofilm from the packing surface, m
δ	Biofilm thickness, m
ϕ	Thiele Modulus defined as $\phi = \sqrt{\delta(k_f / D_e)}$, dimensionless

Abbreviations

ACGIH	American Conference of Governmental Industrial Hygienists
EC	Elimination capacity
EBRT	Empty Bed Residence Time
EPA	Environmental protection agency
HAP	Hazardous air pollutants
VOC	Volatile organic compound
MCB	Mono-Chlorobenzene
NVOC	Nonvolatile organic compounds
OSHA	Occupational Safety and Health Administration
PEL	Permissible exposure limit
SVOC	Semi-volatile organic compound
TBAB	Trickle bed air biofilter
TLV	Threshold limit value
TWA	Time-weighted-average

Chapter 1

Introduction

Over the past few decades enormous quantities of industrial pollutants have been released into the environment. Due to high releases of wide variety of pollutants in environment results in an increasing number of environmental related problems. These xenobiotic compounds are usually removed slowly and tend to accumulate in the environment. Due to the high degree of toxicity, their accumulation can cause severe environmental problems. With increasing public concern about deteriorating environment air quality, stringent regulations are being enforced to control air pollutants.

Volatile organic compounds (VOCs) belong to a special category of air pollutants that can adversely affect our health. Yet they receive little attention in India. Industrial operation is an important source of VOCs and there are various technologies that can curtail VOC emissions from these industrial processes. Environmental biotechnology is an option to curtail the VOC emission.

Environmental biotechnology refers to the utilization of microorganisms to improve environmental quality. Chemical engineers are uniquely poised to contribute in this emerging area since many of the potential solutions require a combined perspective from modern biology and process engineering, two areas where chemical engineers excel. A deeper inspection reveals that the design of biological catalysts, based on defined techniques from biochemistry and biology is indeed parallel to our understanding of chemical kinetics, transport, separation, and control.

Scientists have generally considered biological treatment processes too inefficient to challenge chemical treatment processes, particularly in treating large volumes of waste. The typically long contact time of 10 s or even longer between the pollutants and microbes would require an impractically large process for a practical treatment plant. However, it is well known that biological processes are generally safer, greener, and cheaper to run. The obvious challenges are whether similar conversions of chemical treatment processes into biological processes could be achieved, offering the same treatment capacity that are much cheaper and safer. Considering the cost benefit and environmental impact of switching to biological treatment processes, this is one opportunity that chemical engineers cannot afford to miss.

1.1. Definition of VOC

Volatile Organic Compounds (VOCs) are organic chemicals that have a high vapor pressure and easily form vapors at normal temperature and pressure. VOC is any volatile compound containing the element carbon, excluding methane, carbon monoxide, carbon di oxide, carbonic acid, metallic carbides or carbonates, ammonium carbonate, and exempt compounds. More precisely, if an organic compound has a vapor pressure greater than 0.1 mm Hg at 20°C, it is considered volatile. Hundreds of VOCs can be found in the air and have been documented from a variety of sources.

Organic compounds can be divided into three categories based on volatility. Volatile organic compounds (VOCs) exist in the vapor phase at ambient temperature and have vapor pressure greater than about 1 mm Hg. Semi-volatile organic compounds (SVOCs) have vapor pressure in the range of 10^{-7} to 0.1 and are present both in vapor and particle-bound states. Nonvolatile organic compounds (NVOCs) are those that are present only as particles and have a vapor pressure of less than 10^{-7} mm Hg. The U.S. Environmental protection agency (EPA) defines VOCs as any organic compounds that participate in atmospheric photochemical reactions. EPA has identified 188 hazardous air pollutants (HAPs), 150 are included in VOC and SVOC category. In Table 5.1, some of the VOCs are listed.

1.2 Mono-Chlorobenzene

The Clean Air Act Amendments of 1990 list chlorobenzene as a hazardous air pollutant. Chlorobenzene (also called Mono-Chlorobenzene or MCB) is a flammable liquid. It does not occur naturally. Chlorobenzene is produced by bubbling chlorine gas through liquid benzene in the presence of ferric chloride catalyst. Chlorobenzene and hydrochloric acid are produced in the reaction. Because of environmental concerns for chlorinated organic chemicals in general, future demand for MCB is likely to decline. The largest users of MCB are companies that make Nitrochlorobenzene. Companies also use MCB to make adhesives, paints, paint removers, polishes, dyes, and drugs. In the past, companies have used MCB to make phenol and related chemicals, pesticides (like DDT), and aniline.

Mono-Chlorobenzene evaporates when exposed to air. It dissolves slightly when mixed with water. Most releases of Chlorobenzene environment are to air. MCB also can evaporate from water and soil exposed to air. Once in air, MCB breaks down to other chemicals. Because it is a liquid that does not bind well to soil, MCB that makes its way into the ground can move through the ground and enter groundwater. Plants and animals are not likely to store Chlorobenzene.

Table 1.2: Physical Properties of Chlorobenzene:

Synonyms	Mono-Chlorobenzene; Benzene Chloride; Chlorobenzene; Phenyl Chloride
Molecular formula	C_6H_5Cl
Molecular Weight	112.56
Boiling Point	131 - 132 °C
Melting Point	-45 °C (solidifies at -55 °C)
Flash Point	85 °F (closed cup)
Vapor Density	3.88 (air = 1)
Vapor Pressure	11.9 mm Hg at 25 °C
Density/Specific Gravity	1.107 at 20 °C (water = 1)
Log Octanol/Water Partition Coefficient	2.84
Conversion Factor	1 ppm = 4.6 mg/m^3
Henry's Law constant	367 Pa.m^3/mol
Water solubility	0.207 g/l at 20 °C

1.2.1 Mono-Chlorobenzene and its health effects

EPA has classified Chlorobenzene in Group D (not classifiable as to human carcinogenicity). Effects of Chlorobenzene on human health and the environment depend on how much chlorobenzene are present and the length and frequency of exposure. Effects also depend on the health of a person or the condition of the environment when exposure occurs. The most probable route of human exposure to chlorobenzene is inhalation.

i) **Acute effects**

(a) Contact with Chlorobenzene liquid or vapor can irritate the skin, the eyes, the nose, and the throat.

(b) Exposure to large amounts of Chlorobenzene causes headaches, muscle spasms, and also causes adverse nervous system effects, including unconsciousness.

ii) **Chronic effects**

(a) Chlorobenzene is a central nervous system depressant, and may cause respiratory tract, eye, and skin irritation and adverse effects on the bone marrow.

(b) Chronic human exposure to chlorobenzene causes central nervous systems effects with symptoms including numbness, cyanosis, hyperesthesia, muscle spasms and reproductive system including teratogenic.

(c) Chlorobenzene may sensitize the myocardium to the arrhythmogenic effects of epinephrine.

(d) Adversely affect the liver, kidneys, and the blood of animals.

Due to exposure associated health aspects of Mono-Chlorobenzene, it is becoming increasingly important to reduce its concentration in the environment.

1.3 Abatement technologies available for controlling VOCs

VOCs emitted into the atmosphere are controlled by two primary ways. The first is source control. Source control consists primarily of implementing substitute technology that reduces emissions at the source or by using less volatile organic compounds in the process or by modifying process equipment. The second involves treatment of the emissions at the stack. Two primary categories of treatment are recovery (capture) and destruction of the VOCs. Some treatment technologies use a combination of both capture and destruction of the VOCs. Source control method's applicability is limited, as it is not possible to change the raw material or modify the process or change the equipment for a specific operation.

Abatement technologies involve physical, chemical or biological methods for the treatment of VOCs. Abatement technologies available for the treatment of the emissions at the stack are presented in Figure 1.1 and they are discussed below.

a) Recovery/removal

Recovery/removal options extract the VOC or odor from the air stream for recycling. The VOC/odor compounds can then be treated elsewhere. Recovery can be particularly effective for processes generating large volumes containing high levels of a single VOC. A key benefit is that recovery makes the organic available for re-use within the process, as an alternating feedstock or for its energy content.

i) Adsorption

This technique is used where VOCs or odors are readily adsorbed onto activated carbon or other adsorbents like silica gel. When both the VOC concentration and the flow rate are low the adsorption/desorption technique is used. Adsorption is often used to recover the solvent. Following desorption of the saturated adsorbent (e.g. with steam or hot gas), the solvent is condensed, dehydrated and either re-used directly or sent for further processing. Activated carbon is generally used as an adsorbent, and it is easily regenerated or disposed.

ii) Absorption (scrubbing)

This is a proven and widely used form of treatment, particularly with gas and particulate emissions. Water is the most commonly used scrubbing liquid; alkaline solutions are used for acidic components and a dilute acid solution for alkaline compounds such as ammonia. If the VOC is not readily soluble in water, then oil or a high boiling point organic liquid in which it has good solubility is used. The saturated scrubbing liquid may itself require further treatment.

iii) Condensation

With high VOC concentrations, the solvent-laden air stream may be cooled sufficiently so as to condense as a liquid. Very low temperatures (i.e. cryogenic condensation) are required to achieve the low emission limits which is difficult to achieve sometimes.

iv) Membrane separation

Polymeric membranes are applied to separate organic vapors/VOCs (to which the membranes are permeable) from air. The membrane separation is an advanced technique to recover the VOC. But, due to the high cost of membranes, and their limited lifetime, this seems to be a quite expensive option.

b) Destruction

Destructive options aim to break down the VOCs and odors to carbon dioxide and water so that no further treatment is necessary.

i) Oxidation

Oxidation (thermal or catalytic) is probably the most widely known method of VOC abatement currently available. Oxidation is generally capable of meeting most current emission limits, but both thermal and catalytic oxidation systems have high capital and operating costs - particularly for emissions with low VOC concentrations. With thermal oxidation, the exhaust gas is raised to a temperature of usually over 800 °C to allow high levels of oxidation of the organic compounds. Most systems incorporate a high degree of heat recovery to minimize the energy use. Catalytic incineration operates at a lower temperature, around 350 °C, with the organic being oxidized in a catalytic bed.

ii) Biological treatment

Within the range of its applicability, biological treatment represents one of the most cost effective technologies available. It has moderate capital costs and low operating costs, and does not produce secondary pollutants. Biotechnology based treatments are capable of degrading a wide range of organic solvents.

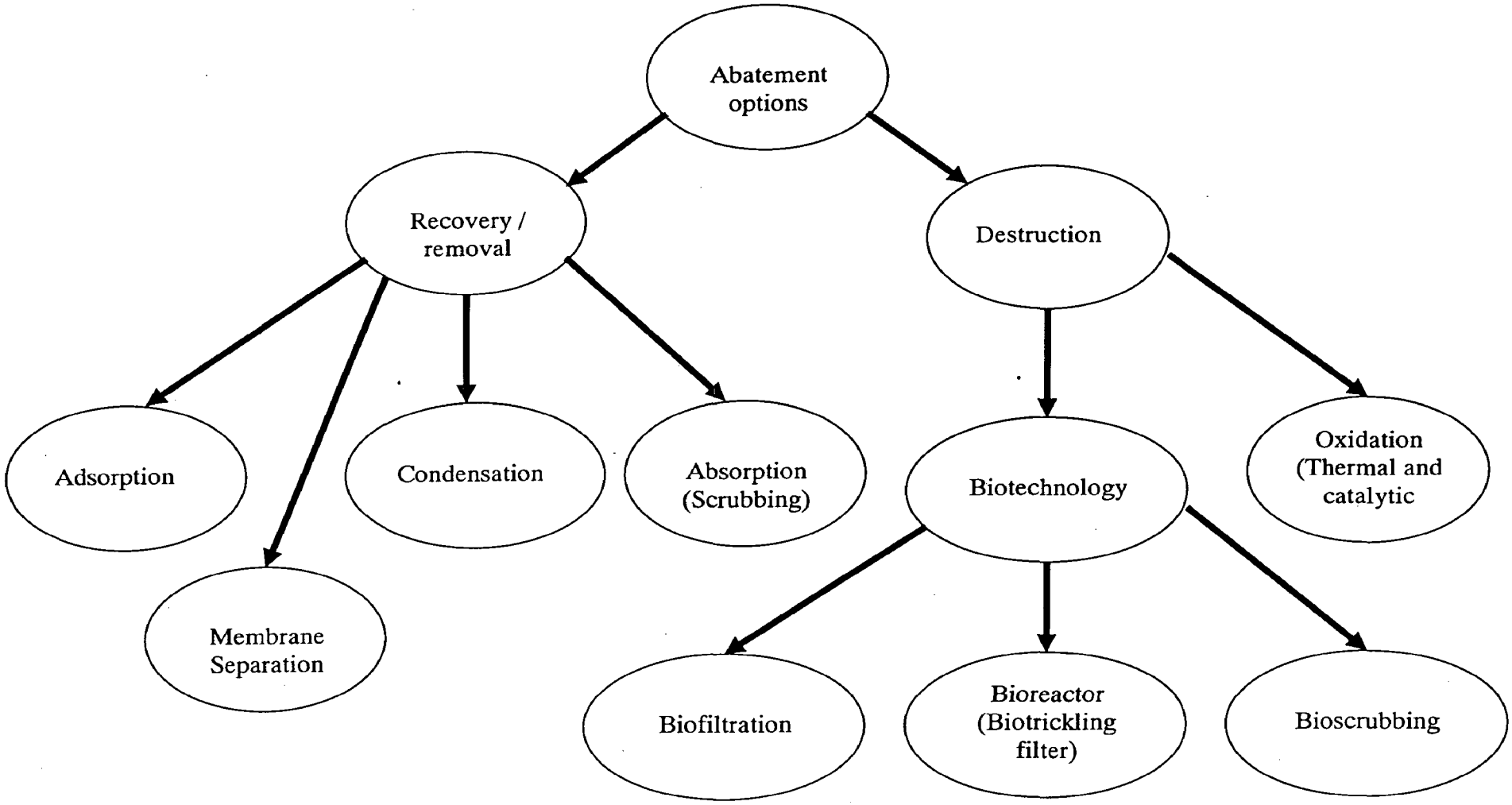


Figure 1.1: Abatement technologies available for the control of VOC (Mike Jones)

1.3.1 Selection of technologies to abate VOCs from waste gases

Although there are numerous technologies available for control of VOC emission but all are not applicable everywhere. Each technology can be applied across a range of concentration and flow rates. However, the optimum choice will be dependent upon individual site requirements. The applicability and availability of a technology for the abatement is restricted by economic consideration, energy consumption, space availability and type of VOC to be treated (as the secondary pollutant can also be produced). Table 1.3a gives a clear idea of potential of various VOC/Odor abatement techniques for VOC removal in various VOC emitting industries.

The abatement technology depends on a wide range of factors. Some of them are discussed below (Cox, et al.,, 2001):

a) The concentration and flow rate of VOC in the exhaust stream
b) The nature of the organic mixture organics in the exhaust stream
c) The biodegradability of the organic constituents
d) The composition of the exhaust stream carrier
e) The temperature, pH and humidity of the exhaust stream
f) The destruction efficiency required to meet the regulation restriction of local controlling bodies
g) Physical and Chemical properties of the VOC to be treated and its end product after the treatment.

Table 1.3a: Potential for VOC/Odor abatement technique (Jones, et al.,)

Sector/process	Biofilters	Bioreactors and Bioscrubbers	Thermal Oxidation	Catalytic Oxidation	Absorption	Adsorption
Chemical industry	††	†††	††††	††	††	†††
Pharmaceutical industry	††	†††	†††	††	††	†††
Automotive industry	††	†††	††††	††	††	††††
Foods/semi-luxuries	†††	††	†	†	†††	††
Electrical engineering and electronics	†	†††	†††	††	†	†††
Paint shops	††	††††	††††	††	†	†
Printing	††	††††	†††	††	†	††
Plastics processing	††	†††	††	††	††	†††
Tank depots	††	†	††	†	†	††
Composting	††††	†	†	†	†	†
Sewage treatment plants	††††	††	†	†	†	†
Animal carcass disposal	††††	††	†	†	†	†
Commercial kitchens	†	††	†	†	†	†††

Note: †††† High ††† Medium †† Low † Very Low

1.3.2 Biofiltration – A biological air pollution control technology:

The removal of VOC emissions in recent years necessitates the development of innovative, cost-effective treatment alternatives. Traditional VOC control technologies such as adsorption, absorption, thermal and catalytic oxidation have been commonly used to remove VOC vapors in air streams. However, even the desired VOC removal efficiencies are achieved, but they suffer from high operating costs and secondary waste stream issues (Corsi, et al., 2002). Compared to the above processes, biological air treatment methods are very cost effective and degrade VOCs to non-toxic material such as carbon di oxide and water.

Biological methods exploit the natural ability of micro-organisms (microbes, e.g. bacteria and fungi) to degrade and transform waste to simple and harmless substances. Among biological air treatment methods, biofiltration have attracted most interest. Biofiltration basically originated from Europe and its application was growing all over the world (Swanson, et al., 1997). The basic concept of biofiltration is to remove gaseous contaminants by passing them through microbial layers in a packed bed. The biofiltration process utilizes a biological microbial film fixed on a support medium where the contaminants are adsorbed from the waste gases and biologically converted to benign end products such as water, carbon di oxide and biomass (Sorial, et al., 1997).

The advantages of the biofiltration are as follows:

- Biofiltration is an simple and cost-effective technology
- Biofiltration has a very high odor and VOC removal efficiency
- Biofilters have low investment and operation costs
- Biofiltration process results in a complete decomposition of the pollutants, creating no secondary pollutants

There are three types of biofiltration methods available for treating VOCs and odors (Jones, et al.,). They differ each other in their complexity, process design, equipment dimensions and working parameters, but based on the same principle. The applicability, advantages, and issues to be considered for the three types are summarized in Table 1.3b.

Table 1.3b: Comparison of Biofilter, Biotrickling filter and Bioscrubber (Cox, 2001), (Jones et al.,)

Method	Application area	Advantages	Disadvantages
Biofilter	➢ Odors and low VOC concentrations ➢ VOC concentration less than 0.5 g/m^3 ➢ Flow rates of 500 to over 200,000 m^3/h, depending on filter design	➢ Low capital costs ➢ Low operating costs ➢ Degrades a wide range of compounds ➢ Can handle insoluble VOCs ➢ Easy to operate and maintain	➢ Low specific productivity ➢ Control of operating conditions required ➢ Large area required ➢ Biomass bed is heavy and bulky to replace ➢ Long retention time ➢ Susceptible to channeling
Bioreactor (Biotrickling filter)	➢ Low/medium VOC concentrations ➢ VOC concentration less than 3 g/m^3 ➢ Flow rates of 500 to 50,000 m^3/h	➢ Medium capital costs ➢ Low operating costs ➢ Low retention time/high volume throughput ➢ Small size and weight	➢ Requirement to design system for fluctuating concentrations
Bioscrubber	➢ Low/medium VOC concentrations ➢ VOC concentration less than 3 g/m^3 ➢ Flow rates of 10,000 to 50,000 m^3/h	➢ Able to deal with high flow rates and severe fluctuations ➢ Good control of reaction conditions	➢ Treats only water soluble compounds ➢ Can be complicated to operate and maintain ➢ Extra air supply may be needed ➢ Excess sludge will require disposal

1) **Biofilter** - The VOCs or odour-causing compounds present are degraded as the contaminated air passes through a bed of naturally-occurring microbes immobilized on a natural support, e.g. peat, bark, compost, soil and heather. Both the bed and air stream are kept moist to encourage microbial activity. The solvents and other organic compounds present in the air stream provide a source of carbon for the microbes, while the organic support acts as a source of other nutrients. Because of the low density of microbes, which are generally present as a mixed culture, the specific performance of a biofilter is relatively low.
2) **Bioreactor (Biotrickling filter)** - The VOC-laden air stream is passed over microbes immobilised as a biofilm on synthetic material with a high surface area. The microbes are kept moist by the recirculating water, to which nutrients are added. The VOCs dissolve in the aqueous phase and are destroyed by the growing microbes.
3) **Bioscrubber** - The VOCs are first absorbed in a liquid phase (usually water) in a tower or tank packed with an inert support. The solution is then pumped to an aerated tank containing suspended biomass in the form of activated sludge where biodegradation takes place. Nutrients are added to the circulating water. The mixture of biomass and treated water is separated in a settling tank; the wastewater is discharged and the biomass returned to the activated sludge bioreactor.

Relatively uncomplicated design and simple operation and maintenance requirements make biofiltration a good option than other air control technologies. Table 1.3c gives some examples of the application of biofiltration in various industries. Table 1.3d gives the degradability of VOCs by the biofiltration technique.

Table 1.3c: Examples of the use of biofiltration to abate VOC/odour emissions

Application	VOC/odour
Cable production plant	Xylene
Chemical plant	Formaldehyde
Coach works	Phenol, Formaldehyde, Ethanol
Composites plant	Cyclohexanone, Methyl ethyl ketone
Furniture factory	Hexane, Ethanol, Acetone, Styrene, Ethyl Acetate, Toluene, Xylene
Glass fibre plant	Styrene, Epichlorhydrin
Leather factory	Ethyl acetate, Butyl acetate, Acetone, Toluene, Ethanol
Meat processing plant	Odorous Aldehydes, Acids
Rubber factory	Ethyl acetate, Butyl acetate, Acetone
Shoe factory	Ethyl acetate, Butyl acetate, Acetone
Printing	Ethyl acetate, alcohols

Table 1.3d: The biodegradability of VOCs by microorganisms (Swanson, et al.,1997)

Readily degraded	Moderately degradable	Difficult to degrade
Petrol	Crude oil	Perchloroethylene (PCE)
Diesel	Creosotes	Carbon tetrachloride
Benzene	Pentachlorophenol (PCP)	Polychlorinated biphenyls
Xylene	Long chain aliphatic	(PCBs)
Toluene	hydrocarbons	Chlorinated pesticides such
Phenols	Phthalates	as (Dichloro-Diphenyl-
Alcohols, eg methanol	Trichloroethylene (TCE)	Trichloroethane) DDT,
Ketones, eg acetone	Vinyl chloride	heptachlor and
Hydrocarbons	Ethers	chlordane
Acrylonitrile	Ammonia	
Esters, e.g. ethyl acetate		
Hydrogen sulphide		
Styrene		

1.4 Objective of the Present Research Work:

The objective of the research work is to use a biological air treatment method to control the Mono-Chlorobenzene which is widely used in many industries as discussed in Chapter 1.1. Biofiltration technique was employed in this study. Biotrickling filtration is chosen in this work because of its advantages over the other biofiltration techniques. Coal was used as the packing material because of its characterstics like high surface area, good adsorbitivity, cheaper cost and long life. MCB, a halogenated aromatic hydrocarbon which produces secondary pollutants when treated by other air pollution control technologies was degraded in biotrickling filtration. The capability of microorganisms obtained from the activated sludge to degrade the MCB was studied in this work. The degradability of MCB and the performance of the biotrickling filter were also studied.
The main objectives of the work are:

1. To examine the capability of the biotrickling filter for degrading the MCB gas stream
2. To study the performance of coal as a packing material
3. To study the influence of inlet concentration, gas flow rate and residence time on the performance of the biofiltration system
4. To study the effect of change in temperature and pH on the performance of the biotrickling filter
5. To determine the Michealis-Menten kinetic constants
6. To develop a suitable model for the biotrickling filter degrading the MCB.

Chapter 2

Literature Review

2.1 Biotrickling Filtration Fundamentals

2.1.1 Biofilm

In the biofiltration system, the pollutants are removed due to biological degradation rather than physical straining as if the case in normal filters. Biofilm is a group of microorganisms (aerobic, anaerobic, and facultative bacteria, fungi, algae and protozoa) which attach themselves to the packing media and form a biological film or slim layer of a viscous, jelly like structure (Peavy, et al, 1985). The development of biofilm may take few days or months depending on the microorganisms concentration. The crucial point for the successful operation of a biofilter is to control and maintain a healthy biomass on the surface of the biotrickling filter. There are three main biological processes that can occur in the biotrickling filter, (i) attachment of microorganism, (ii) growth of microorganism, and (iii) decay and detachment of microorganisms (called as Sloughing). Since the microorganisms are attached to the surface, the supply of organics or substrate (food) to the microorganisms in a biofilm is mainly controlled by the bulk and substrate transport phenomena. The substrate must be transported from the bulk liquid to the biofilms outer surface where it has to diffuse into the bulk liquid into the biofilm for its metabolism. The factors influences the rate of substrate utilization within a biofilm are (i) substrate mass transport to the biofilm, (ii) diffusion of the substrate into the biofilm, and (iii) utilization kinetics of the biofilm. Biomass detachment is one of the most important mechanisms that can affect the maintenance of biomass in the biotrickling filter (Durgananda, et al., 2001).

When the waste gases are passed over these films in thin sheets, the pollutants in the gas stream will pass into the biofilm due to concentration gradients within the film. The pollutants in the waste gases which are retained in the biofilms (sticky surfaces) are biodegraded into CO_2, H_2O, inorganic salts, and biomass. Growth of the biofilm is restricted to one direction i.e. outwards from the solid surface only. The growth, attachment and decay of biofilm depend on many factors such as gas flow rate, pollutant concentration, oxygen supply, nutrient, pH and temperature (Peavy; et al., 1985).

2.1.2 Biotrickling Filter

Biofiltration is actually a gaseous treatment process based on degrading the gaseous pollutants (also called as Trickle bed air biqfilter (TBAB)). Bacteria and fungi are capable of using a wide variety of organic material as food source. These microbes are plentiful in organic soils and decaying vegetable matter. When the pollutant gas stream is passed through the packing medium where microbes are attached, they will degrade the organic pollutants into carbon-di-oxide and water acting like as a filter (Cox, et al., 2001).

Biotrickling filter is one of the biofiltration technologies available for VOC control. The process employs synthetic, inorganic media coated with a steady state biofilm, which results in more uniform VOC distribution and biological contact. Nutrients and moisture are supplied through a nozzle system on the trickling filter. VOC containing streams are transported to the air/biofilm interface, where they are absorbed into the biofilm and employed as a carbon and/or energy sources for the microorganisms.

The principles governing the biofiltration are similar to those of common biofilm processes (Swanson, et al., 1997). Basically, the mechanism of biotrickling filter consists of a three step processes i.e. sorption, diffusion and biodegradation. Figure 2.1 represents the mechanism of biofiltration taking place in the biotrickling filter. VOCs in the gas stream are carried into the biotrickling filter at such rates that the flow is presumed to be laminar, although dispersion occurs because of the tortuosity of the pores in the porous packing. As the gas stream passes through the packing, contaminants are transferred from the gas stream to the water in the biofilm. The contaminants diffuse into the depths of the biofilm, and microorganisms in the biofilm absorb the contaminants and biodegrade them. Contaminants may also be adsorbed at the surface of the packing. The great majority of reactors utilize aerobic respiration, so that oxygen and nutrients must also dissolve in the water or biofilm and diffuse to the microorganisms. During operation at moderate-to-high concentrations of contaminant, the biofilm will gradually grow thicker. At some point, diffusion will no longer provide all the needed compounds to the deeper portions of the biofilm, and they will become inactive. Because the pores within the packing are highly irregular in shape, the growing biofilm will change the pore size distribution. The moving layer of water in biotrickling filters provides a constant biomass as it removes the excess biomass through the sloughing to

avoid clogging. It ensures high water content in the biofilm. It is generally re-circulated from a storage tank, where pH and nutrient concentration are monitored and controlled (Devinny, et al., 2005).

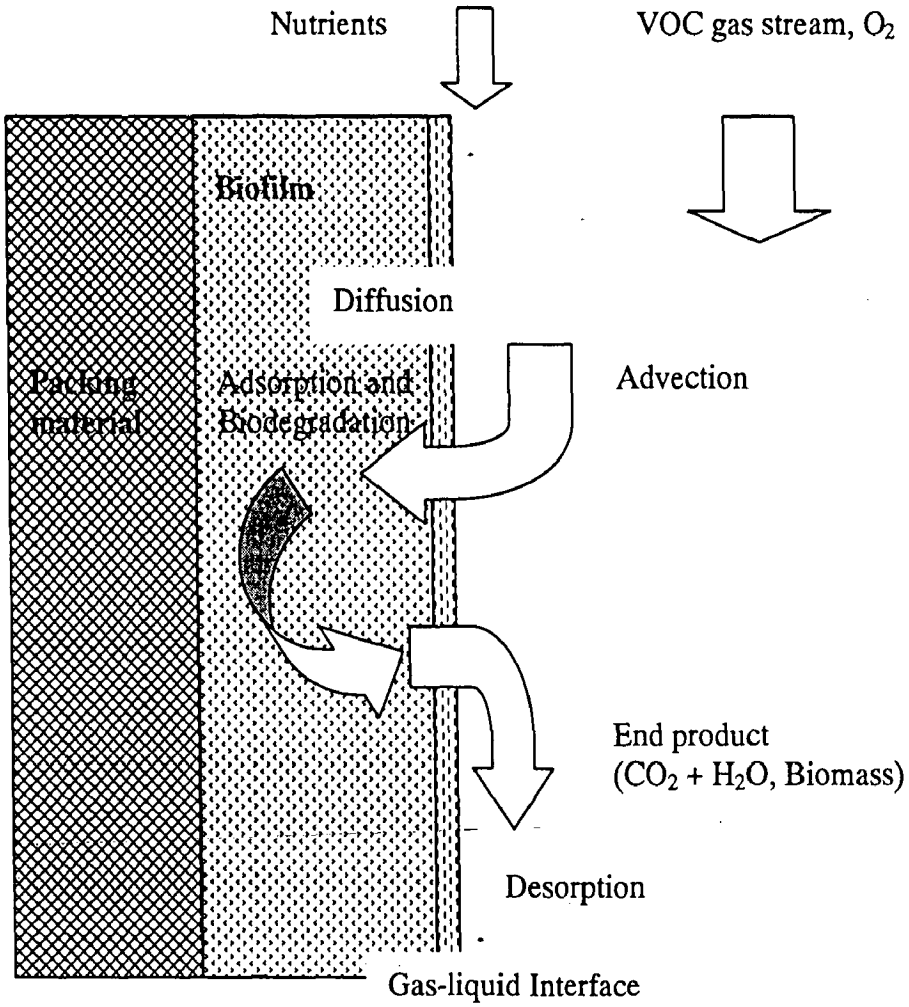


Figure 2.1: The mechanism of biofiltration in the biotrickling filter (Cox, et al., 2001)

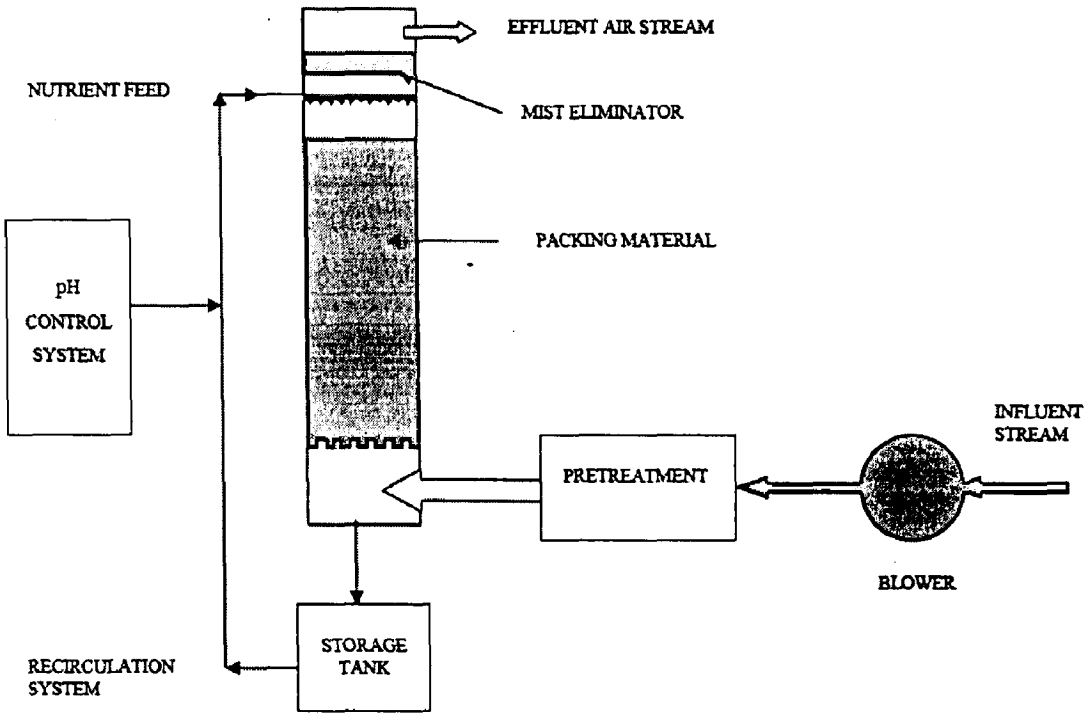


Figure 2.2: Schematic diagram of Biotrickling filter (Liu, et al., 2000)

Finally the microorganisms obtain energy from oxidation of the VOC as a primary substrate, or they co-metabolize the chemical via nonspecific enzymes. Simultaneously, there is diffusion and uptake of nutrients and phosphorous in available forms and oxygen within the biofilm. Utilization of the VOC, electron acceptors, and nutrients, continuously maintains concentration gradients driving diffusive transport in the biofilm. A properly maintained biotrickling filter converts the VOC to end products such as CO_2, H_2O, inorganic salts and biomass. The pollutants treated in the biotrickling filter are degraded into end products such as (Liu, et al., 2000):

1. Hydrocarbons $\longrightarrow$ $CO_2 + H_2O$
2. Hydrogen Sulphide $\longrightarrow$ SO_4^{2-}
3. Reduced Sulphur $\longrightarrow$ $SO_4^{2-} + CO_2$
4. Ammonia or Amines $\longrightarrow$ $NO_2^- (+ CO_2)$
   $\searrow$ N_2

Similarly, the MCB gas stream passing through the biotrickling filter is degraded into CO_2, H_2O, HCl and biomass. In the initial period, the intermediates are formed which is due

to microorganisms adapting to the new environment. Once the microorganism adapted to the environment and condition in the trickling filter, it follows the below stoichiometric equation.

$$C_6H_5Cl + 7O_2 \xrightarrow[\text{Nutrients}]{\text{Microorganisms}} 6CO_2 + HCl + 2H_2O$$

Figure 3.1 illustrates the basic components of a biofiltration system and Figure 3.2 shows an pictorial view of biotrickling filter. Waste gases often require pretreatment to ensure successful biofilter operation (Swanson, et al., 1997). Pretreatment processes include the following:

1. **Particulate removal** – A particulate removal process protects downstream units from possible clogging and or sludge buildup for waste gases containing high particulate concentration.
2. **Load equalization** – If the waste gas VOC concentration is highly variable in time, a load equalization reactor to dampen peak loadings may be needed.
3. **Temperature regulation** – The waste gas may need to be heated or cooled to the optimal range for microbial activity. Temperature adjustment often is incorporated into the humidification step.
4. **Humidification** – The waste gas should be fully saturated with moisture as it enters a biofilter to prevent stripping water from the biofilter medium. Humidification capable of achieving near 100% relative humidity in the waste gas is the critical pretreatment process.
5. **Gas distribution** – Following humidification, the waste gas enters a distribution network designed to uniformly feed the gas to the biotrickling filter medium.

2.1.3 Definitions, Performance Reporting

2.1.3.1. Empty Bed Residence Time (EBRT)

EBRT is a relative measure of gas residence time within the biofilter medium. EBRT is typically used for comparisons of gas residence time in different biofilters or under different loading conditions in the same biofilter. It is one of the most important parameters in the investment cost evaluation of a biotrickling filter (Chantal, et al., 2002). The actual gas residence time in the reactor would be calculated as the EBRT divided by the air-filled porosity available to gas flow, but such porosity is rarely known. While the chemical residence time is greater than the gas residence time due to partitioning between the gas-liquid phase and the adsorbed phases. Thus, EBRT is a simplified, relative measure of chemical residence time in a biofilter. An increase in the EBRT produces an increase in the removal efficiency and elimination capacity (figure 4.1f and 4.2a), a decrease in the environmental costs but it also causes an increase in the investment costs. Sufficient EBRT is necessary to allow transport and degradation of the pollutant to occur, which makes EBRT a critical design and operating parameter (Swanson, et al., 1997). It is often expressed as seconds(s). It has a typical range of 15-200 s.

2.1.3.2 Surface loading rate

Surface loading is a measure of the volumetric gas applied to a biofilter and it is really a loading parameter and it is also called as "face velocity" (Zarook,et al, 1997). Higher surface loading causes shorter EBCT and decreases the removal efficiency. It is expressed as meters per hour (m/h). It has a typical range of less than 200 m/h

2.1.3.3 Mass loading rate

Biofilter mass loading is defined as the VOC mass applied to biofilter per unit medium volume per unit time. The mass loadings include the effects of both flow and concentration of the pollutant stream. However, the plug flow nature of biofilters causes most of the degradation to occur at the influent end, so deeper reaches the biofilter receive smaller mass loads. A single biofilter can perform differently under identical mass loadings. Higher VOC concentrations create stronger driving forces for diffusion into the biofilm and faster

biodegradation kinetics, while low flows (high EBRT) permit longer times for diffusion to occur. From Figure 4.2c the removal efficiency eventually decreases with higher mass loadings. It also results in biomass clogging, and accumulation, and emission of toxic and acidic intermediates (Swanson, et al., 1997). It is expressed as gram per cubic meter per hour ($g/m^3/h$). It ranges from 10-160 $g/m^3/h$.

2.1.3.4 Elimination capacity (EC)

EC is a normalized measure of VOC removal capacity at a given mass loading. It is defined as the VOC mass removed per unit medium volume per unit time. The maximum elimination capacity of the biofilter is the maximum pollutant-loading rate that the biofilter can tolerate without inhibiting its microbial population (Arulneyam, et al., 2000). EC is a function of EBRT, medium type, VOC type and environmental conditions. EC is also a function of mass loading and it is inferred from the Figure 4.2b. That it decreases with the decreasing in EBRT. For the evaluation of biotrickling filter performance, one should consider both the maximum elimination capacity and the removal efficiency. The maximum elimination capacity of the biofilter is the maximum mass loading rate that the biotrickling filter can tolerate without inhibiting its microbial population. But there are limitations to the use of the mass loading rate. It is relatively sensitive to the pollutant inlet concentration, thus extrapolation of low flow-high concentrations to high flow low concentration should be avoided. EBRT and EC determines the biofilter size and process cost. It is expressed as gram per cubic meter per hour ($g/m^3/h$). It ranges from 10-160 $g/m^3/h$.

2.1.3.5 Removal efficiency

Removal efficiency is the operating parameter used to judge the success of a biofilter. The removal efficiency in the biofilter is mainly controlled by the mass transfer rate of the substrate in the biofilm and in the gas boundary layer, which in turn is controlled by the residence time in the biofilter. The removal efficiency is also depends on the temperature and pH (Figure 4.6a & 4.7a). The high efficiencies of about 95-99% are achieved by the biofilters for treating the aromatics such as BTEX and other VOCs with sufficient EBRT.

$$\text{Empty bed Residence time} = \text{EBRT} = \frac{V}{Q} \text{ (s)} \qquad \text{-------- (1)}$$

$$\text{Surface loading rate} = \frac{Q}{A} \ (m^3/m^2/h) \qquad \text{--------} \quad (2)$$

$$\text{Mass loading rate} = \frac{Q\,C_{in}}{V} \ (g/m^3/h) \qquad \text{--------} \quad (3)$$

$$\text{Elimination capacity} = EC = \frac{(C_{in} - C_{out})}{V} \times Q \ (g/m^3/h) \qquad \text{--------} \quad (4)$$

$$\text{Removal efficiency} = RE = \frac{C_{in} - C_{out}}{C_{in}} \times 100(\%) \qquad \text{--------} \quad (5)$$

Where C_{in} and C_{out} are the inlet and outlet pollutant concentrations usually in g/m^3, V is the volume (m^3) and A is the area (m^2) of the packed bed and Q is the airflow rate (m^3/h) (Swanson, et al., 1997).

2.2 Design and Operation considerations

Biotrickling filter works on the principle that when microorganisms brought into contact with the VOC, the carbon source VOC acts as food to the microorganisms. They use their natural ability to degrade the VOC. Biofilter designs are based on the volumetric flow rate of air to be treated, specific air contaminants and concentrations, media characteristics, biofilter size (area) constraints, moisture control, maintenance, and cost. These parameters all play a role in either the efficient cleaning of airstreams or in the economical operation of the biofilter.

For the successful operation of the biotrickling filter some of the design and operational parameters has to be considered and they are discussed in this chapter.

Optimum conditions for biodegradation of VOCs in the trickling filter are (Jones, et al.,):

- Ambient temperature of 15 - 30°C
- High moisture and oxygen content
- Ready supply of nutrients, e.g. nitrogen, phosphorus and iron
- Neutral pH
- Constant ionic strength with no build-up of salts
- No toxic inhibitors, e.g. acid gases and certain heavy metals.

2.2.1 Temperature

Temperature effects in biotrickling filters are expected to be relatively complex. They involve both biological and physicochemical effects. In general, biotrickling filters are operated at temperatures between 10^0C - 40^0C, which typically is the temperature range for growth of mesophilic microorganisms. The biotrickling filter performance is generally limited by the biological reaction rate or by the mass transfer rate. The effect of the temperature should be discussed with respect to the parameters that influence mass transfer such as Henry coefficient, which decreases with increasing temperature. On the other hand, the diffusion coefficient increases, facilitating mass transfer inside the biofilm. These two effects may counterbalance each other. The decline of microbial activity occurs when the temperature goes beyond the optimum temperature range of 10^0C - 35^0C and also even leads to the death of microorganism. Low operating temperature will enhance sorption of odorous compounds into the biofilm but will slow down the microbial growth. Higher temperature will have reverse effect. Therefore, thermophilic treatment is expected to be a promising new area of application of biotrickling filters. The use of thermophilic microorganisms adapted to high temperatures is an interesting area (Cox, et al., 2000), as it allows for the treatment without prior cooling and also sustains at a higher temperature which makes the process easier and as well as reduce the operating cost. In the current study, the biotrickling filter was operated between 12^0C - 40^0C. The effect of temperature on removal efficiency is discussed in Chapter 4.7.

2.2.2 Oxygen

The oxygen concentrations in most waste gases are in several orders of a magnitude higher than the pollutant concentration, whereas the oxygen solubility in water is very low. The oxygen concentration indirectly affects the biotrickling filter performance by limiting the mass transfer of oxygen into the biofilm or diffusion into the biofilm. Both the low gas-liquid mass transfer resistance and the internal structure of packing material contribute to the high oxygen penetration within the biofilms. When the oxygen partial pressure in the gas is increased, the elimination capacity also increases and the removal rate is also limited by the oxygen availability (Kirchner,et al., 1996).

Oxygen limitation occurs when the diffusion of oxygen is less than that of the pollutant, which causes the anaerobic layers in deeper parts of the biofilm. Anaerobic zones in the biofilm are unwanted but they can facilitate the biodegradation of compounds that require anaerobic conditions for biodegradation. The separation efficiency of MCB depends strongly on the oxygen concentration. Indeed, the pollutant removal in biotrickling filters becomes more sensitive to oxygen-related parameters at high inlet concentrations of the pollutant.

2.2.3 Packing material

Any porous material capable of adsorbing gaseous compounds and of supporting biological growth can be used as a packing material. As the removal efficiency of a biofilter depends on the microbial breakdown of VOCs, the packing material should be selected such that the number of microorganisms to be attached should be more and also the type of microorganisms that is adaptable on the surface of the packing medium also to be considered. The requirements of a good packing material are (1) high water-holding capacity, (2) high porosity and large specific surface area, (3) less compacting nature, (4) low pressure drops, high chemical stability over long periods of use, (5) lightness, (6) low cost and appropriate adsorbing capacity for contaminant gases. Requirements (3), (4), (5) and (6) are related to the construction and maintenance of the biological apparatus and (1), and (2) are related to biological activities (Jang, et al., 2004). Packing materials are classified into two groups: organic materials, which include soil, peat and compost, and inorganic materials, which include activated carbon, ceramic, peat, polyurethane foam and perlite.

Critical properties of media material include (David,et al., 2004):

1. Porosity,
2. Moisture holding capacity,
3. Nutrient content, and
4. Slow decomposition.

Natural media materials such as peat, loam soil, and compost normally contain sufficient microorganisms for a biofilter treating air from a livestock building or manure storage. From various research works, the inorganic or inert packing materials (such as perlite, polystyrene) are replacing the organic packing materials. The characteristics of the

packing material (coal) used in this work was given in the Chapter 3.2. The removal efficiency of the biotrickling filter using the coal as packing material achieved 95.20%.

2.2.4 Inoculation and Microbial ecology

The microorganisms in biofilters treating the VOCs are heterotrophs such as bacteria, fungi, protozoa, and invertebrates. The fungal growth rates were much lower than those for bacteria and mycelial growth appeared to cause severe clogging problems (Lars, 1998). Unlike biofilters with an indigenous microbial population, biotrickling filters need to be inoculated with microorganisms so as to fix the microorganisms on the surfaces of the packing material. Many microbial species have been shown to be capable of degrading VOCs. These microbes are used either as a mixture or as a culture of a single strain. The selection is based upon developing a microbial content to provide the maximum efficiency for degradation of specific VOCs in the exhaust gas (Cox, et al., 2001). The following sources are commonly used for obtaining the microorganisms:

- Activated sludge from wastewater treatment plants.
- Soil or water samples from sites or plants contaminated with the pollutant of interest.
- Consortia that are enriched in the laboratory on the pollutant of interest.
- Pure cultures, degrading the pollutant of interest and obtained either from culture collections or isolated from mixed consortia.

Selection of the inoculums source becomes increasingly important when the pollutant is more difficult to degrade. One of the problem occurs in the filter is the stratification, where high microorganism densities exist in only a small fraction of the bed which causes a slow response of filters to shock loads (Swanson, et al., 1997).

2.2.5 Nutrients and Toxicity:

The toxicity and mutagenicity are the two factors that impact the efficiency as well as the microorganisms in the biofilter. The toxicity in the biofilter arises due to the specific VOC on which the microorganisms are not able to survive and also due to acid producing VOCs during the degradation. Low VOC feed concentration generally eliminates toxicity where the toxicity complications are due to specific contaminant.

Carbon, nitrogen and phosphorus are three important nutrients for microbial growth and metabolism. Organic media such as compost have some amount of nutrients in the available form itself. However, nutrient availability to microorganisms also be concerned in some situations (Cox, et al., 2001). It is necessary to provide nutrients to trickling filters operating with inert media like granular activated carbon (GAC). Carbon is supplied by the VOCs in the air stream; however the filter material must provide both nitrogen and phosphorus. Nitrogen can make up about 15% of microbial cell dry weight and therefore it is a major constituent of microorganism proteins and nucleic acids (Shareefdeen, et al., 2003). Since nitrogen is such a large percentage of cell mass, it can be a limiting nutrient if adequate amounts are not available in the biofilter material. Inorganic nitrogen (ammonia, nitrate, or nitrite) is water-soluble and can be considered as the available nitrogen nutrient for microorganisms utilization. Common forms of nutrients, which can be supplied in solution, are KNO_3, NH_4NO_3 and K_2HPO_4 (Swanson, et al., 1997) and the nutrient solution used in the experiment is given in Chapter 3.3.3.

Increasing the nutrient concentration as high enough as to maintain an active, growing culture, increase the elimination capacity of the VOC. The nutrient addition is an important factor in biofilter design and operation as excessive nutrients lead to produce the excess biomass in turn clogging of the filter occurs. The nutrient supply combined with air-sparging treatment and limited nutrient supply removes the excess biomass.

2.2.6 Moisture Content

One of the most important and troublesome operating parameters is maintaining the proper water content in the packing bed material. Excessive water leads to elevated pressure drops as water displaces air in the void spaces, thereby restricting the flow of air. Higher water content means more dissolved contaminants, more opportunity for decomposition, and more rapid and effective treatment. But the over wet biofilter medium causes high back pressures, low gas retention time, oxygen transfer problem and nutrient washing whereas dry biofilter medium causes depletion in microorganisms, contraction and consequent cracks in the medium. Peat and compost have good water holding capacities. Heat generated by biological activity in a biotrickling filter may increase the temperature of the bed medium above that of the inlet gas phase. Even if the gas enters the biotrickling filter saturated with

water, it will be unsaturated as its temperature rises after contact with the bed medium. Drying of the bed medium will inevitably occur. Therefore optimal moisture content has to be maintained. Optimal moisture content ranges from 40 to 60% (wet weight) (Swanson, et al., 1997).

Moisture maintenance has been traditionally approached in the following ways:

- Direct water addition to the surface of biofilter media with a spray-like irrigation system.
- Water and influent gas flowing counter currently through a packed tower and the water is sprayed either through an atomizer or spray nozzles.

2.2.7 pH

Different biofilters may have different pH values, depending on the contaminant being treated and the characteristics of the microbial ecosystem. The pH in a biofilter may also change during the operation due to carbon dioxide formation during degradation and the pH variation due to CO_2 is expressed in the equation (6) (Chang-Tang, et al., 2004).

$$CO_2 + H_2O \longrightarrow H_2CO_3 \quad \text{--------} \quad (6)$$

$$H_2CO_3 \longrightarrow H^+ + HCO^-_3 \quad \text{--------} \quad (7)$$

When microorganisms degrading some VOCs result in acid end products, these acid end products disturb the microorganism growth in the filter as well as disturb the performance of the filter. Change in the pH affects the EC and removal efficiency also. It is discussed in figure 4.6a. Several of the most widely encountered situations (Cox, et al., 2001) are as follows:

- H_2S and sulphur containing organics leads to H_2SO_4 buildup.
- NH_3 and nitrogen organics leads to HNO_3 buildup.
- Chlorinated organics leads to HCl buildup.

The pH around 6.5 to 8.0 is maintained in the biotrickling filter. The removal efficiency increased with increase in pH from 6.5 to 7.6 and then the removal efficiency decreased when further increase in pH. The optimal pH for the biotrickling filtration is 7.0-7.6 (from the experiment). The acidity effects in the biofilter are controlled in a biofilter medium with the ability of resisting pH changes, a property known as buffer capacity. The

removal or neutralization of the acids is required when using an inorganic media or a media with a low buffer capacity. In order to maintain pH, limestone, crushed oyster shells and marl are added, which does the buffering, and they are proven very effective (Swanson, et al., 1997).

2.2.8 Acclimation

Acclimation time is the biofilter startup period during which removal efficiencies steadily increase until they reach a sustained maximum value. This phenomenon occurs as microorganisms adapt enzymes and degradative pathways to metabolize the substrate. It is often measured as the time necessary to reach 90% maximum removal efficiency. Acclimation is an issue in two instances: during initial startup and restart following shutdowns. Following are important points regarding acclimation (Swanson, et al., 1997):

- Restart acclimation times are generally shorter than those during initial startup. Once a biofiltration process has been established, its ability to recover from shutdown and other disruptions can be quite good.
- Acclimation time can be longer for mixtures, especially for mixtures containing some difficult compounds to degrade.
- For media lacking indigenous microorganisms, acclimation times may be longer because the microorganisms need to multiply and distribute themselves throughout the biofilter.
- Acclimation is dependent on substrate, concentration, media, operation and environmental conditions.
- To speed up acclimation upon restart, the biofilter medium should be kept humid, aerobic and of near optimal temperature during the shut down.

2.3 Review of Research Papers

From the literature survey, it was found that many works on biofiltration was done. This review gives an idea about the work done on biofilter and biotrickling filter for treating various VOCs, the effect of operating conditions on the performance of biofiltration system, the application of various microbial culture used, and the characterstics of different packing material for treating different VOCs.

Van Groenestijn et al. (2002) conducted an experiment on the removal of alpha-pinene from waste gases using biofilters containing fungi. They found from their experiment that fungi were more resistant to acid and dry conditions than bacteria, which was a helpful property in the aspect of biofiltration. They used the perlite, compost and polyurethane foams as the packing medium for the biofilter, where start up took 1–2 months; the volumetric removal capacity of the biofilter was 24-38 $gm/m^3/h$, which was higher than found in bacteria based biofilters. The removal efficiency was generally between 50% and 90% even in the pH range of 4.0-6.8. From their experiment they suggested that the use of polyurethane foam cubes were preferred because of the low gas pressure drop in combination with high volumetric elimination capacity.

Strauss et al. 2004 investigated the mesophilic and thermophilic BTEX substrate interactions for a toluene-acclimatized biofilter. They investigated the (BTEX) substrate interactions on toluene-acclimatized biofilter for a mesophilic range of (25°C) and thermophilic range of (50°C) toluene-acclimatized in a composted pine bark biofilter. They observed the removal efficiencies at the selected retention time (0.8 min) were 99.6% and 86.7% degradation under mesophilic and thermophilic conditions, respectively. They found that the 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 ethyl benzene >benzene >o-xylene >m-xylene >p-xylene. Under thermophilic conditions overall BEX compound degradation was ranked as benzene >o-xylene >ethyl benzene >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, under both mesophilic and thermophilic conditions.

Lambert Otten et al. (2004) conducted an experiment to evaluate the removal efficiencies of butyric acid, a volatile fatty acid. They found that the removal efficiencies nearing 100% by both compost and compost/perlite filled biofilters at all times during a run period extending 2000 h. They also found that the bed sterilization, nutrient addition, extraction results and changes in nitrogen composition of the bed were mainly responsible for the microbial activity for the removal and conversion of butyric acid. They observed the

compost and perlite mixtures had less compaction, maintained better porosities, resulting in lower pressure drops, uniform moisture profile and removal efficiencies remained identical to those of compost alone.

Spigno et al. (2003) studied the removal of hexane (which is poorly water soluble and hardly metabolized by most bacteria) through a gas-phase bioreactor inoculated by Aspergillus niger, a fungi. They used expanded clay as the packing material for their study. They found that the system was more efficient for lower pollutant concentrations (2–7 g/m^3) with a maximum EC of 200 $g/m^3/h$ and having removal efficiency of 80% and the system was revealed to be stable for longer periods.

Sene et al. (2002) conducted an experiment to evaluate the feasibility of using sugarcane bagasse as an alternative packing material for the biofiltration of air streams contaminated by benzene. The benzene-degrading strain of Pseudomonas species NCIMB 9688 was grown aerobically at 25^0 C and pH 6.8 ± 0.2. The benzene degradation in the biofilter was between 78-97% and the elimination capacity was in the range of 3.5-3.8 $g/m^3/h$. They demonstrated that sugarcane bagasse can be used as an effective and cheap alternative packing material for biofiltration systems.

Sorial A. George et al. (1997) conducted an experiment to evaluate the performance of trickle bed biofilter in removing the BTEX components. They used randomly packed 6 mm R-635 Celite pellets as packing medium. They investigated the operational parameters such as BTEX loading, EBRT, biofilter removal efficiency, backwashing frequency and duration recovery of biofilter removal efficiency after backwashing. From their results , the removal efficiency by the celite packed biofilter was around 90% overall removal efficiency for an BTEX loading of 6.2 kg $(COD)/m^3/d$ for an EBRT of 0.67 min. They found that periodic addition of Nutrient-P combined with reduced backwashing frequency may permit long-term, stable operation at high removal efficiencies for reduced BTEX loadings.

Lars Elsgaard (1998) studied the removal of ethylene by immobilized bacteria in a peat-soil packed biofilter. The removal efficiency of peat-soil packed biofilter was around 89-99% and the elimination capacity was 21 $g/m^3/h$. The observations from their work were (i) the operational stability of the biofilter extended for more than 75 days, (ii) the biofilter adapted to C_2H_4 removal at 10°C, and (iii) storage of the inoculated peat-soil for 2 weeks at 20°C caused only a halving of the C_2H_4 removal rate.

Chantal Seignez et al. (2002) studied the effect of operating parameters on biotrickling filter performance degrading chlorobenzene and *o*-dichlorobenzene mixture. They used bacterial consortium attached in a structured packing media from Sulzer mellapack and they studied the operating parameters of biotrickling filter at 30^0C and 6.8-7.2 pH. They found that the maximum removal efficiency was 62 and 72% for CB and DCB, respectively with an elimination capacity of 1.1kg/m^3/day. They observed that the influence of biotrickling filter operating parameters on the removal efficiency and elimination capacity of CB and DCB mixture was based on the inoculum preparation including biomass adaptation and cultivation, empty bed retention time, recirculation liquid flow rate, and nutrient liquid flow rate. The optimal values will depend on the nature and mass load of contaminants on the particular biofilter.

Jang et al. (2004) studied the degradation of styrene in biofilter packed with organic and inorganic materials. Pseudomonas sp. SR-5 was used as the microbial organism for the degradation of styrene with peat and ceramic as organic and inorganic packing material. They observed that styrene removal efficiency differed due to the difference in chemical and physical properties of the two materials as the peat contains organic materials, which has high adsorption capacity for styrene, high water-holding capacity, and a large specific surface area. These properties were favorable for microbial growth compared to those of ceramic. The disadvantage of peat as a packing material was its weakness against compression due to its fine structure, which tends to lead to a high pressure drop during operation. Ceramic was inferior to peat in that it has no organic materials, but the change in pressure drop is small due to its solidity. The mixed packing material biofilter had a removal efficiency of >90% with an elimination capacity of 170 g/m^3/h.

Hicham Elmrini et al. (2004) conducted an experiment on the removal of xylene vapors in a biofilter and studied the response of biofilter for the variation of inlet pollutant concentration and gas flow rate. They used peat as the packing material inoculated by a microbial consortium. The experimental study was conducted over a period of 2 months in two phases. In the first phase, the biofiltration column was fed with an air stream characterized with a constant xylene inlet concentration of 1.39 g/m^3, and the empty bed residence time was varied between 150 and 56 s. In the second phase, the biofilter was operated under a constant empty bed residence time of 150 s but various inlet concentrations

of the contaminant were tested 0.48–2.69 g/m^3. They found that the removal efficiency of the biofilter above 96% in less than 24 h following the change to low concentrations and gas flow rate. They also found that the temperature variation strongly depends on the intensity of the microbial activity for the degradation of the pollutant. They observed increase of temperature from 26^{0}C to 28^{0}C in the average temperature of the filter bed was accompanied with an increase from 12 to 61 g/m^3/h in the elimination capacity. They observed from their results that the xylene removal was eliminated exclusively by aerobic biodegradation only.

Kwotsair Chang et al. (2004) studied the performance of trickle bed biofilter treating the isopropyl alcohol and acetone mixtures. They used the mixed culture as packing material inoculated with mixed culture. They observed the applicable operating conditions were temperature between 25^{0}C-35^{0}C and EBRT of 20-30 s. They observed removal efficiency of 80-85% with an elimination capacity of 90-128 g/m^3/h. They found that the elimination capacity of isopropyl alcohol was higher than that of acetone indicating that the inhibition which exerts on the removal of acetone was stronger than the inhibition exerted by acetone on the removal of isopropyl alcohol.

Mpanias et al. (1998) conducted an experiment on the removal of MCB in trickling filter using Intalox saddles as packing material and microbial consortium as the biomass. They studied the performance of biotrickling filter by varying the operating conditions such as inlet MCB concentration, residence time, liquid circulation rate, pH and frequency of medium replacement. They observed that the removal of MCB was high under all conditions. The effect of pH was found to be much less. They suggested that the concentration profiles of MCB along the filter bed follows either zero or first order rate law, depending on the inlet MCB concentration. They observed the removal efficiency of 80-90% was achieved for inlet MCB concentration of 1.7-2.7 g/m^3 with an elimination capacity of 12-55 g/m^3/h.

Table 2.1 gives a list of VOCs degraded by the biofiltration process by the different microorganisms in different packing mediums. It also gives an idea about the average removal efficiency, elimination capacity, temperature and pH for a particular type of a VOC on a particular type of medium. Still some more research works are going all over the world on different VOC with different packing mediums and different microbial community.

Table 2.1: Review of Literature

No.	Volatile organic compounds (VOCs)	Type of biofilter	Type of packing material	Removal efficiency (%)	Elimination capacity ($g/m^3/h$)	Microorganisms	pH	Temp ^0C	Ref.
1.	Alpha Pinene	Biofilter	Perlite, Compost, Polyurethane foam cubes	50-90%	24-38	Fungi (mycelia)	4.0-6.8	25	Van, et al., (2002)
2.	Acrylonitrile + Styrene	Biotrickling filter	Coal particles	>80%	<22	Activated sludge	-	-	Lu, et al., (2002)
3.	Benzene	Biofilter	Sugarcane bagasse	78-97%	3.5-3.8	Pseudomonas species	7	20-22	Sene, et al., (2002)
4.	Benzene + Toluene	Partitioning bioreactor	Aqueous phase	99% (Benzene), 94% (Toluene)	62.4 (Benzene), 47.9 (Toluene)	Alcaligenes xylosoxidans	6.6	30	Colin, et al., (2003)
5.	BTEX	Biotrickling filter	Celite pellets	>90%	87.5	Mixed culture	7.2-7.6	32	Sorial, et al., (1997)
6.	Butyl acetate	Biotrickling filter	Coal particle	79-100%	95-162	Activated sludge	7.3-8.5	25-30	Chungsying, et al., (2004)
7.	Ethanol	Biofilter	Compost and Polystyrene	>90%	195	Mixed consortium of activated sludge culture	7.2	-	Arunelyam, et al., (2000)
8.	Ethyl acetate + Toluene	Compost Biofilter	Compost and soil	More than 90%	400	Bacteria and Fungi	5.5-7.08	20-25	Liu, et al., (2002)
9.	Ethylene	Biofilter	Peat-soil	89-99%	21	Ethylene-oxidizing bacteria strain RD-4	-	10-20	Lars, et al., (1998)
10.	Chlorobenzene + Dichlorobenzene	Biotrickling filter	Sulzer mellapack, 125.4, PP	62%CB 72%DCB	1.1kg/m^3/day	Bacterial consortium	6.8-7.2	30	Chantal, et al., (2002)

Table 2.1 Contd..

11.	Gasoline	Compost Biofilter	Compost	80% for TPH 85% for BTEX	40gTPH/m^3/h 5.3gBTEX/m^3/h	-	8.8	20	Wam, et al., (2003)
12.	Hexane	Biofilter	Clay	80%	200	Aspergillus niger	-	30	Giorgia, et al., (2003)
13.	Isopropyl alcohol + acetone	Biotrickling filter	Coal particle	80-85%	90-128	Mixed culture	7.6-8.3	25-35	Kwotsair, et al., (2003)
14.	Mono-Chlorobenzene	Biotrickling filter	Intalox saddle	80-94.6%	11-50	Microbial consortium	6.5-7.0	-	Mpanias, et al., (1998)
15.	Styrene	Biofilter	Ceramic and peat	>90%	170	Pseudomonas species	4.78-6.5	20-26	Jang, et al., (2004)
16.	Toluene	Trickling filter	Raschig rings	94% for inlet conc. <400ppm	-	Pseudomonas putida	6.8	25-30	Peixoto, et al., (1998)
17.	Toluene and Styrene	Biofilter	Peat	~100%	242-Toluene 63-Styrene	Acinetobacter Rhodococcus	-	25	Mario, et al., (2001)
18.	Trichloroethane	Biotrickling filter	Coal particles	>95%	0.45-6.2 kg/m^3/d	Activated sludge	7.8-8.5	16.9-26.8	Chungsying, et al., (2003)
19.	Trichloroethylene	Biofilter	Composted poultry litter and Pine bark	100% for loading rate of 0.28-2.35 g/m^3/h	0.05-1.0	TCE degrading consortium	-	Room temp.	Laura, et al., (2002)
20.	Trimethylamine	Bioreactor	Cellulose triacetate	90-99%	-	Arthrobacter oxydans and Pseudomonas Putida	4-10	25	Chang, et al., (2004)
21.	Xylene	Biofilter	Peat	>98%	12-61	Microbial activated consortium	-	26-28	Hicham, et al., (2004)

Chapter 3

Experimental Design

3.1 General design considerations

Biotrickling filter system offer a number of benefits in terms of capital and operating costs. To realize these benefits and achieve the required reduction in VOC emissions essential consideration of the following factors in the design of the system are required (Jones, et al.,):

- Microbial reactions take place in the aqueous phase. Pre-humidification of the air stream or frequent spraying of the support material to a preset moisture level will ensure that excess moisture is present.
- The rate at which a particular VOC dissolves in water affects the volume of the equipment capable of treating it. Therefore the system has to be designed such a way to maximize mass transfer and degradation rate.
- The optimum temperature range for biodegradation is 15 - 30°C. The system has to be designed to incorporate a heating and cooling device to maintain this temperature.
- High particulate levels in the air stream may cause blockages. This would lead to channeling and a fall-off in performance of the reactor. Particulate filtration is often included in system design.
- Any biocides or other inhibitors present in the inlet VOC stream may affect the microbes in the bioreactor. The system has to be designed to remove these prior to the air stream entering the bioreactor.
- VOC degradation frequently leads to the production of acids and acid build-up can be a problem in certain systems. A mechanism for adjusting pH can be incorporated to maintain neutral conditions.
- When emission is not continuous (e.g. from batch processes and starvation periods), a buffering mechanism for smoothing out the air stream should be incorporated.
- Specific design criteria will apply according to the degree of process control and operational complexity of the system.

The efficiency of the biological system measured as a proportion of the VOC or odour removal, which is a function of the design of the system (Jones., Cox, 2001). The efficiency of the system depends on:

- VOC residence time in the bioreactor
- Fluctuations in the VOC/odour concentration and/or flow rate
- Temperature fluctuations
- Device downtime.

The above-mentioned design aspects were considered in carrying out the work.

3.2 Experimental Trickling filter

The Trickling filter system consists of the following components:

a) Air compressor
b) VOC generation system
c) Humidifier
d) Nutrient chamber
e) Trickling filter unit
f) Trickling filter packing media

The schematic diagram of the laboratory biotrickling filter system is shown in the Figure 3.1. Figure 3.3 gives a pictorial view of the laboratory biotrickling filter.

a) Air compressor

The VOC gas stream to the Biofilter unit was provided by Air compressor (Surya Pvt. Ltd) equipped with filter and automatic pressure regulator switch. The filter provided along with the compressor removes the oil, water and particulate matter from the air. The Automatic pressure regulating switch which restarts and switch off the compressor operates between 20 to 40 PSI. The needle valve was used for controlling the airflow rate from the compressor to the trickling filter unit. The Rotameter (Star Flow meters) (range 1-10 lpm) was used for the measurement of the air flow rate. The air stream from the rotameter was distributed into two sections in air distributor: (1) humidifier and (2) VOC generation system. The flow of air stream into two sections was controlled by valve 1 and 2. The distribution of gas to all the units from the air compressor to

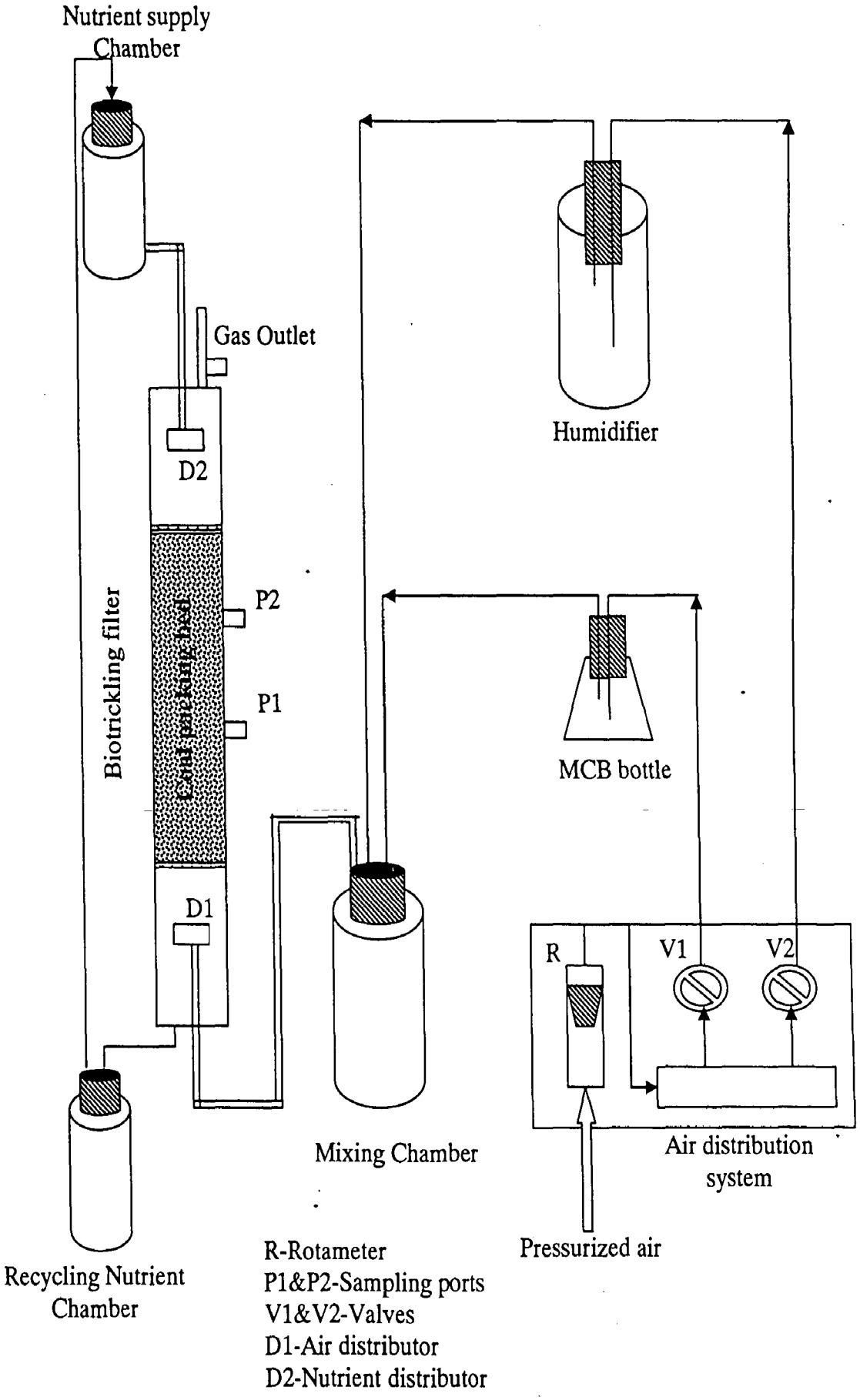


Figure 3.1: Schematic diagram of the laboratory biotrickling filter system

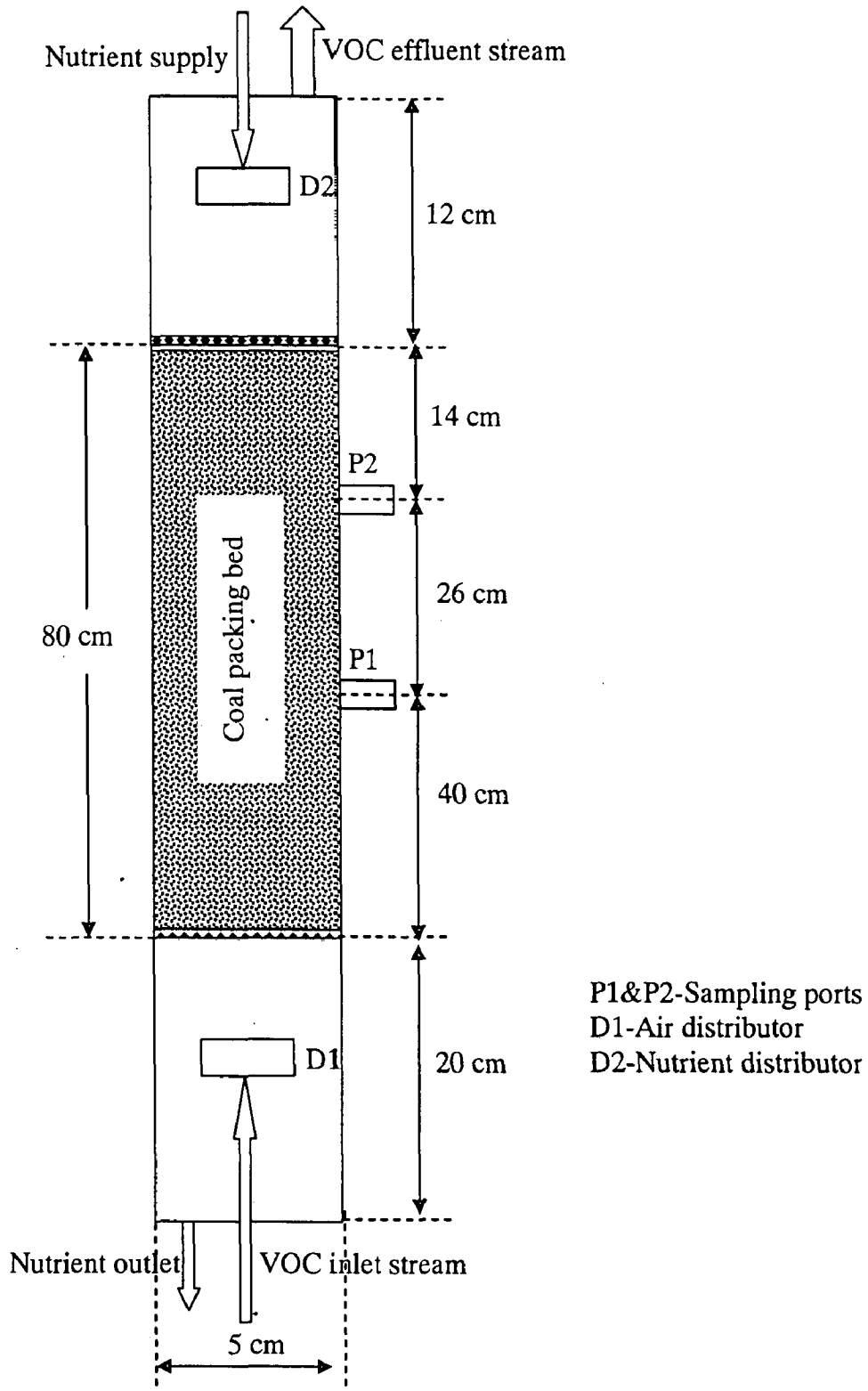


Figure 3.2: Schematic diagram of the laboratory biotrickling filter

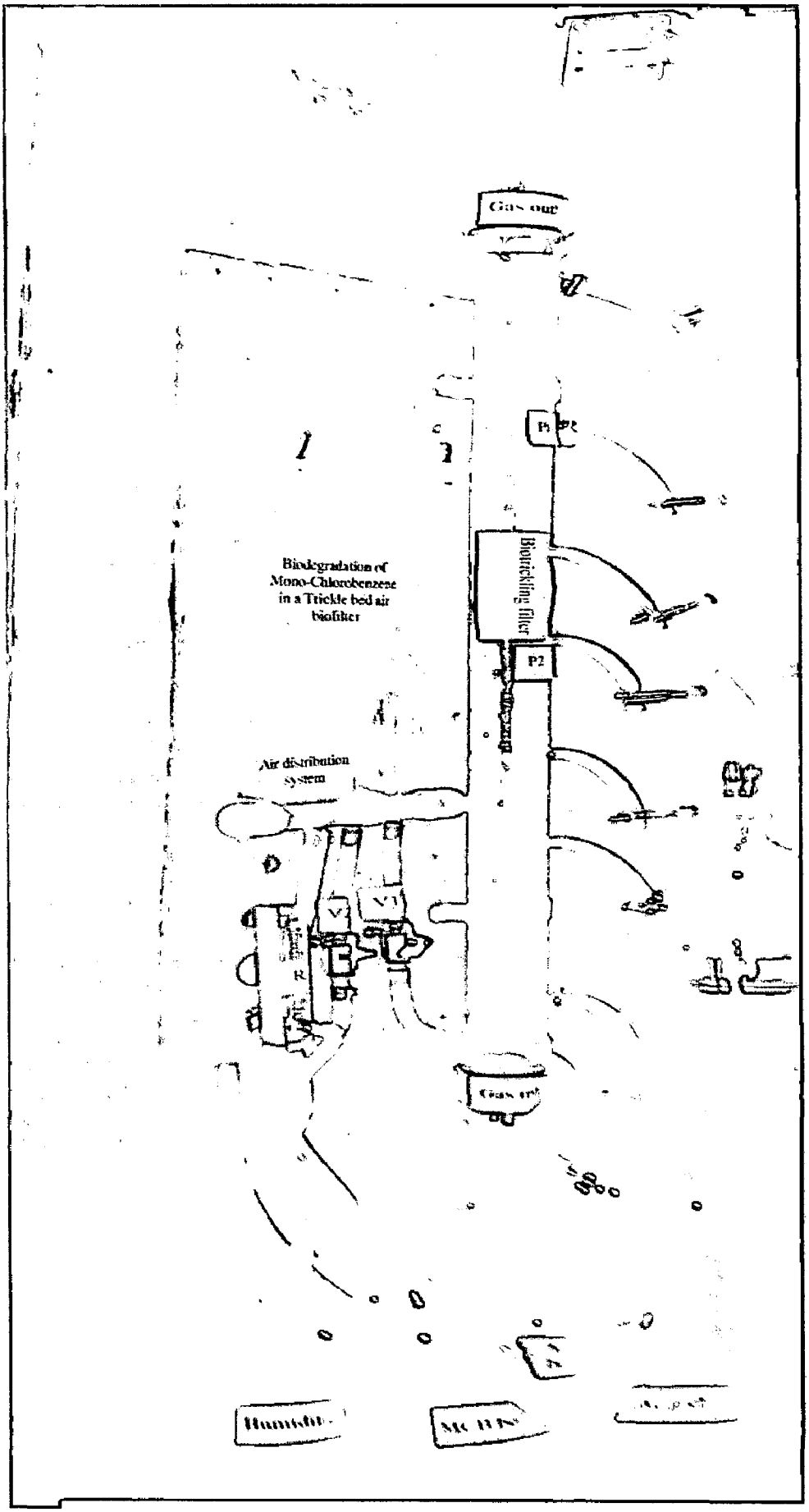


Figure 3.3: Pictorial view of biotrickling filter

trickling filter unit was done by Petropex (solvent resistant) flexible tubing of ¼ inches.

b) VOC generation system

The VOC generation system was a conical flask of 1 litre volume containing 200 ml of MCB with air inlet and air outlet. The air stream from the air distributor was sent to the conical flask to produce the VOC gas stream. By the principle of stripping, the MCB in liquid phase got stripped into gas phase by having direct contact of air with the MCB. The artificially produced MCB gas stream was taken for the study. The amount of liquid stripped was controlled by a valve to restrict the amount of air contacting the MCB liquid.

c) Humidifier

The Humidifier was a conical flask of 1 litre volume containing 500 ml of distilled water with air inlet and air outlet. The other air stream from the air distributor was sent to the humidifier to produce 100% RH air. The humidifier also follows the same principle of stripping. The main purpose of the humidifier was to provide 100% RH to the bed. After that, the streams from the VOC generation system and humidifier were mixed in a mixing chamber and sent as a single stream to the trickling filter unit.

d) Nutrient Chamber

The nutrient to the trickling filter was provided by means of a 500ml bottle at the top of the unit. The flow rate of the nutrient was controlled by means of a valve. The flow rate of the nutrient is maintained in between 3 ml/min to 5 ml/min.

e) Trickling filter unit

The laboratory set up of biotrickling filter was made up of Persplex (acrylic glass) and was designed and fabricated by Workshop, Department of Chemical Engineering, IIT Roorkee. The dimensions of the filter are given in the Table 3.1. The schematic representation of trickling filter is shown in the figure 3.2. The trickling filter was a cylindrical tube with packing material supported by the acrylic sieve plate at the bottom and as well as top. The coal was used as the packing material with the packing bed height of 80 cm and the internal diameter

of the cylinder was 5 cm. There were two distributors in the cylinder (1) gas distributor at the bottom to distribute the gas evenly to the packing bed, and (2) liquid distributor at the top to distribute the liquid evenly to the packing bed to avoid channeling and dry spots. There were two sampling ports P1 and P2 at 40 cm and 66 cm from the bottom along the cylinder to collect the samples. There was a drain port at the bottom to drain the liquid, the nutrient drained were collected in a recycle chamber and recycled back to the trickling filter by manually.

f) Trickling filter packing media

The coal used was bought from the local market and it was crushed and sieved to the required size. The coal in the range of 10-20 mm diameter was used as the packing media in the trickling filter. Critical properties of a good packing material are high porosity, low pressure drop, high moisture holding capacity, high surface area and slow decomposition. The coal almost satisfied the above characteristics and was used as a packing material in the trickling filter. The characteristics of the coal used were given in the Table 3.2.

Table 3.1: Design and Operational parameters for the Trickling filter

Design parameters	
Material of construction	Transparent acrylic plastic
Internal diameter of trickling filter	5 cm
Height of column	100 cm
Bed height	80 cm
Packing material	Coal
Operational parameters	
pH	6.5 – 8
Gas flow rate	0.5 – 2.5 lpm
EBRT	188.52 – 37.704 s
MCB inlet concentration	0.133 – 7.187 g/m^3

Table 3.2: Characteristics of the coal packing material

Parameter	Value
Particle diameter	+ 10 mm
Specific gravity	2.514
Moisture content	42%
% porosity	66.1

3.3 Analytical Methods

Analytical methods were used for the measurement of concentration of MCB at various sampling ports. Following method was used for the measurement of gas concentration in this experiment.

3.3.1 Gas sampling and Analysis

Influent and effluent MCB gas concentrations were determined by using a HP 5895A Gas Chromatograph equipped with a capillary column type HP 1 of column length 30 m, internal diameter of 0.53 mm and capillary film thickness of 2.65 μm, and a Flame Ionization Detector was connected with a computing integrator. The Injector, Oven and Detector temperature were maintained at 200°C. The fuel gas and the carrier gas was hydrogen with a flow rate of 5 ml/min. The air samples were collected from the various sampling ports in an air tight syringe of volume 6 ml. 50 μl of air samples were injected into the FID gas chromatograph with a 100 μl air tight syringe. The gas standards for MCB were prepared by injecting the pure MCB and analysis its concentration by gas chromatography. This procedure was carried out several times during the experiment to ensure the correct measurement of unknown concentration of MCB. The unknown MCB concentrations in the samples were determined by comparing with standard results.

3.3.2 Selection of VOC

In the present study, Mono-Chlorobenzene was used as the VOC to study the trickling filter capacity to degrade it. The artificial VOC gas stream is produced by direct contact between air and the MCB liquid. The Mono-Chlorobenzene of 99% purity supplied from Thomas Baker (Chemicals) was used in this experiment.

3.3.3 Nutrient solution and Microorganism

The nutrient solution was continuously supplied to the microorganisms with a flow rate of 3 ml/min to 10 ml/min and it was recycled manually. The nutrient feed contains inorganic salts and vitamins vital to the growth of attached microorganisms and $NaHCO_3$ as a pH buffer to maintain pH values of 6.5 – 8. The composition of the nutrient feed in 1 litre of distilled water was listed in Table 3.3. The nutrient solution was sprayed from the top of the trickling filter using a liquid distributor.

Microbial seed was used to start the process. Activated sludge which had a Sludge Volume Index (SVI) of 150, mixed liquor suspended solids (SS) of 3000 mg/l, and mixed liquor volatile suspended solids (VSS) of 2100 mg/l was obtained from the secondary clarifier of Kankhal Sewage Treatment Plant in Kankhal near Haridwar. The suspended solids were allowed to settle for 5 h and the supernatant was discarded to obtain concentrated sludge. The seeding step consisted of mixing concentrated sludge for 1 day and $CaCO_3$ was added to prevent acidification in the bed.

Table 3.3: Chemical composition of the Nutrient solution

Chemical	Concentration	Manufacturer
KH_2PO_4	1.19 g/l	S.D.Fine Chemicals
$Na_2HPO_4.12H_2O$	3.13 g/l	S.D.Fine Chemicals
KNO_3	3.88 g/l	Thomas Baker (Chemicals)
$(NH_4)_2SO_4$	2.58 g/l	Loba Chemie (Chemicals)
$FeSO_4$	0.28 g/l	Qualigen Fine Chemicals
$MgSO_4.7H_2O$	0.35 g/l	Loba Chemie (Chemicals)
$NaHCO_3$	0.90 g/l	Thomas Baker (Chemicals)
$MnSO_4$	1.52 mg/l	S.D.Fine Chemicals
Na_2MoO_4	1.0 mg/l	S.D.Fine Chemicals
$CaCl_2$	3.0 mg/l	Thomas Baker (Chemicals)

3.4 Experimental Plan

The sequence of the experimental program conducted was presented in the Table 3.4.

Table 3.4: Sequential Experimental Program

Phase	Time (hrs)	Experiment
I	0 – 540	Startup period with MCB as pollutant at EBRT = 188.52 s
II	540 – 744	Performance of trickling filter at EBRT = 125.68 s
III	744 – 840	Performance of trickling filter at EBRT = 62.84 s
IV	840 – 1020	Performance of trickling filter at EBRT = 94.26 s
V	1020 – 1080	Starvation period with nutrient only
VI	1080 – 1176	Performance of trickling filter at EBRT = 47.13 s
VII	1176 – 1320	Performance of trickling filter at EBRT = 37.704 s
VIII	1320 – 1444	Starvation period with nutrient and air only
IX	1444 – 1780	Performance of trickling filter for different pH and different Temperatures

Chapter 4

Results and Discussion

The main objective of the experiment was to investigate the performance, and the effect in performance upon changing the operating parameters and operating conditions in degrading the MCB in biotrickling filter. Totally 9 phases of experiment were conducted to analyze the efficiency and performance of trickling filter. The experiment was conducted for a period of 75 days i.e., 1780 h. After the coal particles were placed in the biotrickling filter, the filter was operated continuously for 540 hrs with EBRT of 188.52 s to attain pseudo-steady state conditions. Pseudo-steady state conditions were assumed only when the daily changes in the MCB removal efficiency were within 20% (Lu, et al., 2001). The experiment had the pseudo steady state for five successive days after startup. The acclimation time required by the biotrickling filter from the startup to attain a maximum removal efficiency of 93.81% was about 16 days from the startup. Figure 4.1a shows the removal efficiency of MCB with operating time.

The Phase I was from 0 h - 540 h, the trickling filter was operated initially with MCB inlet concentration of 0.133 g/m^3 and further increased up to 0.92 g/m^3 with constant gas flow rate of 0.5 lpm. The microorganisms attached on the coal were acclimated with the coal packing within a period of 16 days and they showed a removal efficiency of 93.81% on 16^{th} day for the concentration of 0.92 g/m^3. From the 420 h, the concentration of the MCB was increased to a maximum of 1.52 g/m^3 for the same EBRT. Due to the sudden increase in the concentration of the MCB there was a fluctuation in the removal efficiency. Initially removal efficiency decreased to 51.51% and finally attained a maximum removal efficiency of 92.19%.

The Phase II was from 540 h – 744 h, the gas flow rate was increased from 0.5 to 0.75 lpm with a decreased EBRT of 125.68 s. The effect of the sudden increase of the gas flow rate was observed in the study. The concentration was maintained in the range of 1.56 to 3.861 g/m^3. Initially the trickling filter showed a fluctuation in the removal efficiency, due to sudden increase in gas flow. The removal efficiency was dropped to 36.81% and recovered quickly with a maximum removal efficiency of 92.64%.

The Phase III was from 744 h – 840 h, the gas flow rate was increased from 0.75 lpm to 1.5 lpm with an EBRT of 62.84 s. The inlet MCB concentrations were maintained between 1.101 to 3.293 g/m^3. Due to the sudden increase in gas flow rate, the performance of trickling filter fluctuated initially with a removal efficiency of 48.95% and quickly recovered from the fluctuation and attained a maximum removal efficiency of 85.02%. Then the concentration of MCB was increased to 3.293 g/m^3 where the removal efficiency decreased to 33.89% due to sudden heavy load to the trickling filter.

The Phase IV was from 840 h – 1020 h, the gas flow rate was maintained at 1 lpm from the 1.5 lpm with an EBRT of 94.26 s. The inlet MCB concentrations were maintained between 1.0678 to 4.551 g/m^3. Due to the sudden fluctuation in the gas flow, the trickling filter fluctuated with a removal efficiency of 40.63% and gradually recovered from the fluctuation and reached a maximum removal efficiency of 89.08%. The response of the trickling filter was studied for the sudden increase in the inlet concentration. The removal efficiency decreased to 73.51% when the inlet MCB concentration was increased to 2.012 g/m^3.

The Phase V was from 1032 h – 1080 h, the nutrient at flow rate 4 ml/min was only supplied to the trickling filter for 3 days. The only carbon source for the microorganism was the MCB and the starvation of the microorganism for the carbon source was created in this phase. The re-acclimation period and the recovery of the microorganism to degrade MCB were experimented.

The Phase VI was from 1080 h – 1176 h, the response of the trickling filter due to the absence of carbon source for 3 days was studied. From the experiment, it was observed that the re-acclimation period was very shorter than the acclimation period. The re-acclimation period was 48 h, the microorganisms recovered quickly from the sudden change in the environment. In this phase itself, the gas flow was increased to 2 lpm with an EBRT of 47.13 s. The concentration of MCB maintained in the range of 1.3 to 7.187 g/m^3. After the starvation period the removal efficiency was 36.98% and after recovering from the starvation, the removal efficiency increased to 84.46%.

The Phase VII was from 1176 h – 1320 h, the gas flow rate was further increased to 2.5 lpm with an EBRT of 37.704 s. The concentration of MCB was maintained in the

range of 1.026 to 2.45 g/m^3. Due to the sudden increase in the gas flow rate, the removal efficiency decreased to 52.94% and reached a maximum removal efficiency of 87.07%.

The Phase VIII was from 1320 – 1444 h, the nutrient flow rate of 4 ml/min and the air flow rate of 1 lpm were only maintained without the MCB gas for 5 days. The phase VIII was considered as a second starvation period with the oxygen supply by means of air without any source of carbon. The detail discussion about the starvation period was discussed in section 4.4.

The Phase IX was from 1444 – 1780 h, the re-acclimation period of the trickling filter due to the starvation was studied. In this phase itself, the operating parameters like temperature and pH were studied. Along this phase, the temperature was maintained in between 35 to 40.2°C. The responses of the trickling filter due to the temperature variations were studied. The pH was varied between 6.5 to 8.0 pH. The response of the trickling filter due to the pH variation was also studied. The concentration of MCB was maintained in the range of 0.324 to 1.626 g/m^3 with a constant gas flow rate of 1 lpm and EBRT of 94.26 s. Due to the variation in temperature and pH, there was fluctuation in the performance of the trickling filter. From the results obtained, the maximum removal efficiency of 85.77% was obtained at temperature 35.2°C and pH 7 for the above gas flow rate and EBRT.

The above Phases from I to IX were the complete experimental plan for this research work and the figure 4.1a represents the corresponding phases conducted during the research work with respect to the operating time. Further discussion on operating parameters and the operation of trickling filter was discussed in the upcoming chapters.

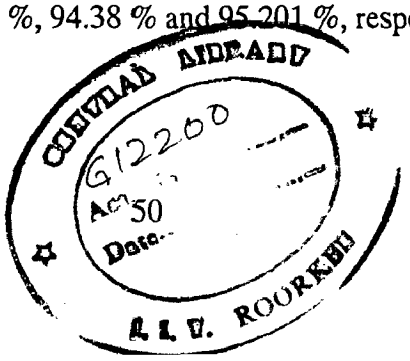
4.1 Removal Efficiency of Mono-Chlorobenzene

The experiment was conducted for 75 days to study the degradation of MCB in the trickling filter. The performance of the biotrickling filter was studied at different operating parameters. From the experimental results, it was observed that the removal efficiency varied throughout the experiment with the operating time. Figure 4.1a shows the removal efficiency of MCB as a function of operating time.

The biotrickling filter achieved a maximum removal efficiency of 93.81% at 372 h after startup. This period of time was called as the acclimation time. Acclimation time can be defined as the time required for reaching a maximum VOC removal efficiency of above 90% (Swanson, et al., 1997). After startup, the removal efficiencies gradually increased and reached steady state, and decreased rapidly after sudden change of EBRT, temperature and, pH in the filter. The maximum removal efficiency 94.35% was achieved after 396 h for an EBRT of 188.52 s and MCB concentration of 0.92 g/m^3. Similarly, for EBRT's 125.68 s, 62.84 s, 94.26 s, 47.13 s and, 37.704 s, the maximum removal efficiencies were 92.64 %, 85.022 %, 89.08 %, 84.46 % and 87.07 % for the corresponding MCB concentrations of 2.88 g/m^3, 1.322 g/m^3, 1.539 g/m^3, 1.3 g/m^3 and 1.47 g/m^3, respectively.

Two periods over the course of the experiment (1020 h to 1080 h and 1320 h to 1444 h) were run without MCB (starvation period) in order to study the response of the microbial community to the changes in the nature of pollutants supplied. Starvation period was the period when the food/substrate was not provided to the microbial community. The food is nothing but the carbon source i.e. the MCB was the food in this work. When the supply of MCB was resumed after starvation the trickling filter recovered quickly within a short period of time.

Figure 4.1b shows the removal efficiency as a function of the inlet MCB concentration. From the figure, it can be observed that with increase in the inlet MCB concentration there was a decrease in the removal efficiency. The microorganisms were not able to fully consume the MCB when the MCB load was increased. For the inlet MCB concentrations 0.324 g/m^3, 0.63 g/m^3, 0.92 g/m^3 and 1.069 g/m^3, the removal efficiencies were 91.67 %, 93.83 %, 94.38 % and 95.201 %, respectively.



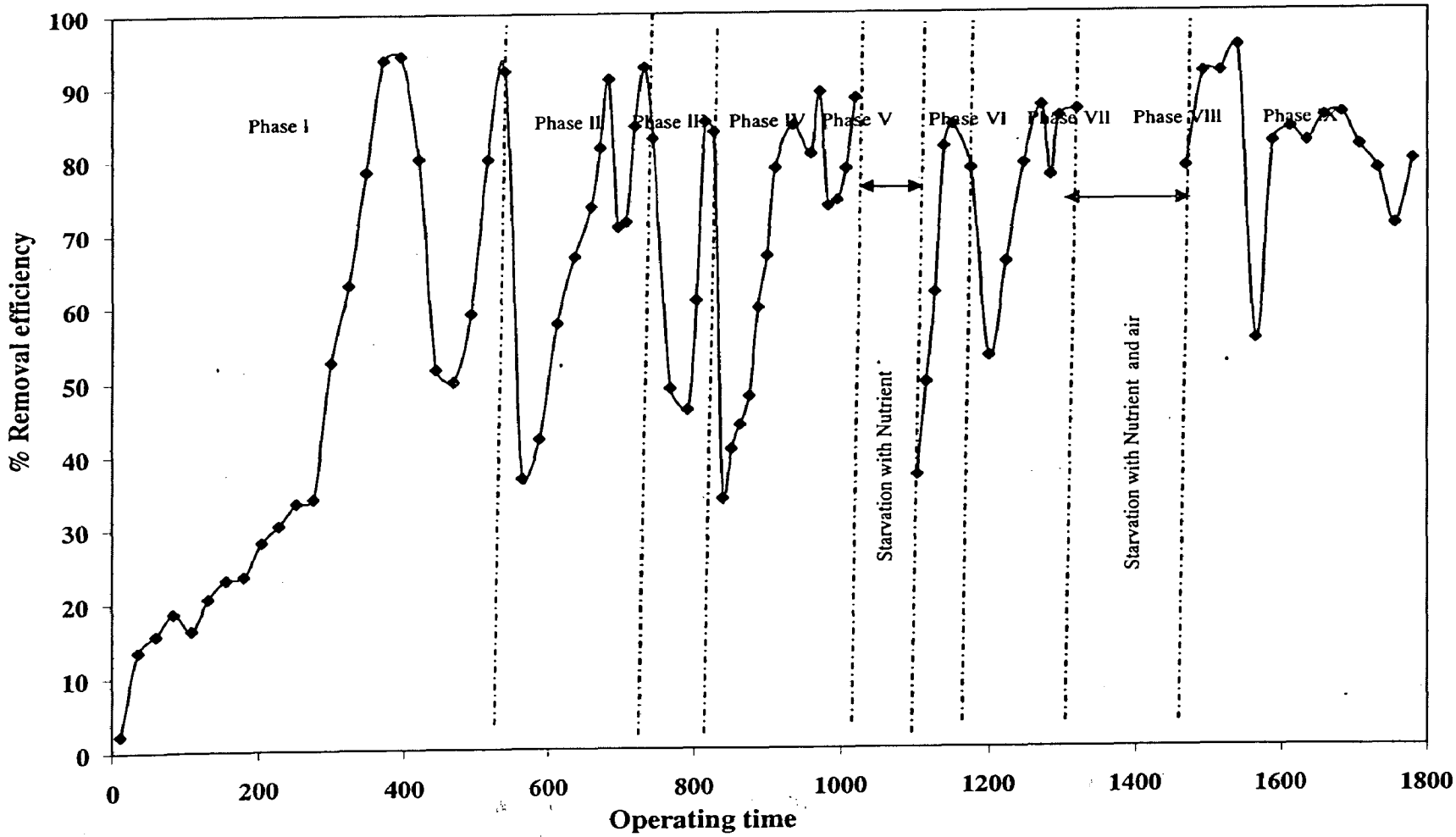


Figure 4.1a: Removal efficiency as a function of operating time

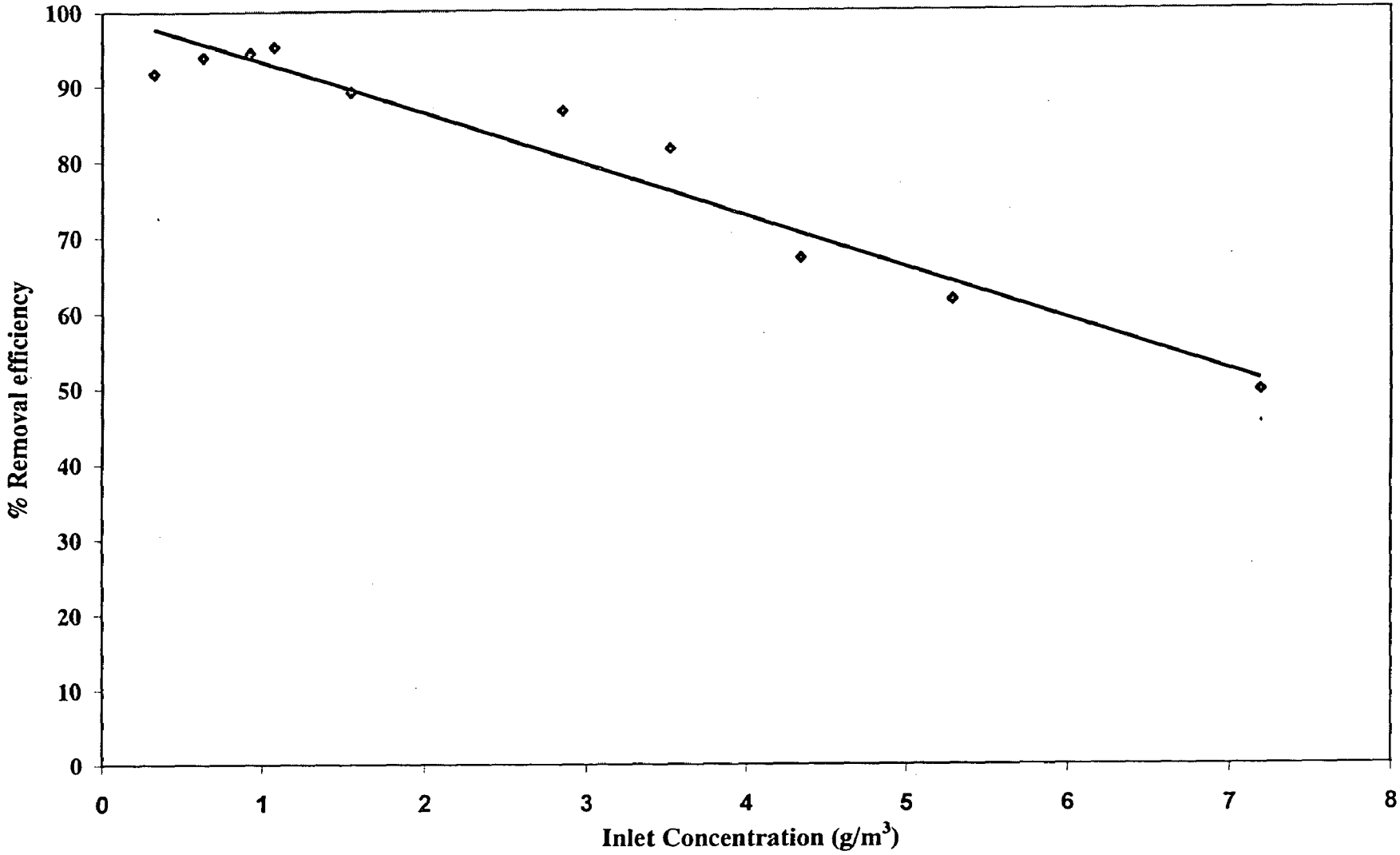


Figure 4.1b: % Removal Efficiency as function of Inlet MCB Concentration

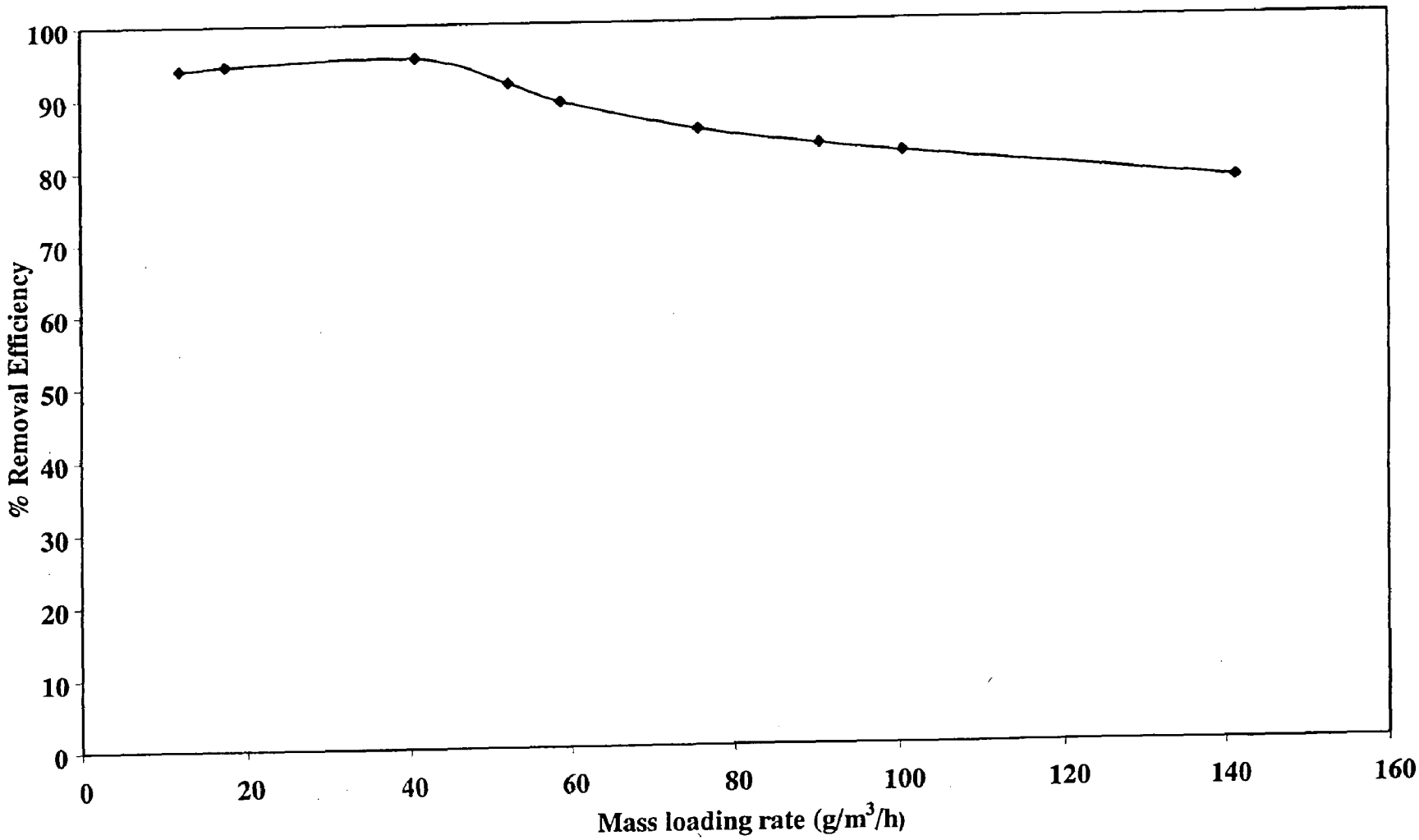


Figure 4.1c: Removal Efficiency as a function of mass loading rate

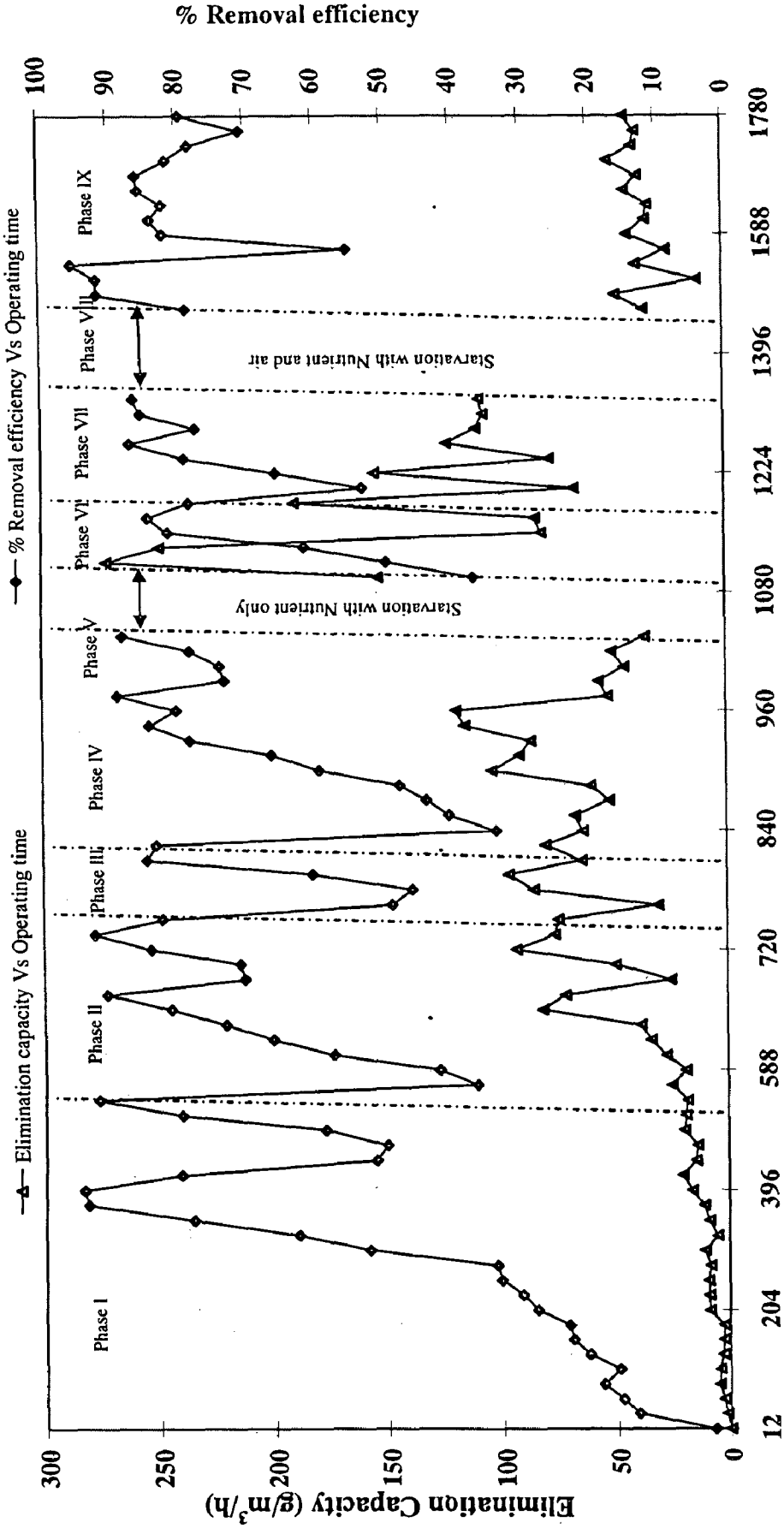


Figure 4.1d: Time dependent of MCB Elimination capacity and Removal efficiency

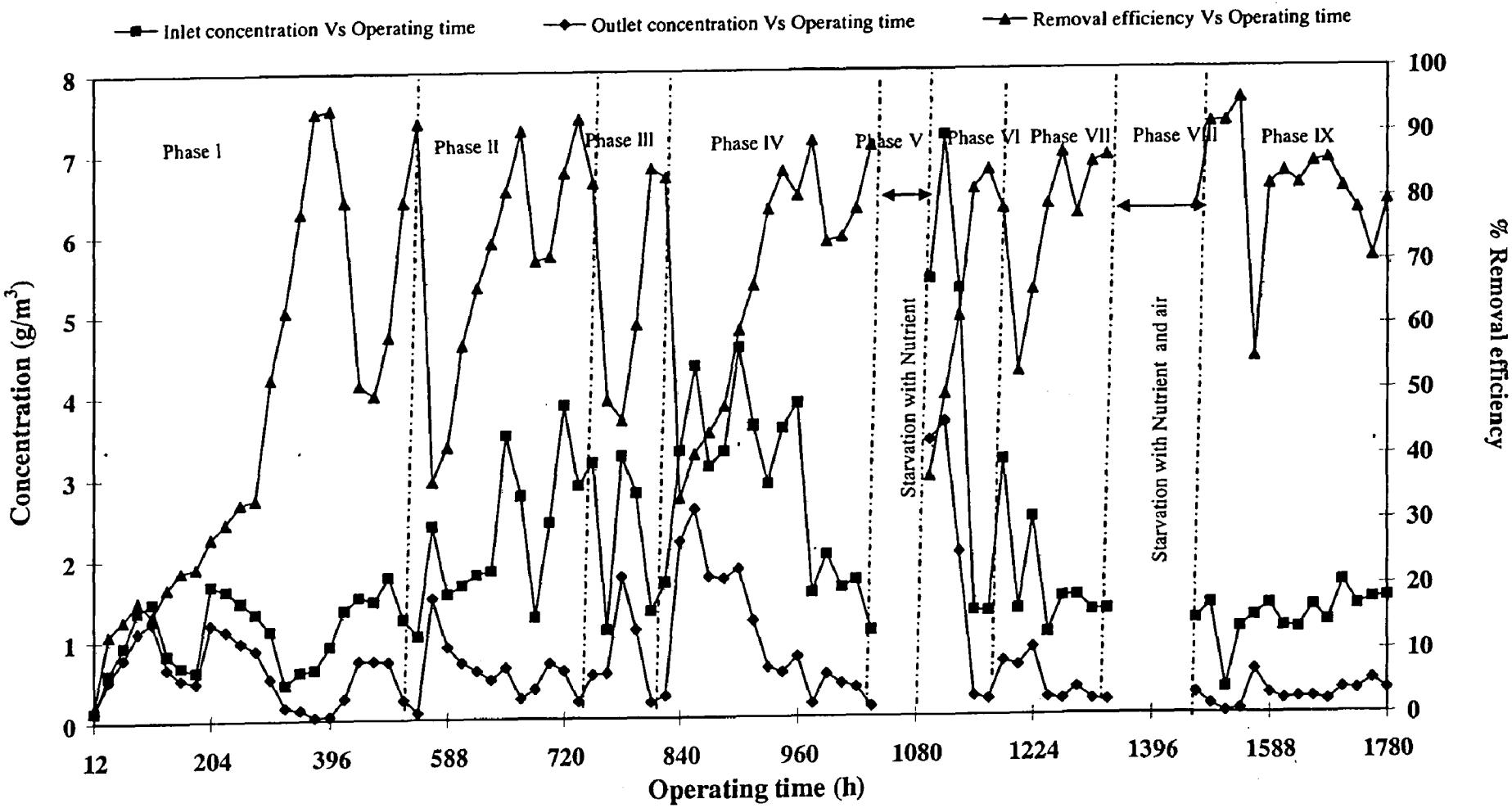


Figure 4.1e: Time dependent of MCB concentration and Removal efficiency

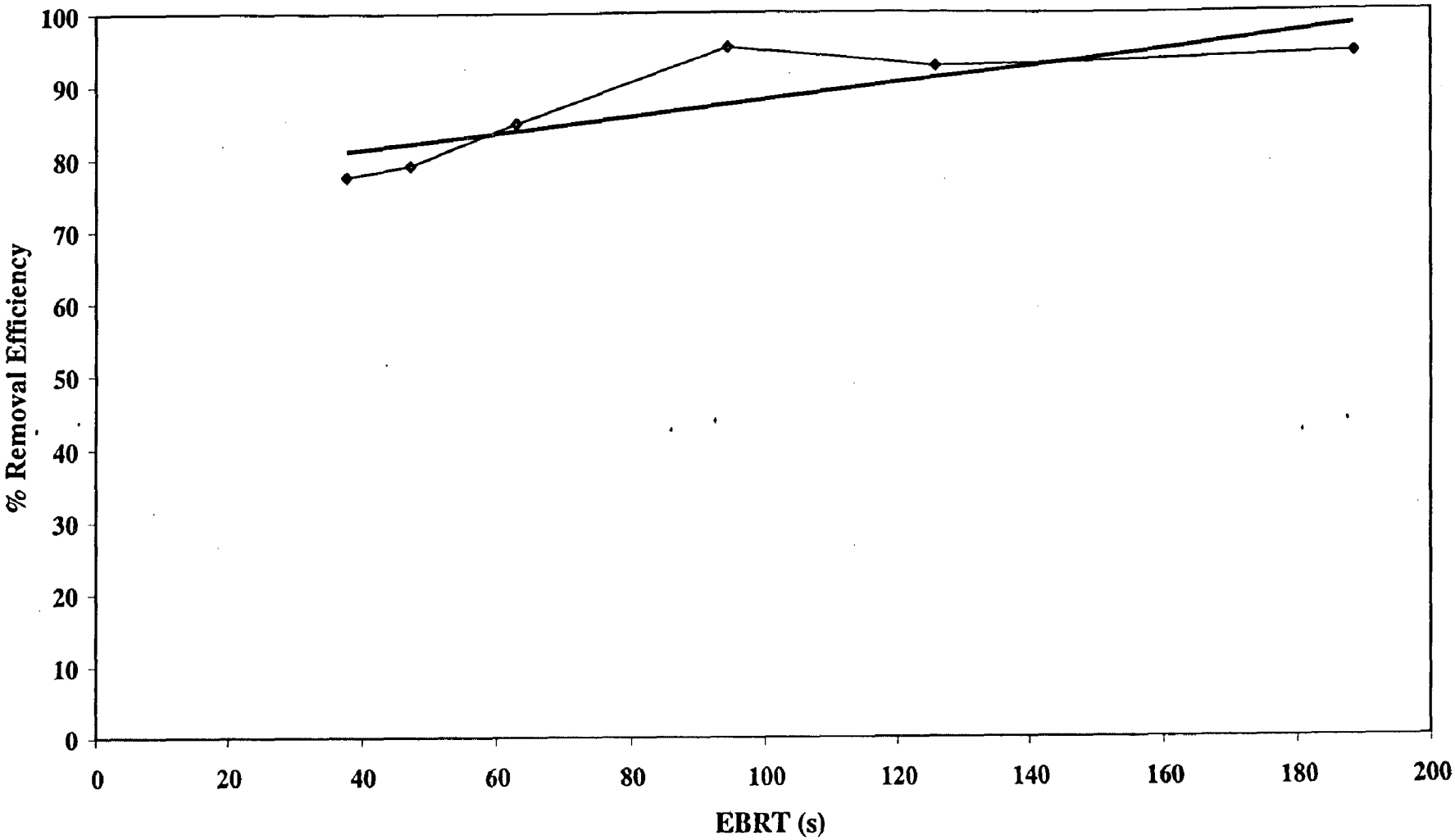


Figure 4.1f Removal Efficiency as a function of EBRT

Figure 4.1c shows the removal efficiency as a function of mass loading rate. The removal efficiency decreases with increase in the mass loading rate. For the mass loading rates of 12.03 $g/m^3/h$, 17.57 $g/m^3/h$, 40.83 $g/m^3/h$ and 52.323 $g/m^3/h$, the removal efficiencies were 93.83 %, 94.38 %, 95.201 % and 91.61 %, respectively.

The maximum removal efficiency during the entire experimental period was 95.20% which was achieved at an EBRT of 94.26 s and inlet MCB concentration of 1.069 g/m^3. Figure 4.1d shows the removal efficiencies for the corresponding elimination capacity as a function of operating time. Similarly, Figure 4.1e shows inlet and outlet MCB concentration and corresponding removal efficiency as a function of operating time.

Figure 4.1f shows the removal efficiency as a function of EBRT. From the figure, it was observed that the removal efficiency increases with increase in the EBRT. The maximum removal efficiencies 94.35 %, 92.64 % and 95.20 % were observed for the EBRT's 188.52 s, 125.68 s and 94.26 s, respectively when the inlet MCB concentration was maintained around 1 g/m^3.

4.2 Elimination Capacity of Mono-Chlorobenzene

Elimination capacity is a function of the inlet concentration and the gas flow rate i.e. VOC loading rate. Figure 4.1d depicts the elimination capacity and removal efficiency for the corresponding inlet and outlet MCB concentrations with the operating time. Figure 4.2a shows the elimination capacity as a function of EBRT i.e. gas flow rate. From the figure, it is observed that the elimination capacity increases with the increase in EBRT for almost same inlet MCB concentration of 1.3 g/m^3 - 1.5 g/m^3. Figure 4.2b shows the elimination capacity as a function of mass loading rate. During the initial period, the elimination capacity increased linearly with increase in MCB loading rate. Above the mass loading rate of 100.54 $g/m^3/h$, elimination capacity almost reached a steady value of around 82.04 $g/m^3/h$. The elimination capacity with respect to MCB loading rate follows the first order Monod kinetics. Figure 4.2c gives a clear representation of the elimination capacity for the corresponding removal efficiency as a function of MCB loading rate. With increase in the mass loading rate, the elimination capacity also increases but the trend was opposite in the case of removal efficiency, it decreased. From the observations, the

elimination capacity varies with the gas flow rate and inlet concentration throughout the experiment. It was observed that for the maximum removal efficiency of 95.201 % and for the inlet MCB concentration of 1.069 g/m^3 with an EBRT of 94.26 s, the elimination capacity was 38.87 g/m^3/h.

4.3 Effect of varying inlet MCB concentration

Effect of varying the inlet MCB concentration during the operation of the trickling filter was studied to give an idea of its effect on the operation. During the experiment whenever there was a fluctuating in the inlet concentration, the biodegradation rate was disturbed and the fluctuation affected the removal efficiency. Figure 4.3a shows the outlet MCB concentration as a function of inlet MCB concentration. From the MCB concentration range from 0.324 g/m^3 to 1.539 g/m^3 the outlet concentration was very low i.e. the degradation was more when the inlet concentration was less, but it followed a opposite trend in the case of concentration higher than 1.539 g/m^3, where the removal efficiency was less and almost the outlet concentration was equal to inlet MCB concentration. The concentration profiles along the bed height at various intervals were studied. Figure 4.3b represents the concentration profile along the bed height for the inlet MCB concentrations of 1.539 g/m^3, 1.3 g/m^3, 0.92 g/m^3, and 0.63 g/m^3. Figure 4.3c represents the concentration profile along the bed height for the inlet MCB concentrations of 3.51 g/m^3, 2.88 g/m^3, and 1.6 g/m^3. From the Figures (4.3b & 4.3c), concentration decreasing along the bed height was observed.

4.4 Effect of starvation on the performance and Re-acclimation period

Operation of full-scale biotrickling filters in industries can face some operational problems, such as repeated periods of non-use. Pollutant starvation may be results of interruption in the plant operation, weekend recess, holiday breaks or equipment malfunction leading to interruption in the feed of pollutant air (Cox, and Dehusses, 2002). In the present study, the effect of pollutant starvation in the trickling filter treating MCB was studied. The experimental protocol consisted of starving microbial community under various conditions, with supply of nutrient only and with supply of nutrient and air. The duration of the starvation period without MCB was

varied from 3 to 5 days. During the starvation, the reactor lost its ability to degrade MCB, regardless of the mode of starvation. The microorganisms significantly decreased during starvation, in particular where the recycle liquid was maintained, but this decrease was not crucial for future re-acclimation. Decrease of biomass may be due to biomass death and lysis, endogenous respiration of the process culture and shear by the liquid recycling. The Figure 4.4a and 4.4b shows the re-acclimation of the trickling filter after starvation with the supply of nutrient only and with the supply of nutrient and oxygen, respectively. From the Figure 4.4a, it was observed that after starvation without air there was a sudden fall in the removal efficiency, which could be due to microbe's death and lysis. But it recovered quickly within 2 days. It reached a maximum removal efficiency of 84.46 % for the concentration of 1.304 g/m^3 and EBRT of 47.133 s. The lower removal efficiencies were due to the higher concentration. From the figure 4.4b, it was observed that after starvation with air there is a slight decrease in the removal efficiency and it attained a maximum removal efficiency of 95.20 % for the concentration of 1.069 g/m^3 and EBRT of 94.26 s. From the experiment it was found that the re-acclimation period was lesser than initial acclimation period. The re-acclimation period was within 2 to 3 days. For the shorter re-acclimation period there was a possibility that the MCB already adsorbed on the coal surface can be consumed during the starvation period by the microorganisms. Comparing the re-acclimation period of both the starvation, it was found that there is no much effect in the trickling filter which was supplied with nutrient and air than the nutrient supplied only.

4.5 Removal efficiencies along the bed height

The MCB concentration and removal efficiency were monitored not only at the entrance and exit of the filter bed but along the filter as well. The MCB concentrations and removal efficiencies along the trickling filter height were studied for various inlet MCB concentrations and various EBRT. The MCB gas flow was flowing upwards, from bottom to top while the nutrient liquid is flowing from the top to bottom. Figure 4.5a and 4.5b shows the removal efficiencies along the trickling filter height at various sampling ports. Figure 4.5a represents the removal efficiencies along the bed height for the low inlet MCB concentrations of 1.539 g/m^3, 1.3 g/m^3,

0.92 g/m^3, and 0.63 g/m^3. Figure 4.5b represents the removal efficiency along the bed height for the high inlet MCB concentrations 3.51 g/m^3, 2.88 g/m^3, and 1.6 g/m^3. The MCB concentration decreased along the bed from the inlet to outlet due to biodegradation. It was observed that the removal efficiency was more in the bottom of the filter. The trend of the concentration and removal efficiency profile changes whenever the oxygen concentration in the bed changes (Baltzis, et al., 1995).

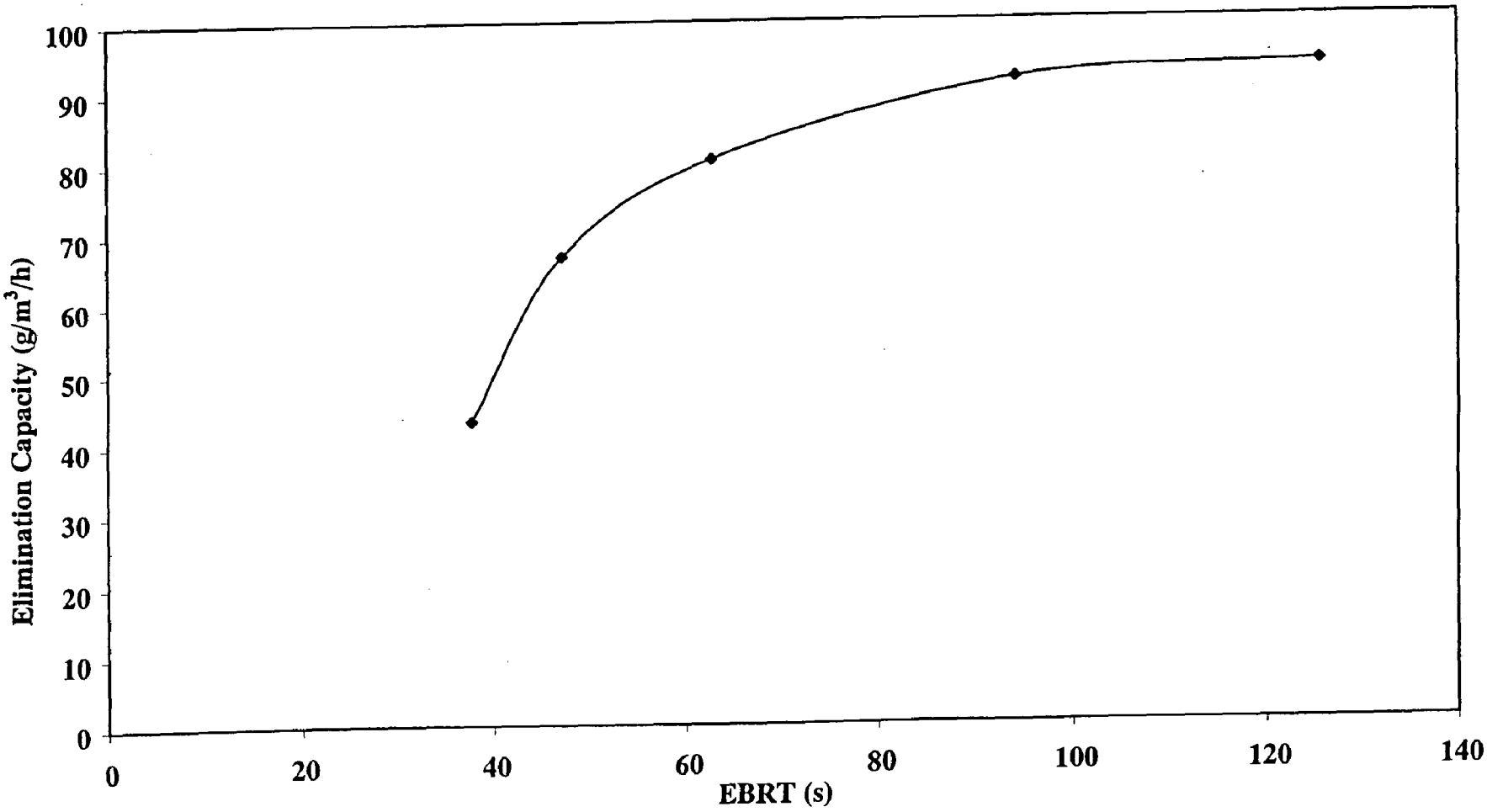


Figure 4.2a: Elimination Capacity as a function of EBRT

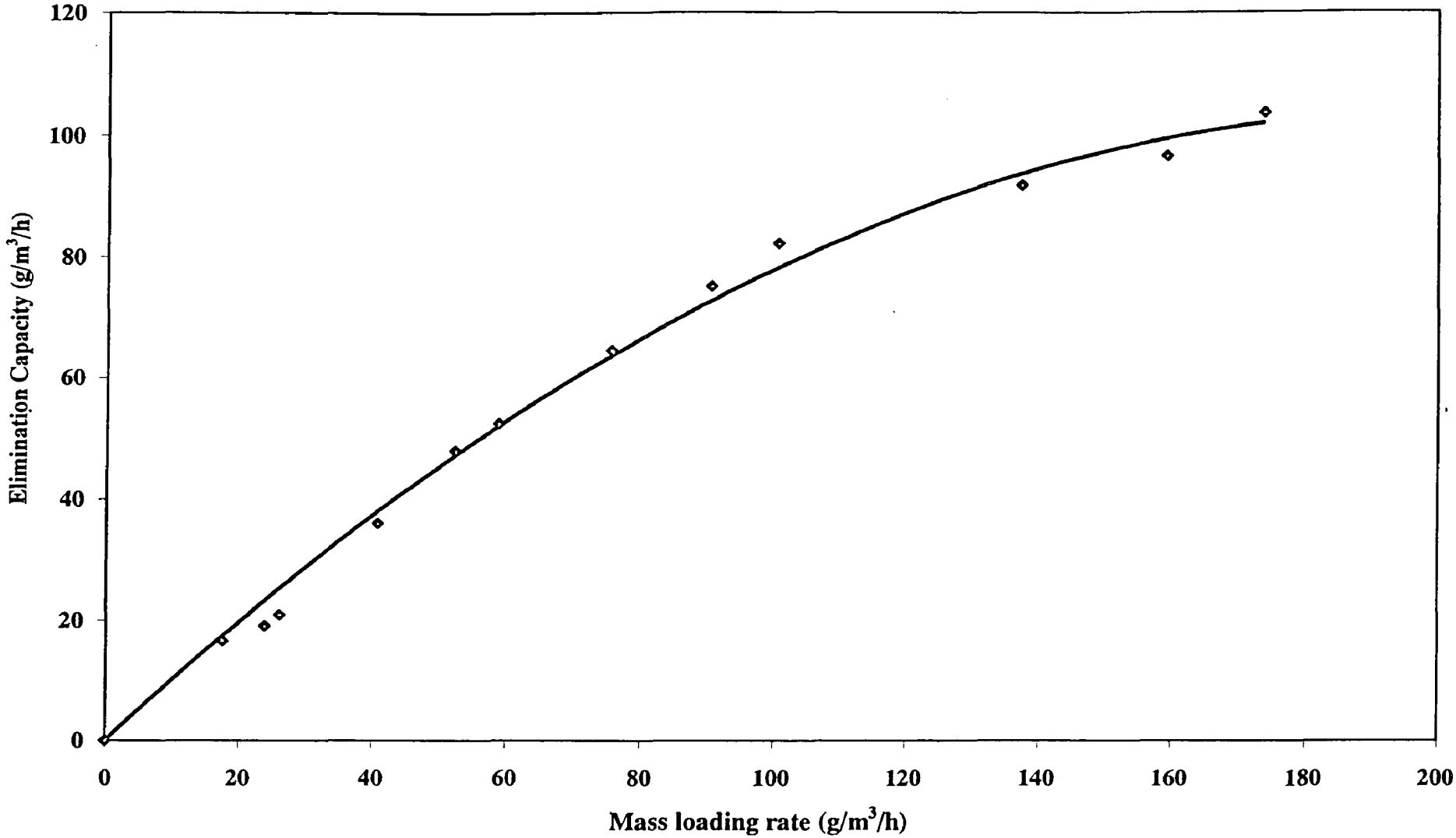


Figure 4.2b: Elimination Capacity as a function of Mass loading rate

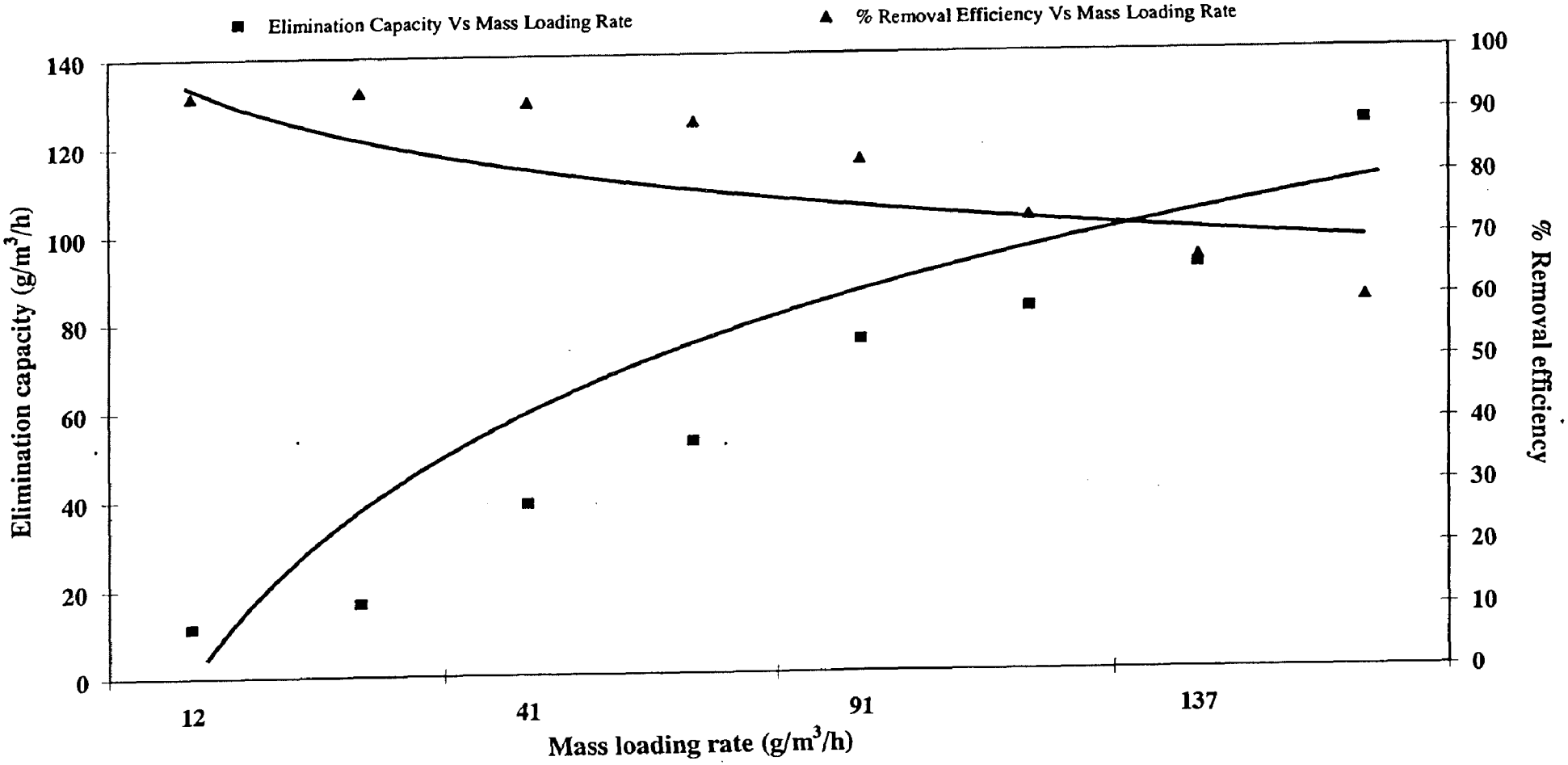


Figure 4.2c: Effect of Mass loading rate on Elimination capacity and Removal efficiency

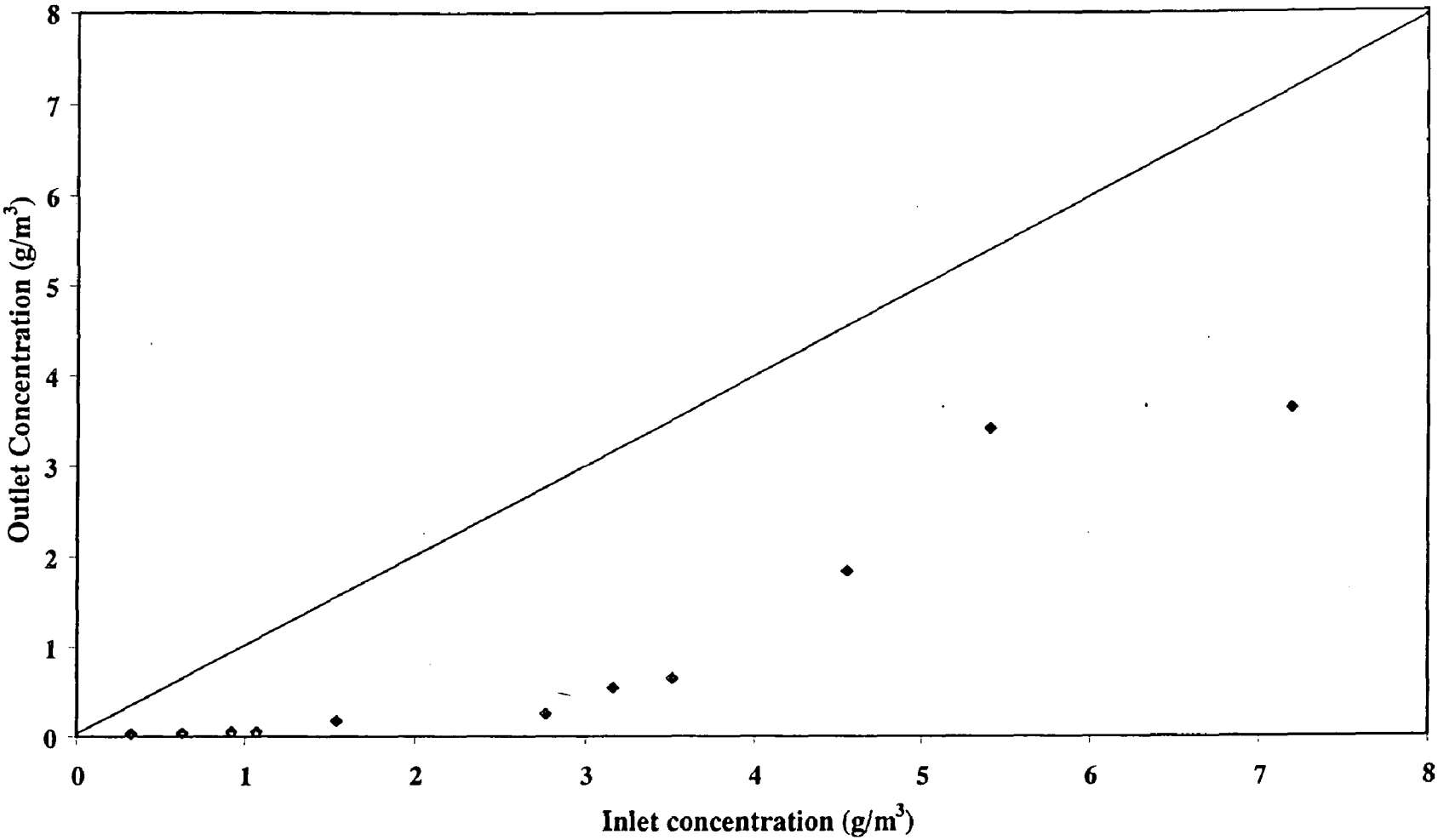


Figure 4.3a: Outlet Concentration as a function of Inlet concentration

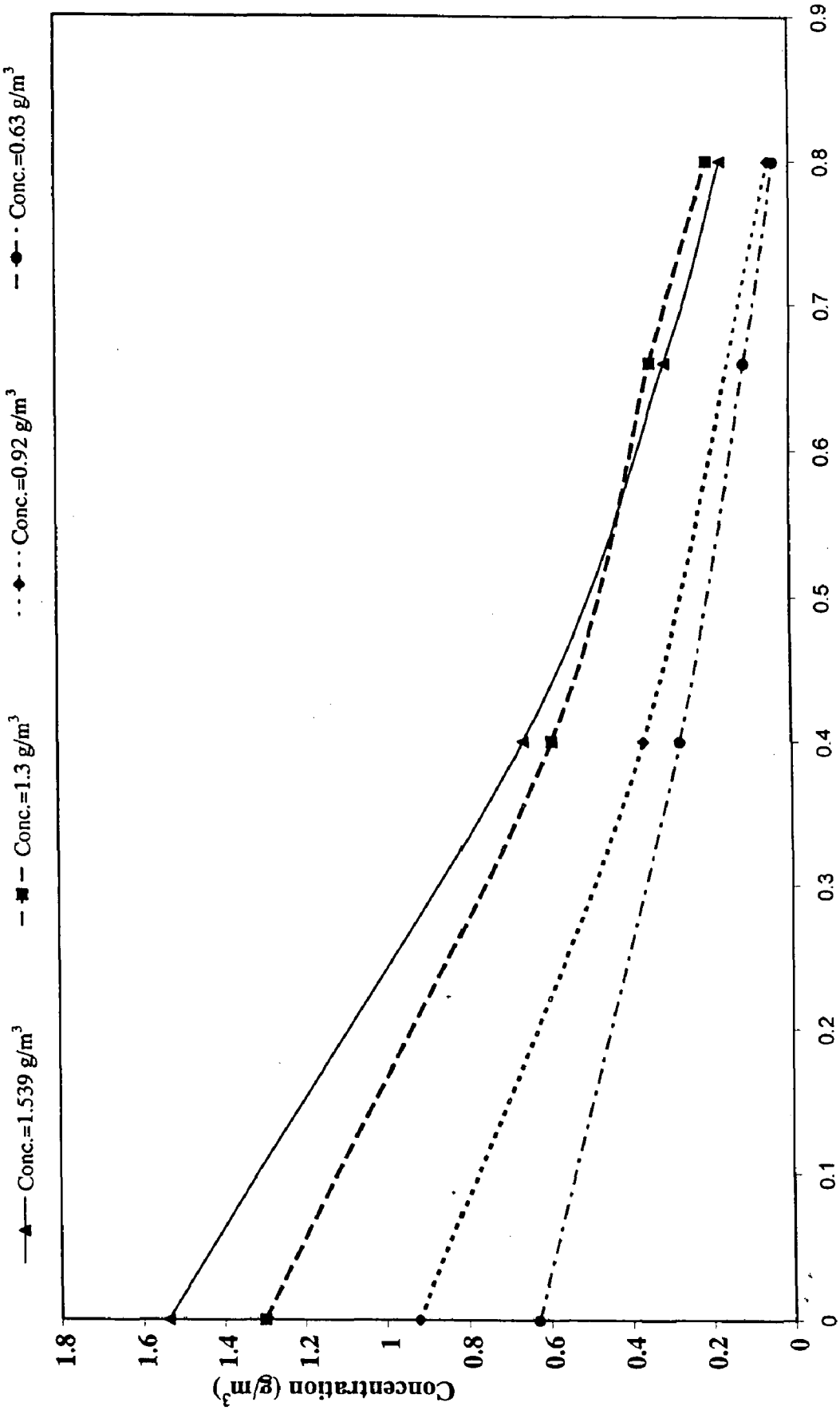


Figure 4.3b: Concentration profile along the bed height for low MCB concentrations

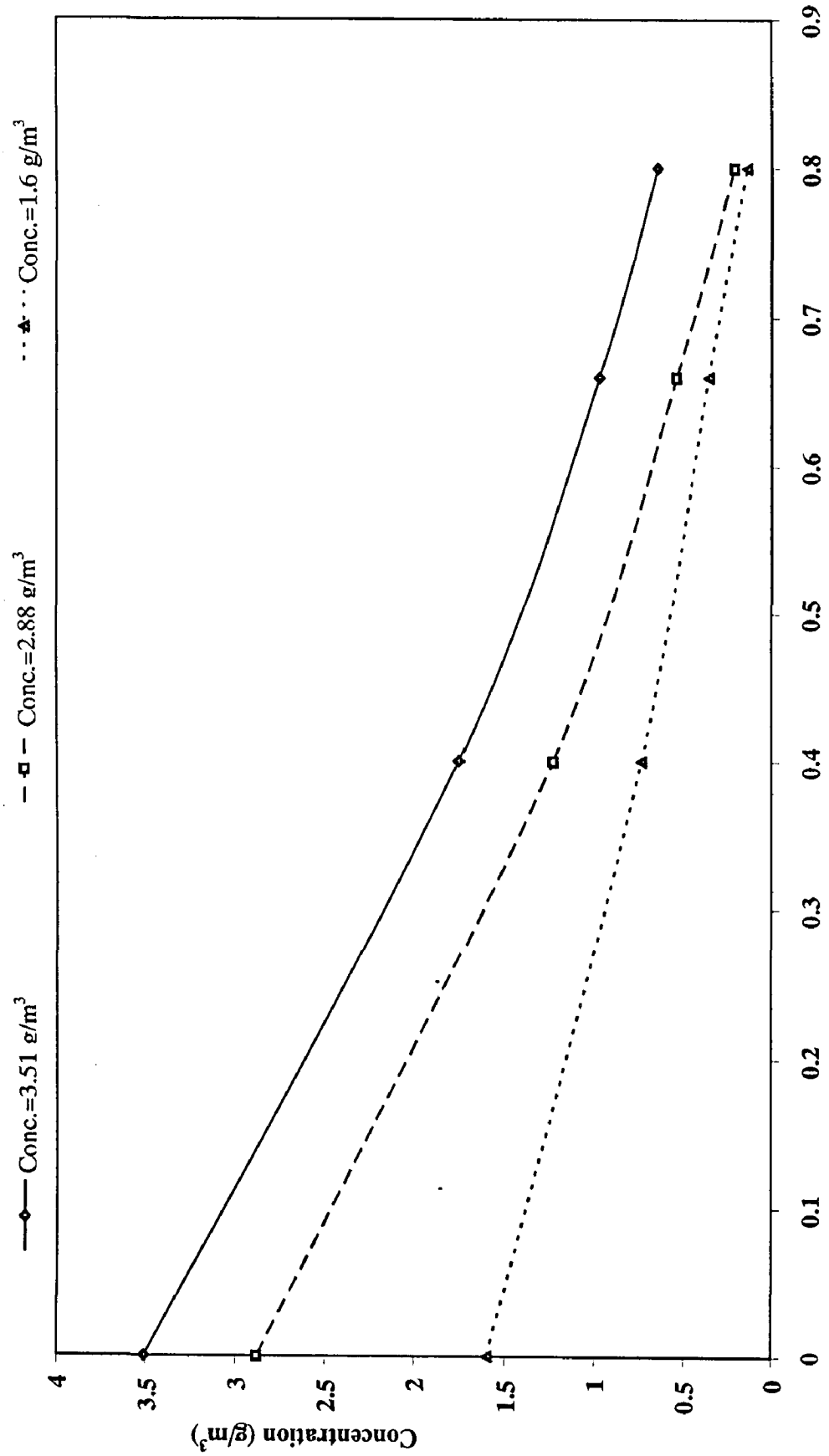


Figure 4.3c: Concentration profile along the bed height for high MCB concentrations

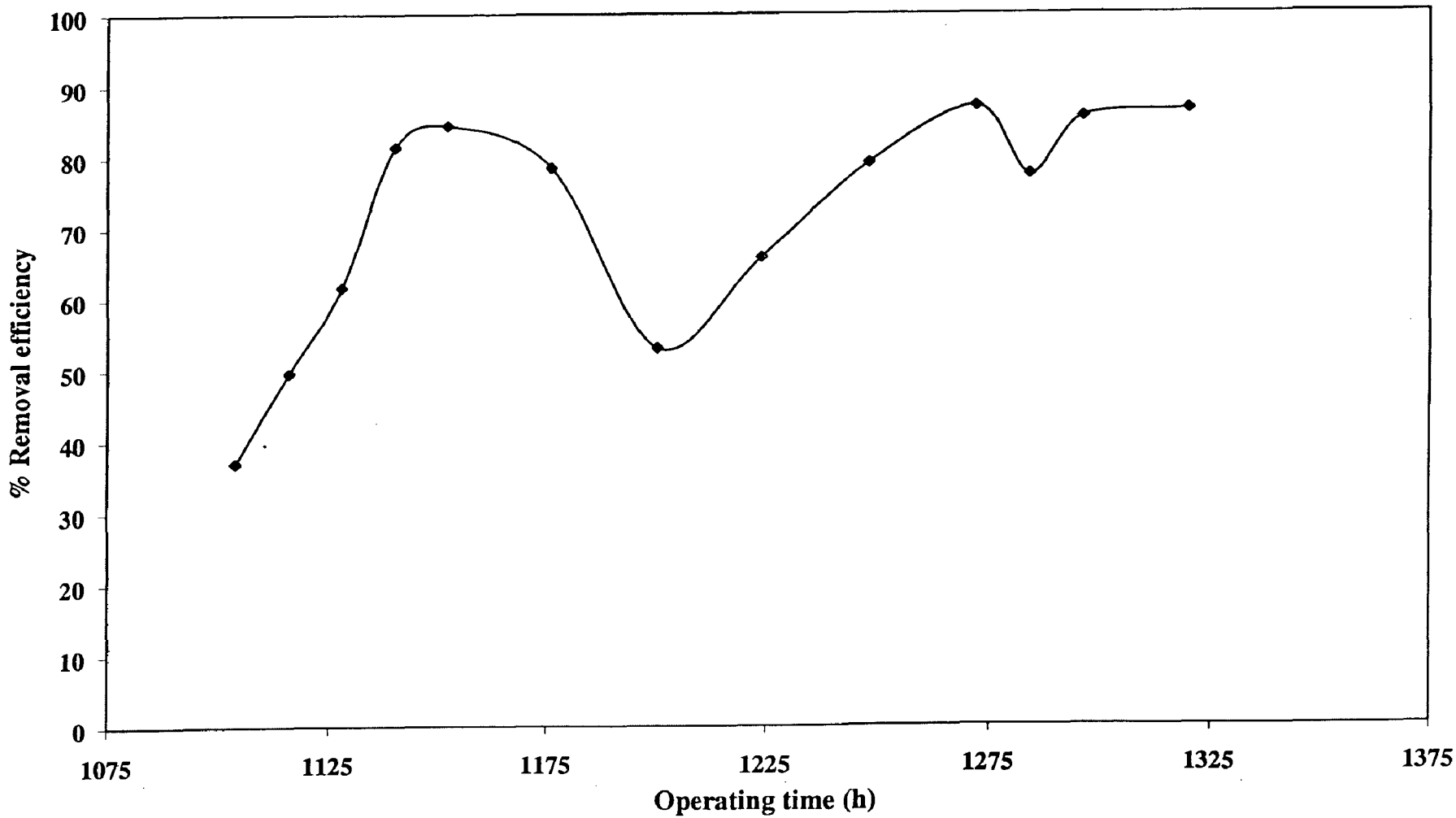


Figure 4.4a: Starvation with Nutrient only

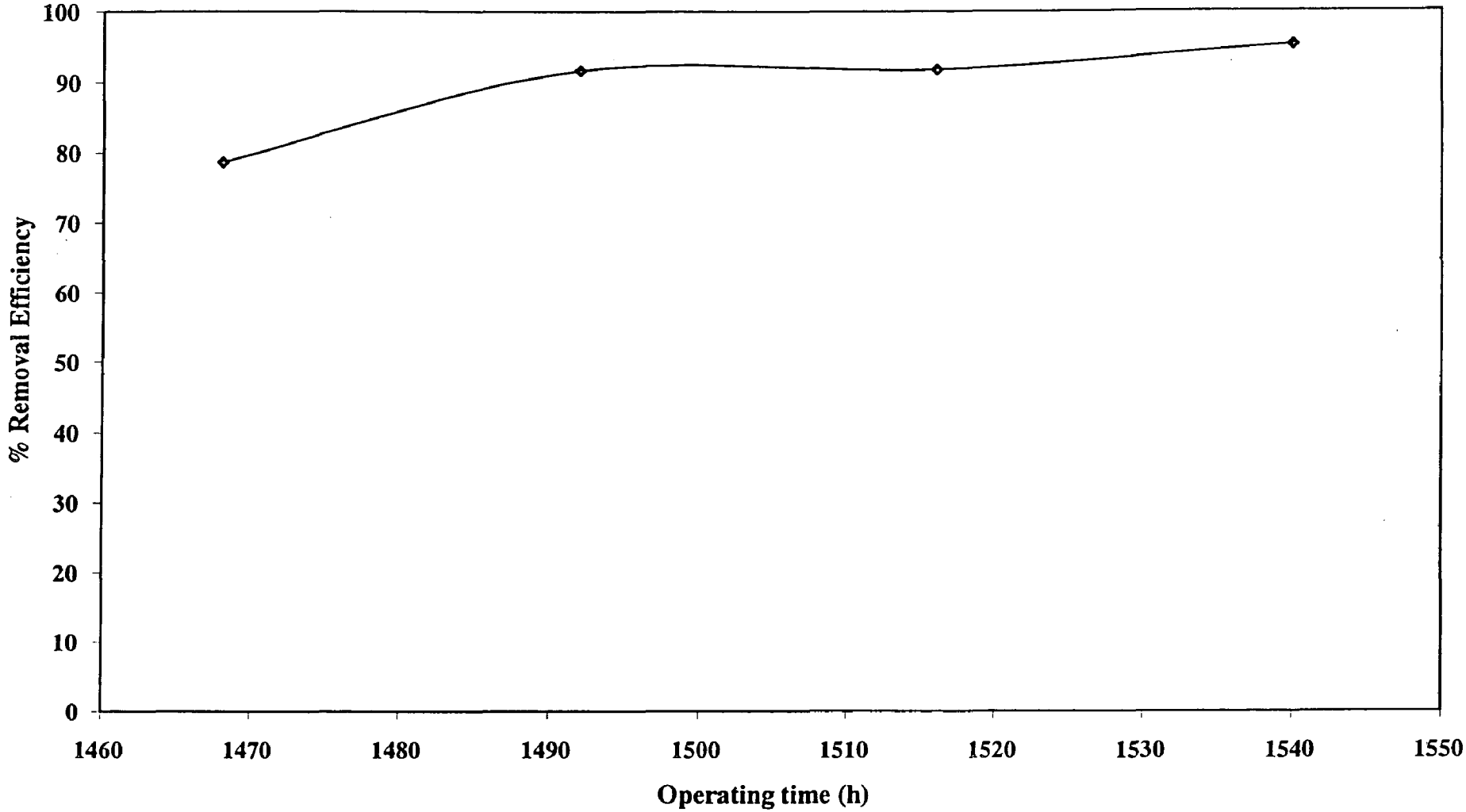


Figure 4.4b: Starvation with Nutrient and Air

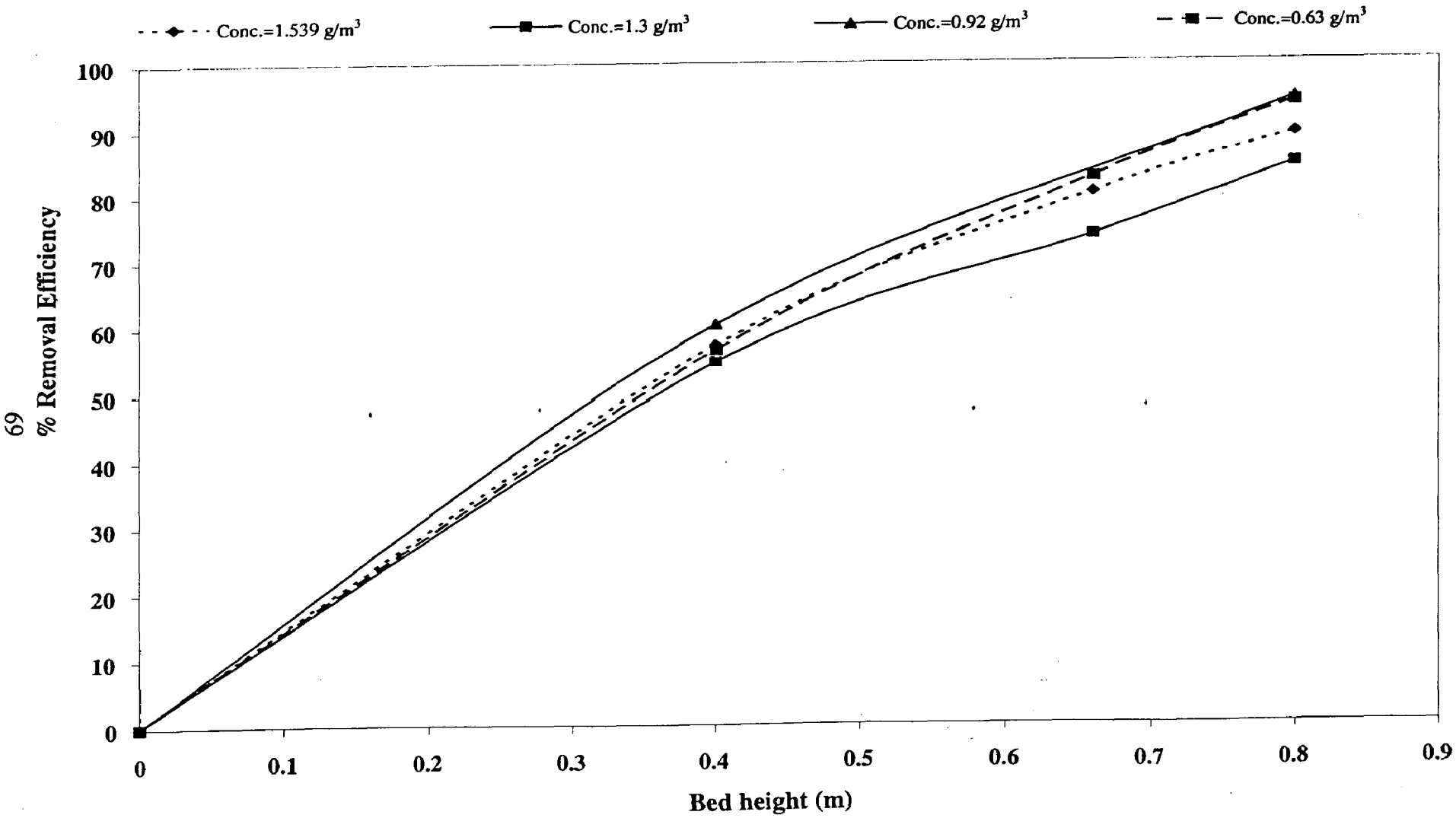


Figure 4.5a: Removal Efficiency along the bed height for low MCB concentrations

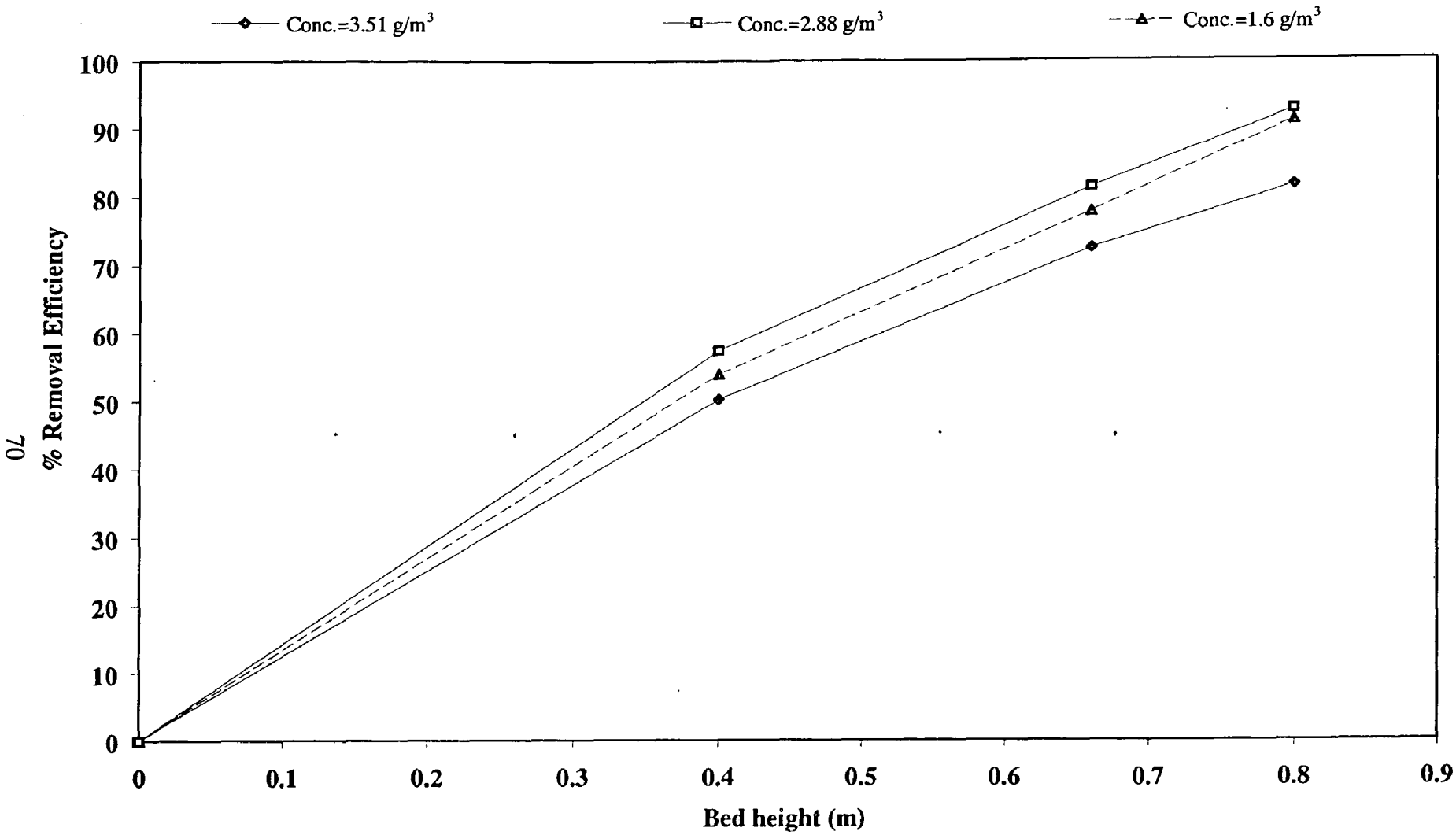


FIGURE 4.5b: Removal Efficiency along the bed height for high MCB concentrations

4.6 Effect of pH on removal efficiency

The pH is one of the important operating parameter for the microorganism growth. The pH values of the nutrient feed and leachate were measured each day throughout the whole experiment period. Initially the pH of the leachate was higher than the pH of the nutrient fed. The higher pH could be due to the intermediate formation before the exact degradation path as given in the stoichiometric equation. The microorganisms could have followed different degradation pathway in the initial operating period by forming intermediates due to new environment condition. Later periods, the pH values of the nutrient and the leachate had difference of 0.1 to 0.3 pH units only. This was due to the HCl formation during the degradation of the MCB. The stoichiometric equation for biodegradation pathway was already discussed. During the experiment, the nutrient liquid was replaced 3 times a week. Figure 4.6a shows the MCB removal efficiency as a function of pH of the nutrient feed. Increase in removal efficiency with increase in pH was observed in the pH range of 6.5 to 7.6 However an opposite trend was observed for pH from 7.7 to 8. The removal efficiency was above 90% when the pH was 7 to 7.7. From the experiment it was observed that the optimum pH for the microorganism growth and degradation was 7 to 7.7 pH.

4.7 Effect of temperature on removal efficiency

During the experiment startup the temperature was maintained at 12°C and gradually increased up to 25°C and it was maintained for a long duration of the operating period. The effect of operating temperature on the performance of trickling filter was studied by varying the temperature from 12°C to 40°C. Figure 4.7a shows the removal efficiency as a function of temperature. As can be seen, the removal efficiency increased with the increase in operating temperature from 12°C to 30°C. However an opposite trend was observed in the temperature above 32°C. From the experiment, it was observed that the optimum temperature for the microorganism growth and for the degradation of MCB is 22 °C to 30 °C. From the results, it was observed that the microorganisms degrading the MCB were mesophilic as well as thermophilic microbial community.

4.8 Determination of Michealis-Menten kinetic constants

The kinetic constants of the bioreaction can be determined either microkinetically or macrokinetically. For microkinetic determination, the microorganisms were isolated from the trickling filter media and inoculated into shake flasks containing a nutrient solution, with the contaminant solution as the sole carbon source. The concentration of contaminant was continuously measured as a function of time to obtain the kinetic constants by plotting the relation of biodegradation rate and the contaminant concentration (Ottengraf, et al., 1983). However, the microkinetic method of determination in biofiltration systems was still controversial because the kinetic behavior of biofiltration systems (a gas phase systems), and suspended cell systems (a liquid phase systems), may be not similar due to the different phases of bioreaction.

In this study, macrokinetic determination was used following the suggestion of Wani (1999). The kinetics of the system can be expressed by a Michaelis–Menten type relationship by assuming that oxygen limitation was not present in the system and the conversion was in the reaction-controlled regime (i.e. the biofilm was fully active). At steady state, the growth rate of microorganisms was balanced by its own decay rate, resulting in the biological equilibrium of the system. Hence, kinetic constants remained constant over the period of time considered.

The kinetic constants were determined using the plug flow model without dispersion at steady state Equation (1).

$$\frac{\partial C_g}{\partial t} = -U_g \frac{\partial C_g}{\partial h} + r \qquad \text{- (1)}$$

Where C_g is MCB concentration (g/m^3), U_g is the superficial velocity (m/s), t is the time interval (s), h is the distance from the bed (m), and r is the overall reaction rate and it is defined as Equation (2).

$$r = \frac{r_{\max} C_g}{K_m + C_g} \qquad \text{- (2)}$$

Where r_{max} is the maximum bioreaction rate per unit biofilter volume (g/m^3/s) and K_m is the saturation (Michaelis–Menten) constant (g/m^3) in the gas phase. At steady state, the accumulation term $\partial C_g / \partial t$ equals zero. Integrating equation (1) under the given

conditions $C_g = C_{gi}$ at $h = 0$ and $C_g = C_{go}$ at $h = L$ where C_{gi} and C_{go} are corresponding inlet and outlet MCB concentration (g/m^3), L is the biofilter length (m), Equation (3) was obtained.

$$\frac{V/Q}{C_{gi} - C_{go}} = \frac{K_m}{r_{max}} \frac{1}{C_{ln}} + \frac{1}{r_m} \qquad \text{- (3)}$$

Where C_{ln} the log mean concentration $[(C_{gi} . C_{go})/\ln(C_{gi}/C_{go})]$, V the biofilter volume (m^3), and Q is the volumetric flow rate (m^3/s), r_{max} and K_m for the gas phase can be obtained by plotting $[(V/Q)/(C_{gi} . C_{go})]$ against $(1/C_{ln})$. From the Figure 4.8a, the r_{max} and K_m were calculated as 0.1834 $g/m^3/s$ and 11.55 g/m^3.

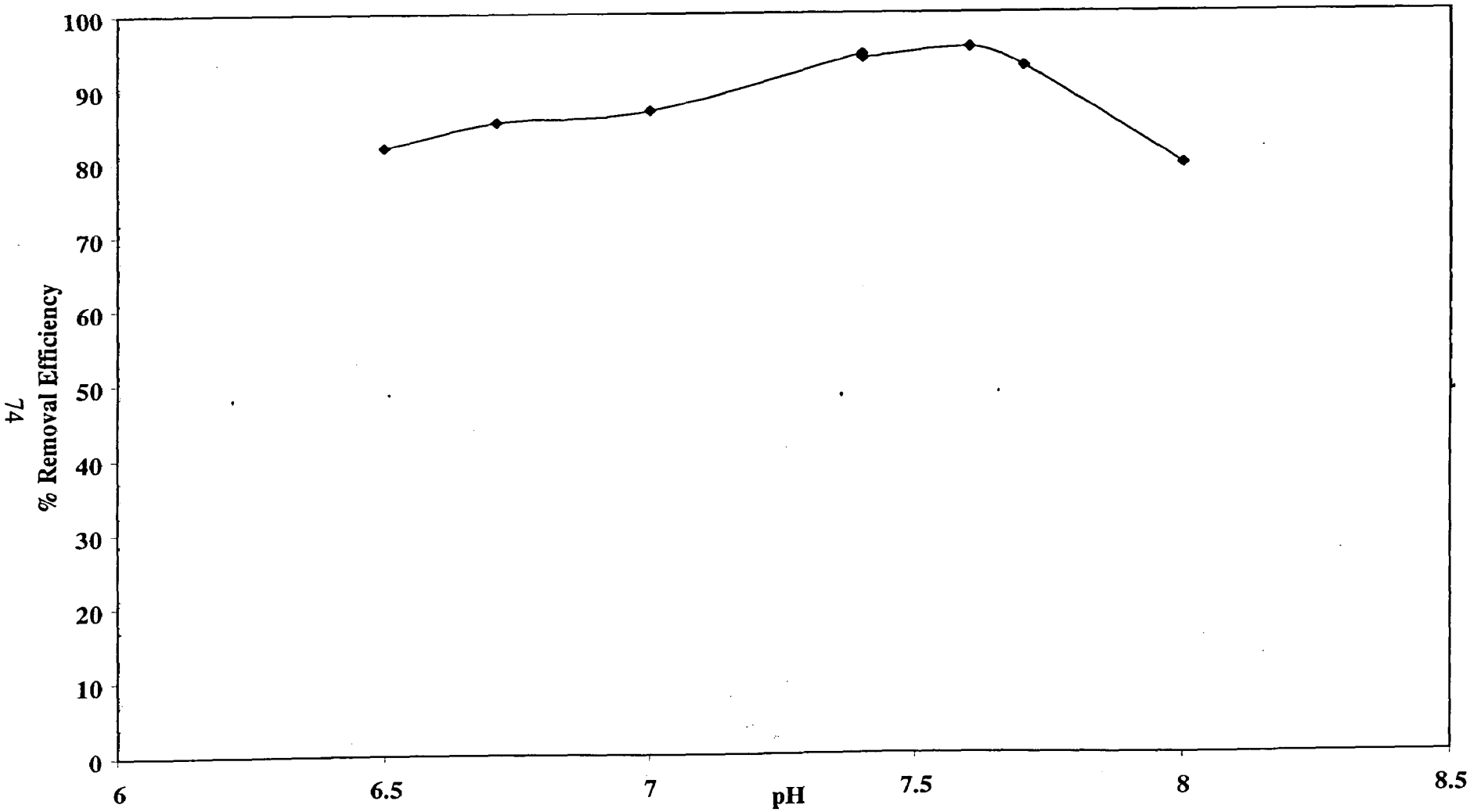


Figure 4.6a: Removal Efficiency as a function of pH

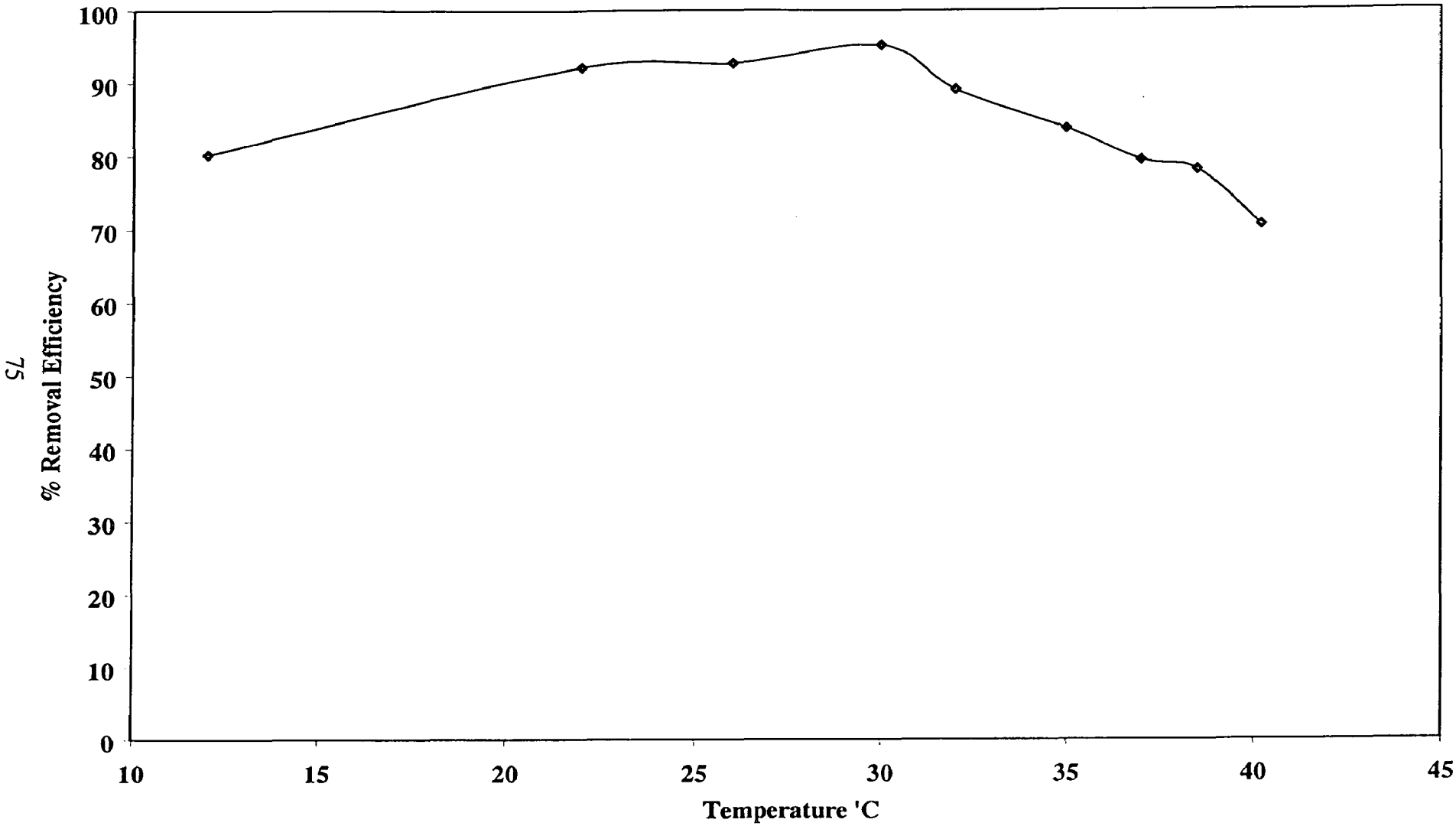


Figure 4.7a: Removal Efficiency as a function of Temperature

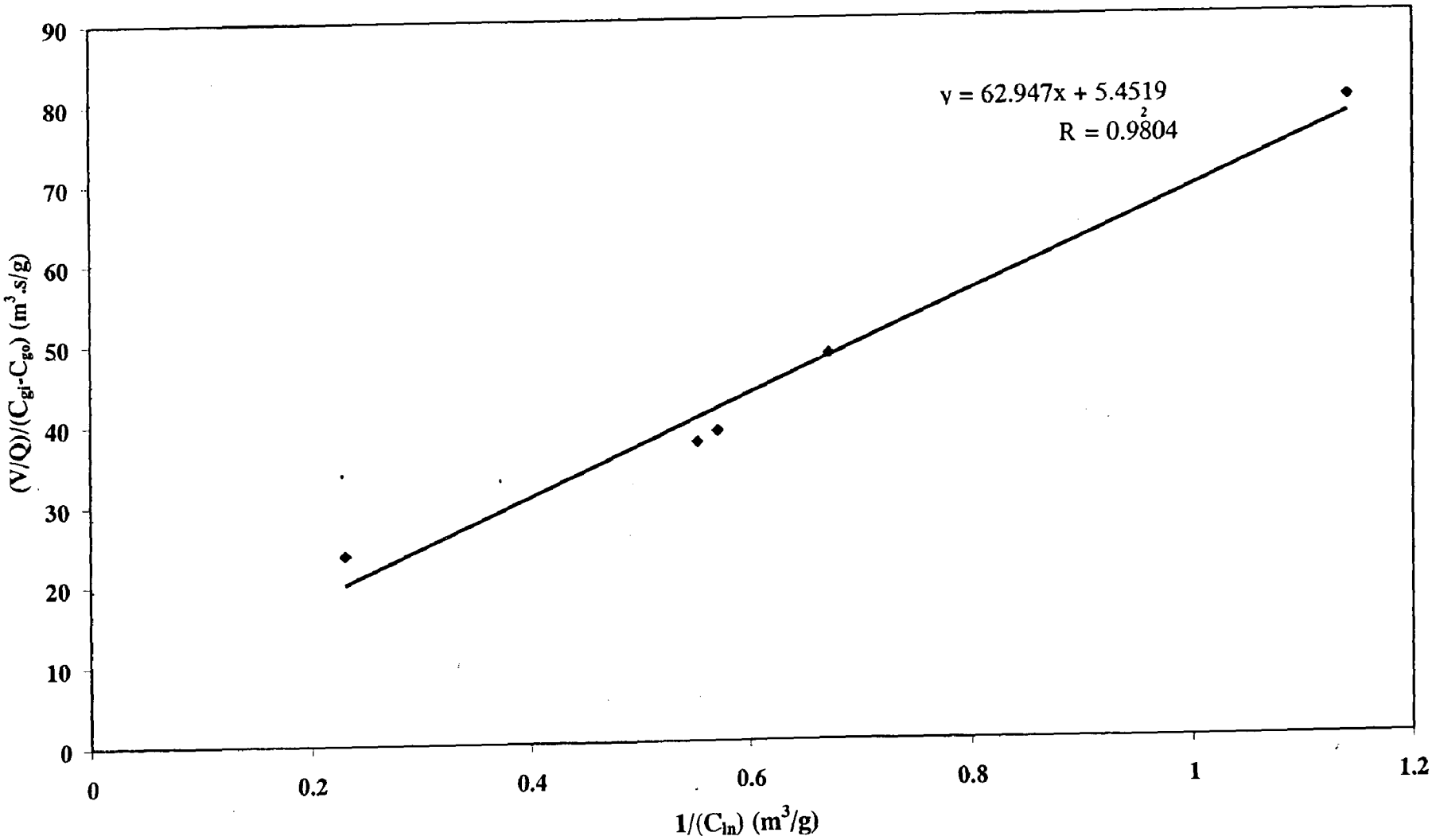


Figure 4.8a: Macrokinetic determination of Michealis-Menten Kinetic constants

4.9 Microscopic Observations:

A Scanning Electron Micrograph (SEM) of microbial growth on peat was taken before biofilm formation and after biofilm formation with low and high magnification. The SEM shows the structure of biofilm formation on the surface of the coal. Figure 4.9a and 4.9b shows the structure of the biofilm on the coal before the experiment with low and high magnification. Figure 4.9c and 4.9d shows the structure of the biofilm on the coal after the experiment with low and high magnification. From the SEM study, it was observed that coal was a good packing material and can be used as a good biological attachment medium for the biofiltration.

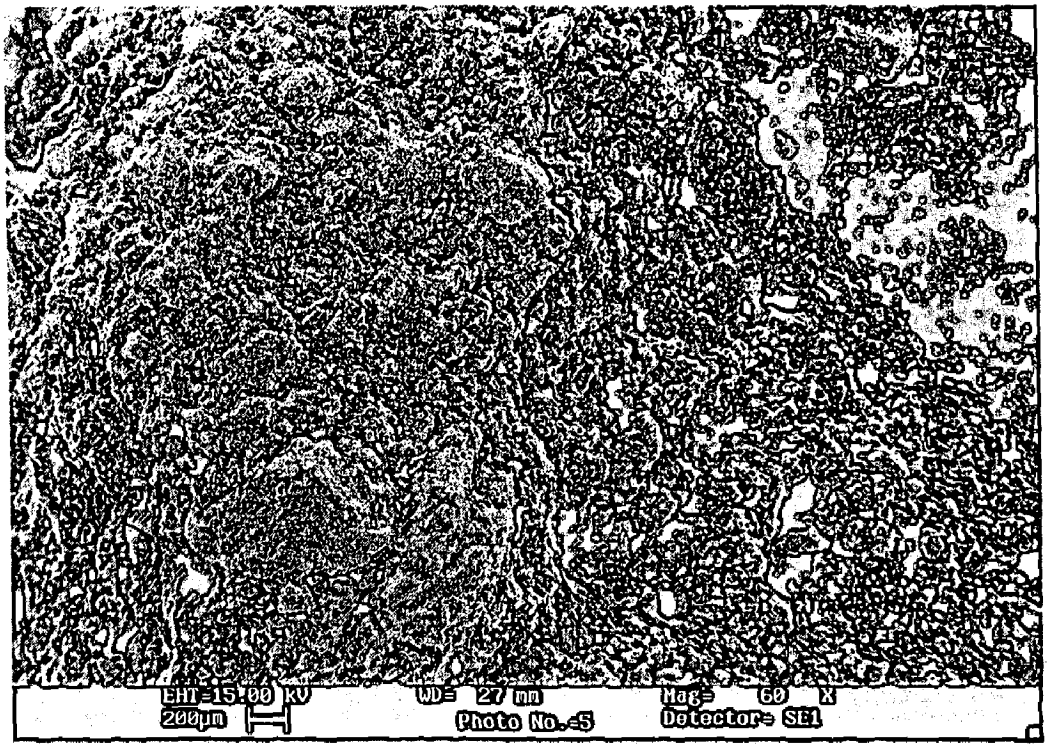


Figure 4.9a: SEM of coal before experiment with low magnification

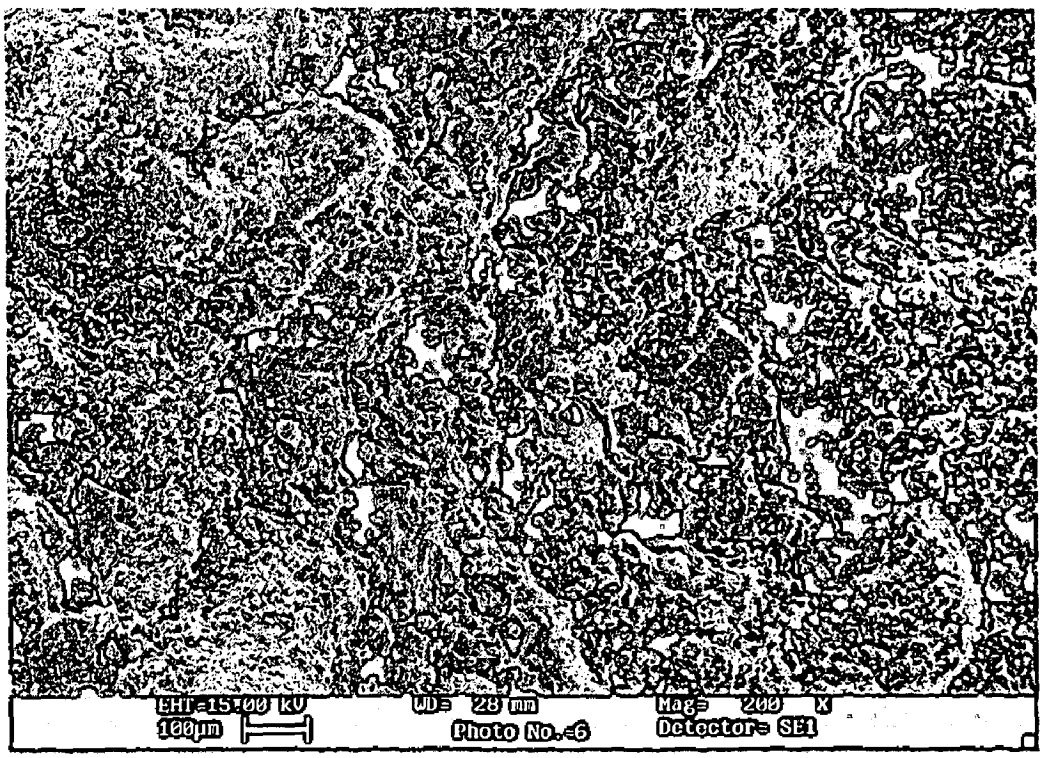


Figure 4.9b: SEM of coal before experiment with high magnification

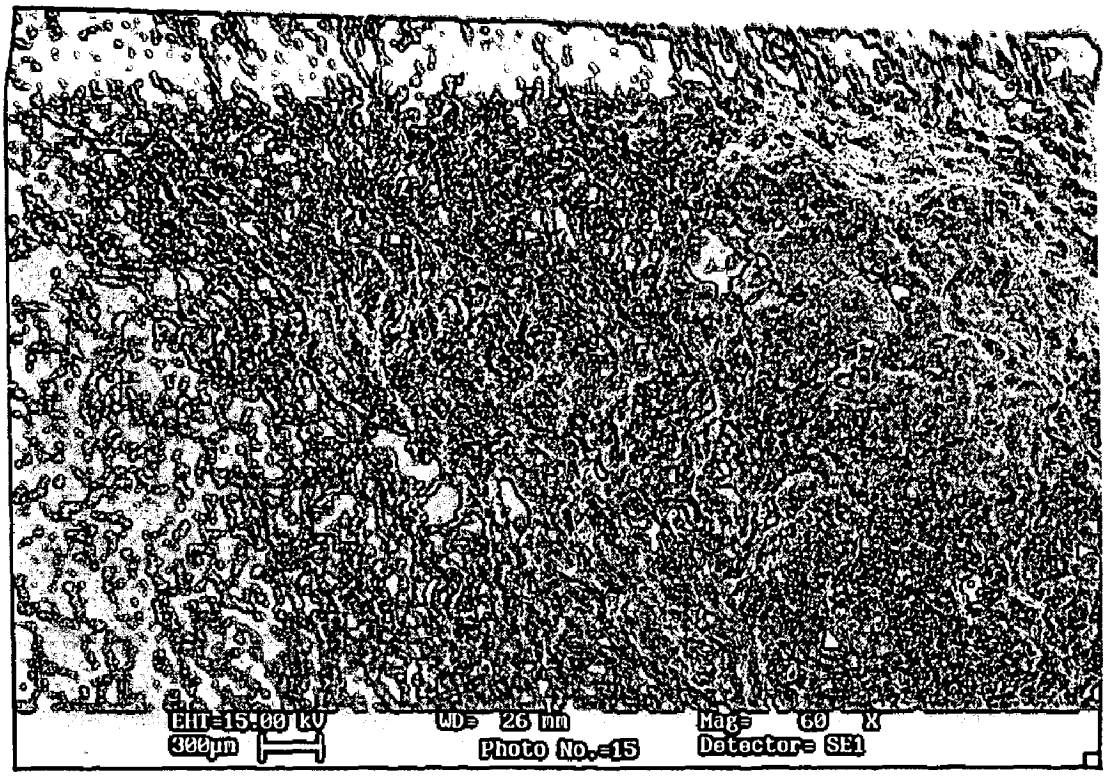


Figure 4.9c: SEM of coal after experiment with low magnification

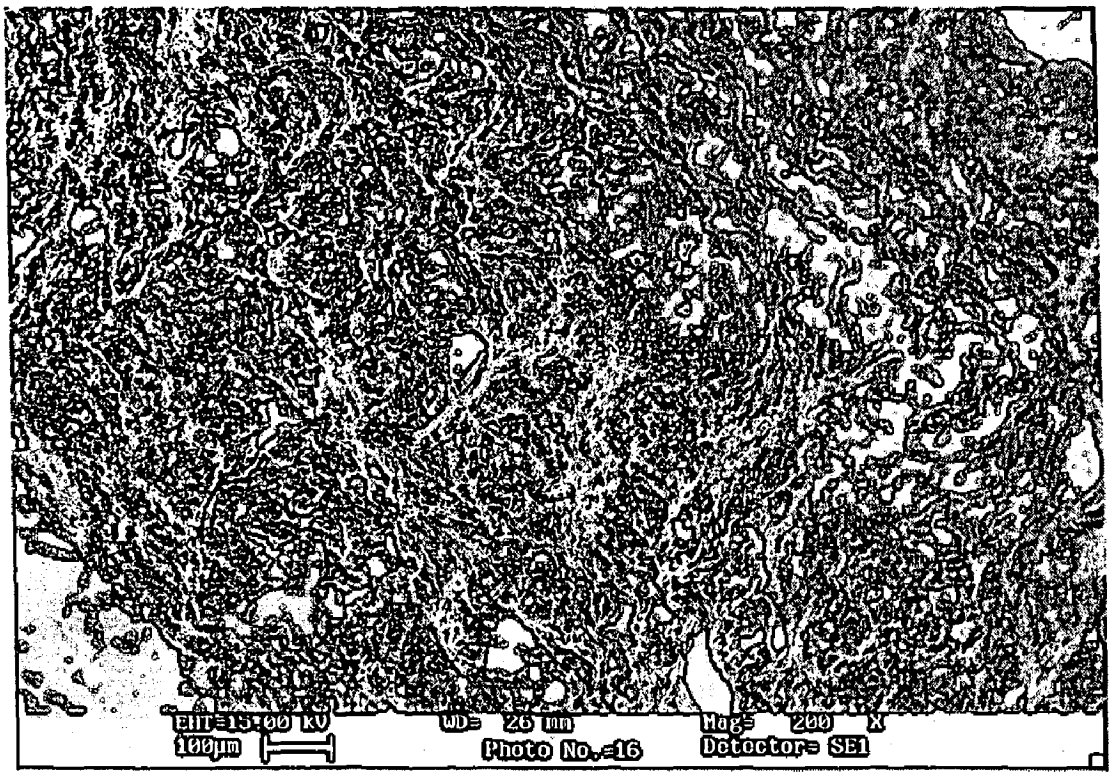


Figure 4.9d: SEM of coal after experiment with high magnification

Chapter 5

Modeling of Biotrickling filter

5.1 Introduction

The biotrickling filter is a relatively new technology which has been proven very efficient for treating many kinds of volatile organic compounds (VOCs) from waste gases by a number of researchers. The process involves mass transfer of VOCs from the gas phase to the biofilm, and subsequent bio-oxidation within the biofilm. Therefore, a thorough understanding of the factors that influence the rates of mass transfer process and biofilm reaction is necessary before practical application of a biotrickling filter in the field can be extensively realized. These considerations result in efforts to develop a valid model for predicting the biotrickling filter performance.

The theoretical description of the biofiltration systems has gained the interest of many researchers with the aim of better understanding the process and optimizing the process and optimizing the design and operation of biotrickling filters. Abumaizer et al. (1997) presented a steady state mathematical model to describe the kinetics of VOC removal in the biofilter that consisted of a mixed compost and granular activated carbon medium. The experimental data were compared with model predictions under steady state conditions for treatment of BTEX vapors. Baltzis et al. (1995) described a general mathematical model for classical biofilter under steady state conditions of operation. The model accounts for potential kinetics interactions among the pollutants, effects of oxygen availability on biodegradation and biomass diversification in the filter bed. Hodge and Devinny (1995) developed a mathematical model that describes basic transport and biological processes for biofilter. The model describes transfer between the air and solid/ water phases, biological degradation of substrate, CO_2 accumulation. They compared the experimental data with the predictive model solutions for steady state and non steady state regimes. Hwang et al. (1997) developed a mathematical model by taking into account diffusion and biodegrading of acetone and diffusion of oxygen in the biofilm, mass transfer resistance in the gas film, and flow pattern of the bulk gas phase. The experimental data was compared with the predictions from the proposed model. Lu et al. (2003) developed a mathematical model that incorporates mass transfer process and

biofilm reactions to predict the performance of biotrickling filter for treating isopropyl alcohol and acetone mixture. The model consists of a set of mass balance equations for both compounds and oxygen in the bulk gas phase within the biofilm. Baltzis et al. (2000) derived a mathematical model for describing removal of MCB and DCB in biotrickling filters. The model accounts for potential process rate limitation by the availability of oxygen as well as for potential kinetics interactions among pollutants during their degradation.

Effective modeling can lead to the development of a trustworthy performance equation that decreases the time and cost of experimentation at the pilot scale (Lu, et al., 2003).

5.2 Mathematical model

In this experiment, VOC containing air stream is passed through a column filled with coal particles that are covered with a steady state biofilm. VOCs are transported to the air/biofilm interface, where they absorbed into the biofilm and employed as carbon and/or energy sources by the microorganisms. A mathematical model describing the transport and biological phenomena involved in the process of contaminant removal in biotrickling filters is developed. The model predicts the concentration profile of the VOC in the gas phase, the biofilm and the sorption liquid retained in the solid particles composing the filter bed at steady state. The figure 5.1a depicts the concentration profile followed by the VOC. The Michealis-Menten constant obtained using the macrokinetic determination was used in this model.

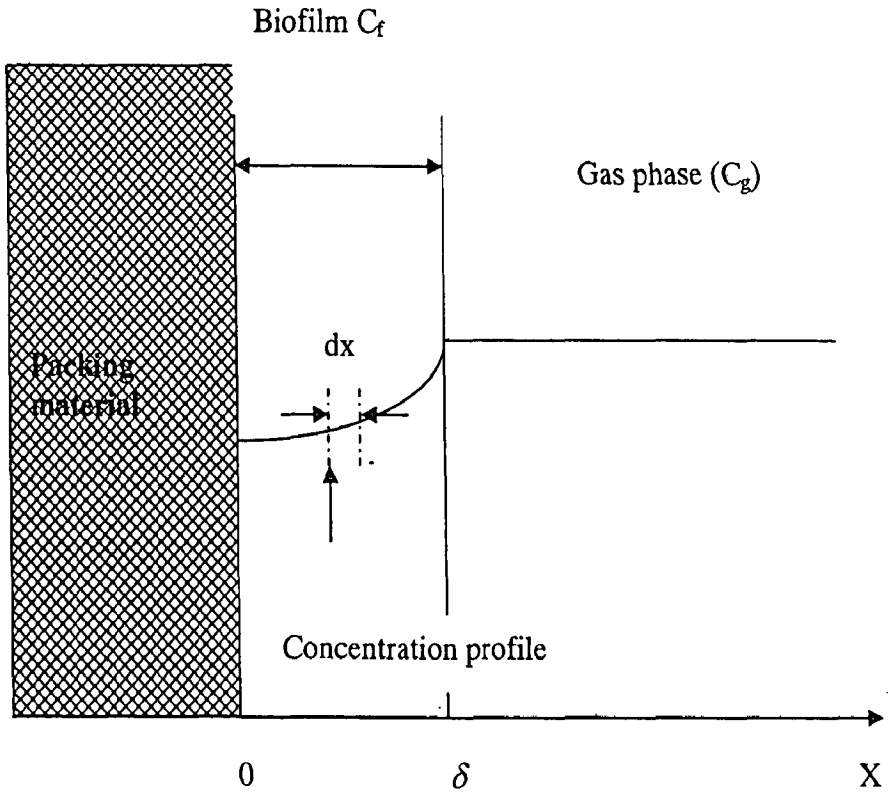


Figure 5.1a: Concentration profile of VOCs along the biofilm

Table 5.1 Model Parameters used in the model

Parameter	Units	Values	Reference
D_e	m^2/s	0.81×10^{-9}	Perry & Green (1984)
r_m	$g/m^3/s$	0.1834	From experiment
K_m	g/m^3	11.55	From experiment
k_f	s^{-1}	0.0159	From experiment
δ	m	0.0001	Mohseni (2000)
m	-	0.167	Baltzis (2000)
d_p	m	0.01	From experiment

5.2.1 Assumptions

Some assumptions are made to derive the governing model equations, they are discussed below.

1. The external surface of the solid particle is completely covered with the liquid biofilm. The biolayer thickness is assumed to be uniform throughout the height of the filter bed (Jorio, et al., 2003).
2. Biodegradation of VOCs occurs only aerobically. The only substances affecting the rate of biodegradation are the VOCs and oxygen. The VOCs are assumed to contact the organisms comprising the biofilm by diffusion as characterized by Fick's law.
3. At steady state, the microorganisms are considered to be uniformly distributed throughout the biofilm and the bed as whole (Jorio, et al., 2003). The kinetics of the substrate reactions in the biolayer surrounding the coal particle follows the Monod type model (Abumaizer, et. al., 1997).
4. The flow of the air stream through the filter bed is of a plug flow type and gas flow rates are sufficiently high to render axial dispersion negligible (Abumaizer, et. al., 1997).
5. The coal particles are assumed to be spherical.
6. The pollutant concentration is assumed to decrease from the particle surface, where the concentration is in equilibrium with the bulk gas phase to a value of zero at some radial distance from the center of the particle. It is illustrated in the Figure 5.1a.
7. The biofilter is isothermic. Ambient temperature prevails uniformly in the trickling filter (Jorio, et al., 2003).

5.2.2 Mass balance in the biofilm

Biodegradation rate is commonly described by the Monod model. The model is based on the two limiting cases, Zero-order kinetics-for sufficiently high VOC concentration, and first order kinetics-for low VOC concentration.

Monod kinetics:

$$-r_b = \frac{r_{max} C_f}{K_m + C_f} \qquad \text{-(1)}$$

Case 1: Zero-order kinetics:

$$-r_b = k_1, \qquad \text{where } (C_f >> K_m) \qquad \text{-(2)}$$

Case 2: First-order kinetics:

$$-r_b = k_1 C_f, \qquad \text{where } (C_f << K_m) \qquad \text{-(3)}$$

Where C_f is VOC concentration in the bulk fluid, r_{max} is maximum specific reaction rate, K_m is half saturation constant, and k_f is biodegradation constant ($k_f = r_{max}/K_m$ for first order), and ($k_f = r_{max}$ for zero order). In this work, the first order kinetics is only considered.

5.2.2.1 First-order biodegradation kinetics in the biofilm

When the substrate concentration is very low, $C << K_m$ reduces to a first order rate equation (equation 3). At steady state, the biofilm is assumed to attain a constant thickness, δ, and there is no accumulation of substrate within the biofilm. Based on the above assumptions, a mass balance in the biofilm of a coal particle (figure 5.1a) is

$$-D_e A_s \left.\frac{dC_f}{dx}\right|_x + D_e A_s \left.\frac{dC_f}{dx}\right|_{x+\Delta x} - k_f C_f A_s \Delta x = 0 \qquad \text{-(4)}$$

Where D_e is diffusion coeffiecient in m^2/s, x is axial distance in m, and A_s is biolayer surface area per volume of packing in m^{-1}. Dividing both sides by A_s and Δx, and taking the limit as Δx approaches zero, yields the following equation:

$$D_e \left.\frac{d^2 C_f}{dx^2}\right|_x - k_f C_f = 0 \qquad \text{-(5)}$$

The boundary conditions, assuming reaction limited kinetics are

$$\frac{dC_f}{dx} = 0 \qquad \text{at } x = 0 \qquad \text{-(6)}$$

$$C_f = \frac{C_g}{m} \qquad \text{at } x = \delta \qquad \text{-(7)}$$

Where m = distribution coefficient which is ratio of (C_g/C_f) at equilibrium condition, the solution of equations (4) – (7) is

$$\frac{C_f}{C_g/m} = \frac{\cosh\left(\phi\frac{x}{\delta}\right)}{\cosh\phi} \qquad \text{- (8)}$$

Where ϕ = 'Thiele Modulus' and is defined as $\phi = \sqrt{\delta(k_f/D_e)}$.

The steady state material balance for gas phase pollutant concentration (C_g) in a coal packed biotrickling filter, h, assuming negligible axial dispersion is (Ottengraf, 1983)

$$-U_g\frac{dC_g}{dh} = N_s A_s \qquad \text{- (9)}$$

Where U_g is superficial gas velocity, m/s, dh is differential length in axial direction, and N_s is mass transport to biofilm given by equation (10).

$$\left(N_s = -D_e\frac{dC_g}{dh}\right) \qquad \text{- (10)}$$

N_s can be calculated by evaluating (dC_f/dx) at $x = \delta$, from equation (8) and then substituting in equation (10).

$$N_s = -D_e\frac{C_g}{\delta m}(\phi\tanh\phi) \qquad \text{- (11)}$$

5.2.2.2 Zero-order biodegradation kinetics in the biofilm

For sufficiently high substrate concentration, the kinetics reduced to equation (2). Once again assuming a constant biofilm thickness and steady state conditions, the equation describing the concentration of substrate in the coal layer is

$$D_e\frac{d^2C_f}{dx^2}\bigg|_x - k_0 = 0 \qquad \text{- (12)}$$

Where k_0 is zero order reaction rate constant, the boundary conditions are same as that of equation (6) & (7). By solving the above equation, we get

$$C_f = \frac{k_0}{2D_e}x^2 + \frac{k_0}{2D_e} + \frac{C_g}{m\delta} \qquad \text{- (13)}$$

For the Zero order biodegradation kinetics, the diffusion rate controlling is considered, therefore the mass transport to biofilm is

$$N_s = -D_e \frac{dC_g}{dh} = KL \qquad \text{- (15)}$$

Where K is the overall mass transfer coefficient and L is the bed height (m). N_s can be calculated by applying the boundary conditions (C_g=C_g) at $x = \delta$, (C_g=C_0) at $x = 0$, then substituting and solving in equation (15). We get

$$\frac{C_g}{C_0} = 1 - \frac{KLA_s\delta}{U_g C_0} \qquad \text{- (16)}$$

The model equation (9) is solved numerically using MATLAB ODE suit. The equation is solved numerically by Fourth order Runge-Kutta Algorithm. The theoretical results and experimental results were compared. The first order and zero order were compared and found that first order kinetics fitted well than the zero order kinetics. The comparison of first order and zero order were not shown because of wide deviation in zero order was found. From the theoretical results, it was observed that the first order model prediction of MCB concentration profiles in the biotrickling filter was in very good agreement with the experimental results.

5.3 Results and Discussion

A mathematical model was developed for the biotrickling filter considering both the zero order and first order monod kinetics. The model was verified by comparing both the theoretical and the experimental values at the different sections of the biotrickling filter. Comparing the theoretical and experimental results, it was observed that the biotrickling filter didn't follow the zero order kinetic. The model developed was verified for the MCB concentrations 0.63 g/m^3, 0.92 g/m^3, 1.4182 g/m^3, and 1.84 g/m^3 for the gas flow rates 0.5 lpm, 1 lpm, and 1.5 lpm, respectively.

Figure 5.3a and 5.3b represent the concentration profiles followed by the model and experimental results for the MCB concentration of 0.63 g/m^3, 0.92 g/m^3 at gas flow rates of 0.5 lpm at various sampling ports in the trickling filter. The experimental and theoretical values follow almost same upto 0.4 m height of the column, and at the end it deviates more.

Figure 5.3c represents the concentration profile followed by the model and experimental results for the MCB concentration of 1.4181 g/m^3 at gas flow rate of 1.0 lpm at various sampling ports in the trickling filter. Along the bed, there was a little deviation of the experimental and theoretical values. The deviation was due to higher concentration as well as the higher gas flow rate.

Figure 5.3d represents the concentration profile followed by the model and experimental results for the MCB concentration of 1.84 g/m^3 and gas flow rate of 1.5 lpm at various sampling ports in the trickling filter. Along the bed, there was a little deviation of the experimental and theoretical values. The deviation ws due to higher concentration as well as the higher gas flow rate.

In conclusion, the experimental first order concentration profiles were generally good predictors of the exponential character of experimental profiles for relatively low inlet MCB concentrations. For the higher concentration, the model predictions were not good. The deviations of experiment and predicted values were due to (1) ignoring the some biochemical aspects such as self inhibition or cross inhibition at higher concentration, (2) the model predictions made does not include the adsorption of VOCs in the packing media, (3) the microorganism would be more near the nutrient supply near

to the outlet, was not considered, and (4) finally some manual errors while taking the samples.

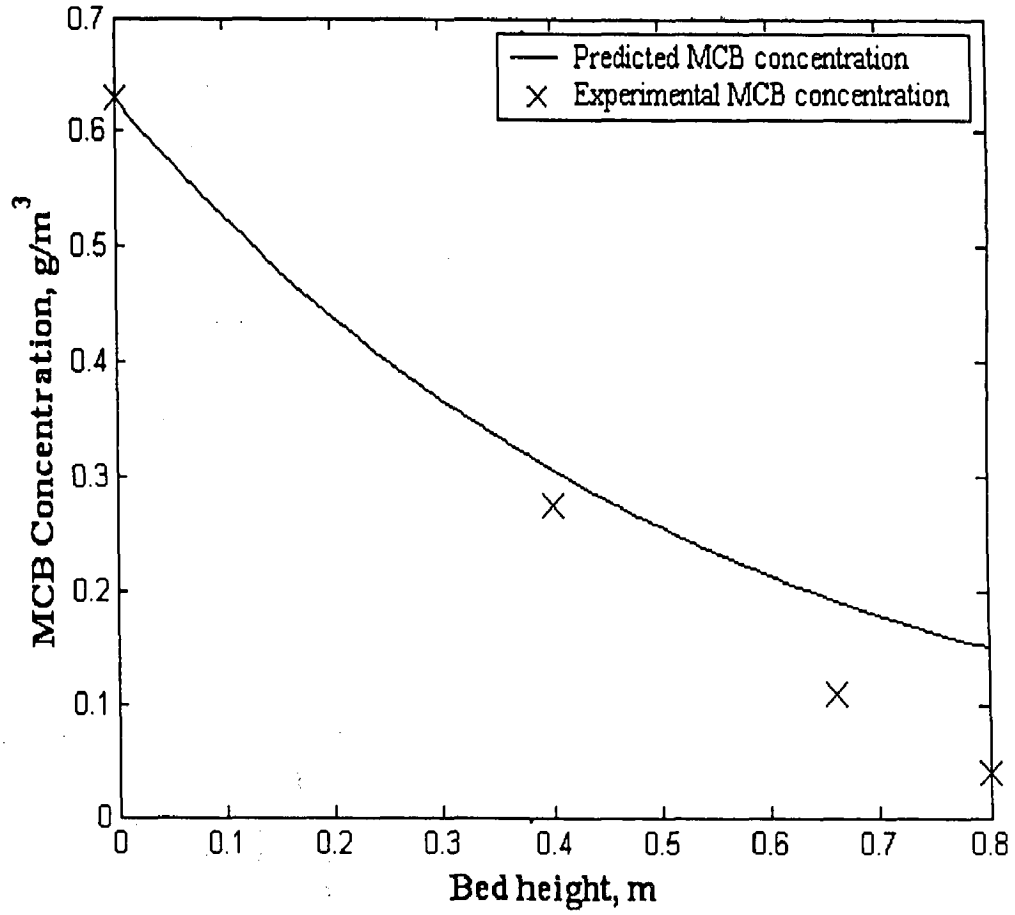


Figure 5.3a: Concentration profile along the bed height for the Inlet MCB concentration (0.63 g/m^3)

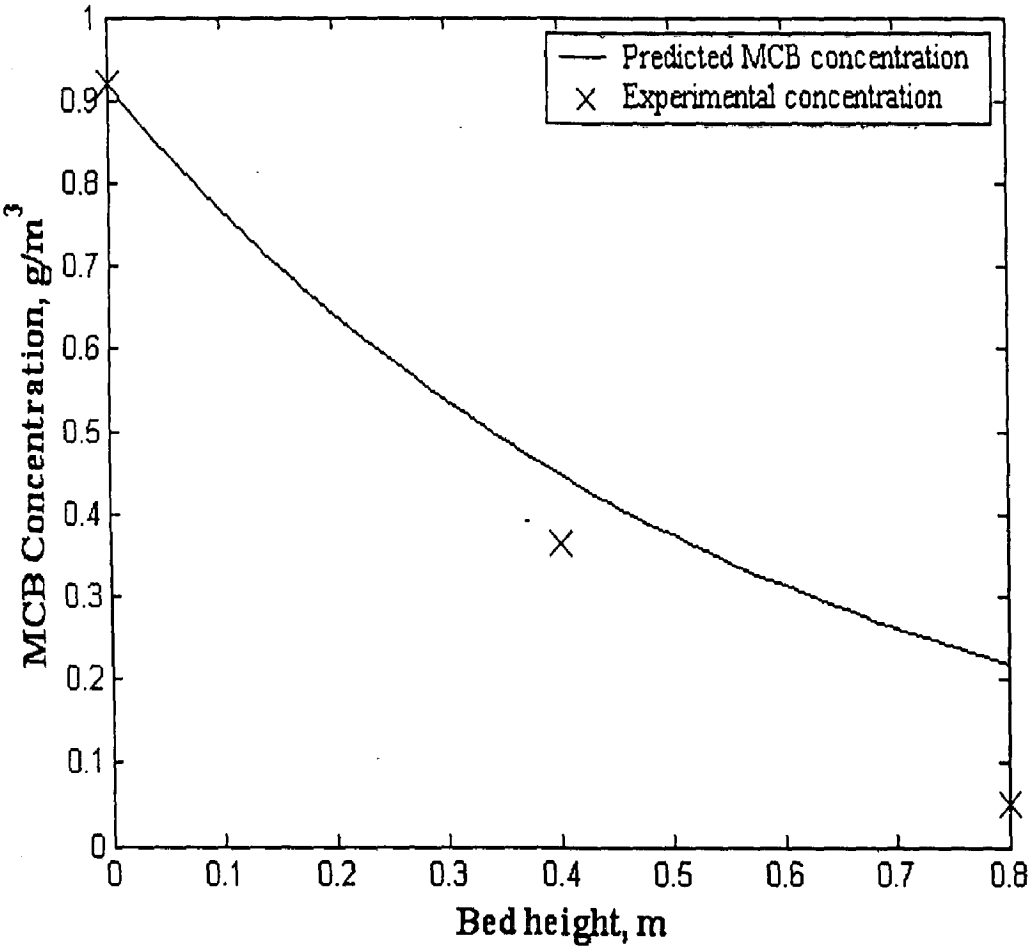


Figure 5.3b: Concentration profile along the bed height for the Inlet MCB concentration (0.92 g/m^3)

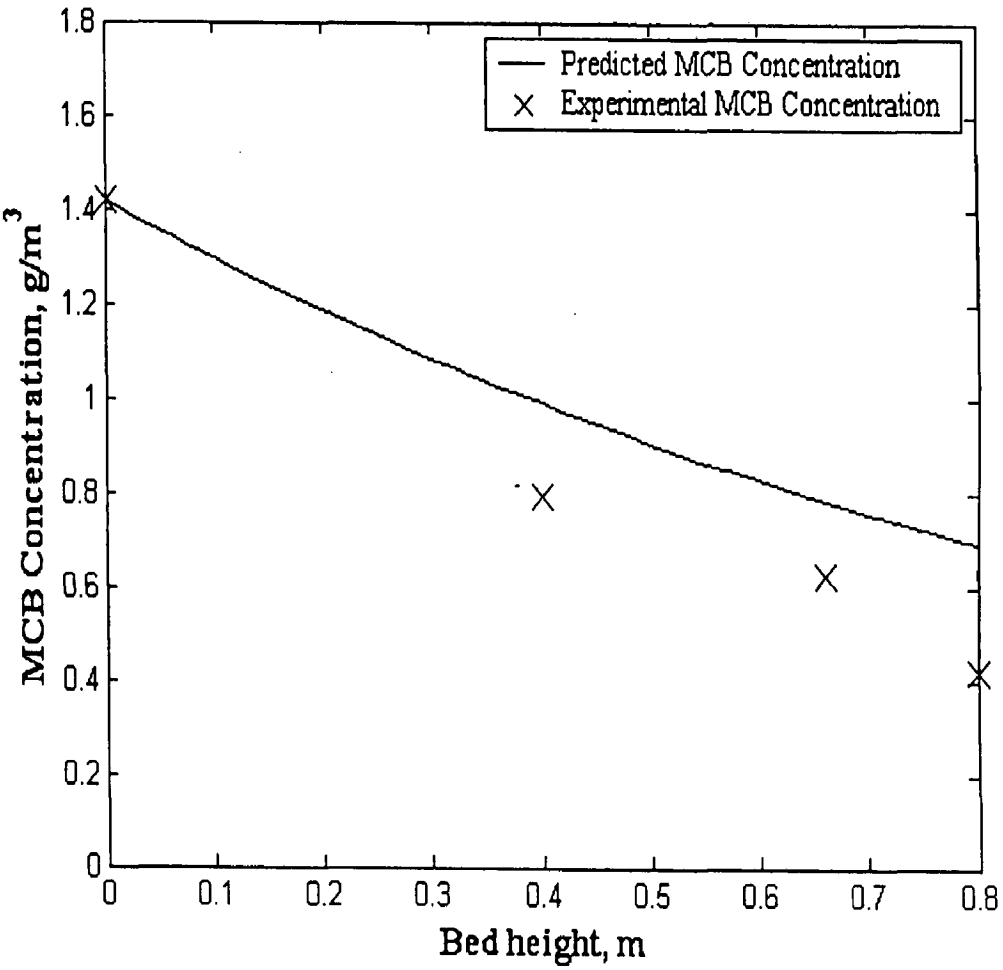


Figure 5.3c: Concentration profile along the bed height for the Inlet MCB concentration (1.4181 g/m^3)

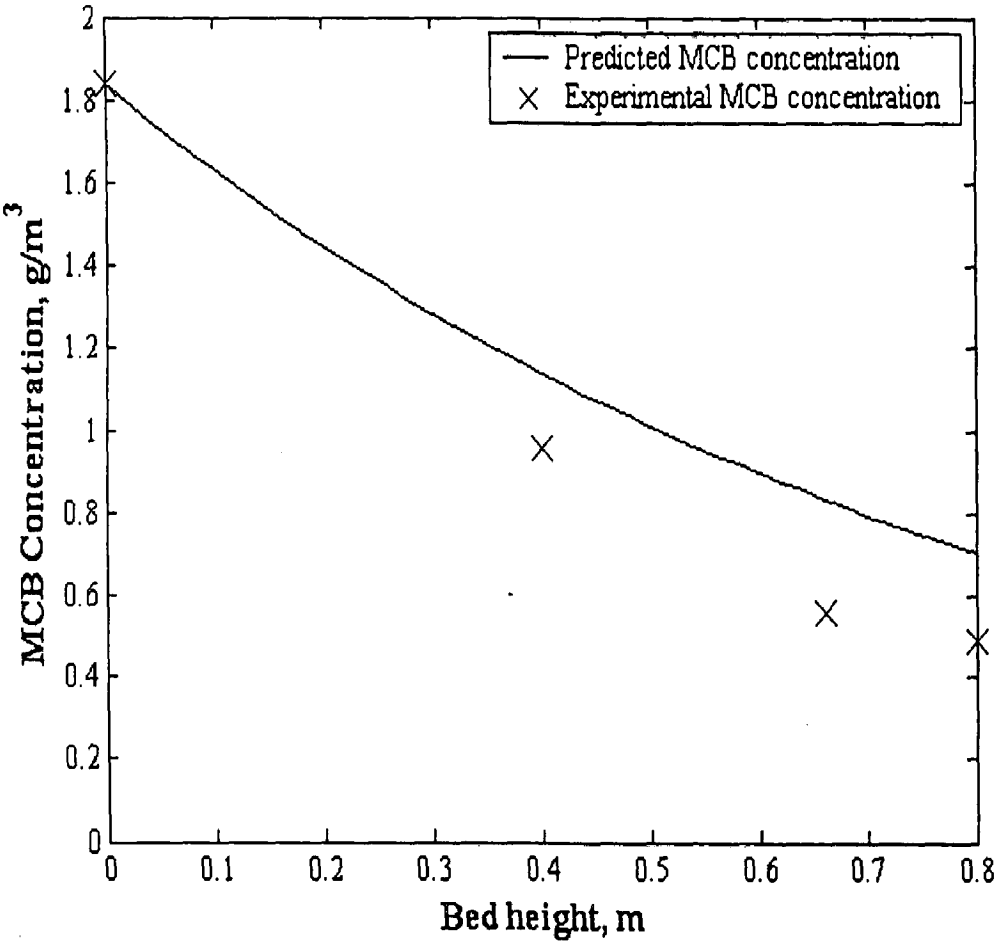


Figure 5.3d: Concentration profile along the bed height for the Inlet MCB concentration (1.84 g/m^3)

Chapter 6

Conclusions and Recommendations

6.1 Conclusions

A laboratory biotrickling filter with coal packing material was studied for the biofiltration of MCB. The performance of the biotrickling filter for different gas flow rate, inlet MCB concentration, and the effect of temperature, and the pH were studied. From the experiment, following conclusions were made:

1. MCB, a halogenated aromatic compound was successfully treated in biotrickling filter with coal as packing material.
2. The maximum removal efficiency of 95.20% and elimination capacity of 40.83 $g/m^3/h$ were achieved in the biotrickling filter for the MCB concentration of 1.069 g/m^3 at EBRT of 94.26 s.
3. The activated sludge obtained from the waste water treatment plant can be used as microbial consortia which is capable to degrade the MCB. Biotrickling filter took an acclimation period of 16 days to attain the pseudo-steady state.
4. The performance of the trickling filter was quite good even when the gas flow rate, EBRT and inlet MCB concentration are changed.
5. Biotrickling filter overcame the starvation within a short period of re-acclimation time.
6. The effects of temperature and pH on the performance of the biotrickling filter were studied. The optimum conditions for the biodegradation of MCB were found to be 7 to 7.7 pH and temperature of 22^0C to 30^0C.
7. The Michealis-Menten kinetics for MCB degradation was determined from the experiment. The r_{max} and K_m were calculated as 0.1834 $g/m^3/s$ and 11.55 g/m^3.
8. A mathematical model was developed for the biotrickling filter. The theoretical and experimental results were compared. The model following first order kinetics well suited for the biodegradation of MCB in the biotrickling filter.

6.2 Recommendations

Although a thorough study was made on the laboratory scale biotrickling filter. Still some more modifications and recommendations are needed to implement in the system for industrial application. Following are some of the recommendations needed in the biofiltration system for the detailed study.

1. Due to lack of time, the performance of biotrickling filter for the change in pH and temperature are not studied in depth.
2. The effect of the moisture content and the nutrient supply to the biotrickling filter has to be studied.
3. The packing material can also be changed to study the biodegradation of MCB on other packing material and their performance can be compared.
4. The mathematical model developed did not take adsorption into account, considering the diffusion only limiting. So the adsorption also has to be taken for the detailed study.
5. Further research works on different VOCs are required to explore the potential of biofiltration systems.

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Appendix I

Table Ia: Exposure limit of Mono-Chlorobenzene

Compound	CAS Number	Exposure limits	
		OSHA PEL	ACGIH (TLV-TWA)
Mono-Chlorobenzene	108-90-7	75 ppm	10 ppm

OSHA PEL

Occupational exposure to Chlorobenzene is regulated by the Occupational Safety and Health Administration (OSHA). OSHA permissible exposure limit expressed as a time-weighted average of the concentration of a substance of a substance to which most workers can be exposed without adverse effect averaged over a normal 8 h work day or a 40 h work week.

ACGIH (TLV-TWA)

American Conference of Governmental Industrial Hygienists emission limit expressed as Time-weighted-average (TLV-TWA) concentration for a normal 8-hour workday and a 40-hour workweek to which nearly all workers may be repeatedly exposed without adverse effects.

Conversion of mg/m^3 to ppm

Reported concentrations of VOCs are usually expressed on a volume basis, C_g^{ppmv} (concentration in parts per million volume), or on a mass basis, C_g^{ppmm} (mg/m^3). In order to compare the two, it is necessary to know the temperature of the air carrying the VOC. At 25^{0}C

$$C_g^{ppmm} = C_g^{ppmv} \times \frac{1}{24465} \times M \times 1000 = \left(\frac{M}{24.465}\right) C_g^{ppmv} \qquad -(1)$$

Where the M (1/gmole) is the molecular mass of the VOC. The Conversion factors for MCB:

1 ppm = 4.7 mg/m^3

1 mg/m^3 = 0.22 ppm

Appendix II

Table IIa. Concentration of Mono-Chlorobenzene with operating time

Time (h)	Gas flow rate (lpm)	Inlet MCB Concentration (g/m^3)	Outlet MCB Concentration (g/m^3)
12	0.5	0.133	0.13
36	0.5	0.599	0.518
60	0.5	0.939	0.791
84	0.5	1.368	1.113
108	0.5	1.473	1.232
132	0.5	0.832	0.66
156	0.5	0.682	0.524
180	0.5	0.621	0.474
204	0.5	1.676	1.202
228	0.5	1.612	1.12
252	0.5	1.47	0.977
276	0.5	1.333	0.878
300	0.5	1.112	0.527
324	0.5	0.4513	0.167
348	0.5	0.607	0.131
372	0.5	0.63	0.039
396	0.5	0.92	0.052
420	0.5	1.368	0.271
444	0.5	1.52	0.737
468	0.5	1.473	0.738
492	0.5	1.77	0.726
516	0.5	1.252	0.25
540	0.75	1.038	0.08
564	0.75	2.393	1.512
588	0.75	1.56	0.902
612	0.75	1.667	0.706
636	0.75	1.797	0.599
660	0.75	1.84	0.487
672	0.75	3.51	0.646
684	0.75	2.766	0.251
696	0.75	1.261	0.369
708	0.75	2.434	0.695
720	0.75	3.861	0.599
732	0.75	2.88	0.212
744	0.75	3.16	0.542
768	1.5	1.101	0.562
792	1.5	3.242	1.75
804	1.5	2.78	1.094

816	1.5	1.322	0.198
828	1.5	1.678	0.275
840	1.5	3.293	2.177
852	1	4.332	2.572
864	1	3.102	1.739
876	1	3.285	1.713
888	1	4.551	1.838
900	1	3.595	1.198
912	1	2.884	0.617
936	1	3.57	0.554
960	1	3.861	0.75
972	1	1.539	0.168
984	1	2.012	0.533
996	1	1.6	0.412
1008	1	1.687	0.362
1020	1	1.0678	0.125
1032	Starvation period with nutrient only		
1056			
1080			
1104	2	5.402	3.404
1116	2	7.187	3.626
1128	2	5.28	2.025
1140	2	1.304	0.241
1152	2	1.3	0.202
1176	2	3.16	0.68
1200	2.5	1.32	0.621
1224	2.5	2.45	0.84
1248	2.5	1.026	0.214
1272	2.5	1.47	0.19
1284	2.5	1.48	0.333
1296	2.5	1.301	0.188
1320	2.5	1.308	0.1761
1348	Starvation period with nutrient and air		
1372			
1396			
1420			
1444			
1468	1	1.182	0.252
1492	1	1.37	0.115
1516	1	0.324	0.027
1540	1	1.069	0.0513
1564	1	1.215	0.5467
1588	1	1.3536	0.2448
1612	1	1.0769	0.1748
1636	1	1.061	0.1917

1660	1	1.3314	0.1952
1684	1	1.1471	0.1632
1708	1	1.626	0.3035
1732	1	1.335	0.2931
1756	1	1.4181	0.4179
1780	1	1.433	0.296

Table IIb. Concentration of Mono-Chlorobenzene at different sampling ports

Gas low rate (lpm)	Inlet MCB Concentration (g/m^3)	Sampling port 1 (g/m^3)	Sampling port 2 (g/m^3)	Outlet MCB Concentration (g/m^3)
0.5	0.63	0.275	0.11	0.0389
0.5	0.92	0.365	-	.0517
1	1.4182	0.7902	0.6243	0.4179
1.5	1.84	0.958	0.56	0.487

Table IIc. Removal efficiency as a function of Temperature

Removal efficiency	Temperature (^0C)
80.19	12
92.2	22
92.64	26
95.2	30
89.04	32
83.7	35
79.34	37
78.04	38.5
70.53	40.2

Table IId. Removal efficiency as a function of pH

Removal efficiency	pH
81.91	6.5
85.24	6.71
86.77	7
94.35	7.4
93.81	7.4
95.2	7.6
92.63	7.7
79.34	8