

CHAPTER II

BACKGROUND AND LITERATURE REVIEW

2.1 Properties of Xylene

Xylene is one of the most concerned hazardous chemicals in the present day. It is a colorless and catches on fire easily. Xylene evaporates quickly from the soil and surface water into the air. It is used as a solvent and in many common products, such as paints, rubber, adhesives, plastic bottles, lacquers, varnishes, adhesives, cements, inks, dyes, cleaners, synthetic fibers, insecticides, pesticides, leather goods, and other chemicals. Xylene has chemical structure as dimethyl benzene with molecular weight of 106.16 and formula as $\text{CH}_3\text{C}_6\text{H}_4\text{CH}_3$. There are three forms of benzene derivatives including ortho, meta, and para isomers of dimethyl benzene. The o-, m- and p- isomers specify to which carbon atoms, the o- isomer has the IUPAC name of 1,2-dimethylbenzene. The m- isomer has the IUPAC name of 1,3-dimethylbenzene. And p- isomer has the IUPAC name of 1,4-dimethylbenzene (Wikipedia, 2007a ; ATSDR, 2005) (Figure 2-1, Table 2-1).

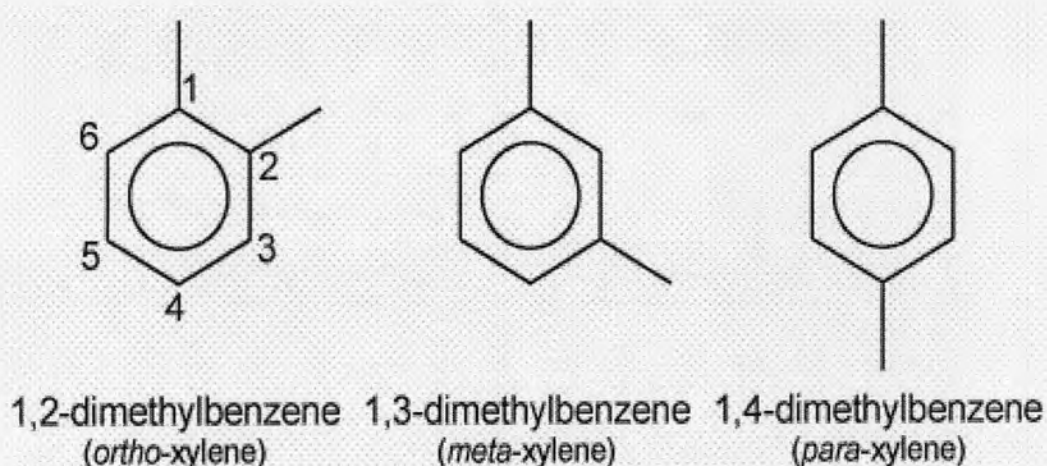


Figure 2-1 Xylene Isomers

Source: Wikipedia, 2007a

Table 2-1 Properties of Xylene

Isomers of Xylene			
General			
Common name	o-xylene	m-xylene	p-xylene
	1,2-	1,3-	1,4-
Systematic name	dimethylbenzene	dimethylbenzene	dimethylbenzene
	o-xylol;	m-xylol;	p-xylol;
Other names	Orthoxylene	metaxylene	Paraxylene
Molecular formula	C ₈ H ₁₀		
SMILES	Cc1c(C)cccc1	Cc1cc(C)ccc1	Cc1ccc(C)cc1
Molar mass	106.16 g/mol		
Appearance	Clear, colorless liquid		
CAS number	[95-47-6]	[108-38-3]	[106-42-3]
CAS number for mixture of xylenes [1330-20-7]			
Properties			
Density and phase	0.88 g/cm ³ , liquid	0.86g/cm ³ ,liquid	0.86 g/cm ³ , liquid
Solubility in water	practically insoluble		
Soluble in non-polar solvents such as aromatic hydrocarbons			
Melting point	-25 °C (248 K)	-48 °C (225 K)	13 °C (286 K)
Boiling point	144 °C (417 K)	139 °C (412 K)	138 °C (411 K)
Viscosity	.812 cP at 20 °C	.62 cP at 20 °C	.34 cP at 30 °C
Hazards			
MSDS	External MSDS	External MSDS	External MSDS
EU			
Classification	Harmful (Xn)		
Flash point	32 °C	27 °C	27 °C
R/S statement	R10, R20/21, R38: S2, S25		
RTECS number	ZE2450000	ZE2275000	ZE2625000
Supplementary data page			
Thermodynamic data	Phase behaviour Solid, liquid, gas		
Spectral data	UV, IR, NMR, MS		
Related compounds			
Related aromatic hydrocarbons	toluene, mesitylene, benzene, ethylbenzene		
Related compounds	xylenols - types of phenols		

Source: Wikipedia, 2007a

2.2 Source of Xylene

Mixed xylenes are distributed to air, rainwater, soils, surface water, sediments, drinking water, and aquatic organisms. They are released into the atmosphere as fugitive emissions from industrial sources, auto exhaust, and volatilization from their use as solvents. They have also been detected at low levels in indoor air; xylenes have been used in home such as fragrances and paints (EPA, 2006).

The worldwide markets for xylene in thousands of metric tons were used. The report provides separate comprehensive analytics for the US, Canada, Japan, Europe, Asia Pacific, Middle East, and Latin America. Annual forecasts are provided for each region for the period of 2000 through 2010. A ten-year historic analysis is also provided for these markets with annual market analytics. The report profiles 57 companies including many key and niche players worldwide such as Total Petrochemicals, BP Petrochemicals, China Petroleum and Chemical Corporation, Exxon Mobil Corporation, Formosa Chemical & Fiber Corp, Koch Industries, Inc., LG-Caltex Oil Corporation, Lonza, Mitsubishi Gas Chemical Co., Inc., Nippon Steel Chemical Co., Ltd, Reliance Industries Limited, Samsung General Chemicals, Shell Chemicals, and SK Corp. Market data and analytics are derived from primary and secondary research. Company profiles are mostly extracted from URL research and reported select online sources (Global Industry Analysts, 2006).

2.3 Health Effect of Xylene

2.3.1 Workplace and Emission Standards of Xylene

In Thailand, workplace concentration standard of xylene is 100 ppm or 435 mg/ m³ according to the regulations of Ministerial Notifications on Safety at Work ; Safety at Work in Connection with Environment (Chemical Substance) issued under the Labour Protection ACT B.E. 2541 (1998). Industrial emission standard of xylene is 200 ppm (Notification of the Ministry of Natural Resources and Environment B.E. 2549).

The OSHA PEL for xylene is 100 ppm (435 milligrams per cubic meter (mg/m³ of air) as an 8-hour time-weighted average (TWA) concentration and 150 ppm (655 mg/m³) as a 15-minute TWA short-term exposure limit (STEL). A STEL is the maximum 15-minute concentration to which workers may be exposed during any 15-minute period of the working day (29 CFR 1910.1000). The National Institute for Occupational Safety and Health (NIOSH) recommended exposure limits (RELs) for xylene are 100 ppm (435 mg/m³) as a TWA for up to a 10-hour workshift and a 40-hour workweek and 200 ppm (868 mg/m³) for 10 minutes as a short-term limit. The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned xylene a threshold limit value (TLV) of 100 ppm (435 mg/m³) as a TWA for a normal 8-hour workday and a 40-hour workweek and a short-term exposure limit (STEL) of 150 ppm (655 mg/m³) for periods not to exceed 15 minutes. The OSHA and ACGIH limits are based on the risk of irritant, narcotic, and chronic effects associated with exposure to xylene, and the NIOSH limit is based on xylene's potential to cause central nervous system depression and respiratory irritation (OSHA, 2000).

2.3.2 Exposure Routes

Three major exposure routes of xylene are oral exposure, respiratory exposure and dermal exposure, dermal exposure also including eyes (OSHA, 2000).

2.3.3 Signs and Symptoms

2.3.3.1 Acute Exposure

The signs and symptoms of acute exposure to xylene are included headache, fatigue, irritability, lassitude, nausea, anorexia, flatulence, irritation of the eyes, nose, and throat, and motor incoordination and impairment of equilibrium. Effect to central nervous system (CNS) is at 100 ppm. Irritation of the nose and throat can occur at approximately 200 ppm after 3 to 5 minutes. Exposures

estimated at 700 ppm have caused nausea and vomiting. Extremely high concentrations could cause incoordination, loss of consciousness, respiratory failure and death. Eye irritation has been reported at vapor levels as low as 200 ppm. Flushing, redness of the face, a sensation of increased body heat, increased salivation, tremors, dizziness, confusion, and cardiac irritability have also been reported (CCOHS, 1998; OSHA, 2000).

2.3.3.2 Chronic Exposure

The signs and symptoms of chronic exposure to xylene may include conjunctivitis; dryness of the nose, throat, and skin; dermatitis; and kidney and liver damage. (OSHA, 2000) The xylene-exposed and unexposed groups were given health examinations, which evaluated haematology, serum biochemistry, and subjective symptoms. Results of analysis of the diffusive samplers showed that workers were exposed to a geometric mean of 14.2 ± 2.6 ppm xylene (arithmetic mean of 21.3 ± 21.6 ppm). This was broken down into geometric means of 1.2 ppm o-xylene, 7.3 ppm m-xylene, 3.8 ppm p-xylene, 3.4 ppm ethyl benzene, and 1.2 ppm toluene. N-Hexane was rarely present and no benzene was detected. Analysis of data from the health examinations found no statistically significant difference ($p < 0.10$) between haematology and serum biochemistry values for xylene-exposed and unexposed populations. The frequency of five symptoms experienced during work was significantly ($p < 0.01$) elevated in either xylene-exposed men or women including: dimmed vision, unusual taste, dizziness, heavy feeling in the head, and headache. The frequency of four symptoms experienced during work were significantly ($p < 0.01$) elevated in both men and women including irritation in the eyes, nasal irritation, sore throat, and floating sensation. Ten subjective symptoms occurring in the previous three months were significantly ($p < 0.01$) elevated in exposed men and women including nausea, nightmare, anxiety, forgetfulness, inability to concentrate, fainting after suddenly standing up, poor appetite, reduced grasping power, reduced muscle power in the extremities, and rough skin. Dose dependency appeared to exist for 3 subjective symptoms noted during work: irritation

in the eyes, sore throat, floating sensation, and for one symptom occurring in the last three months, poor appetite (Air Toxics NEPM, 2003).

2.3.4 Carcinogenicity

There is no direct evidence of carcinogenicity in humans although this has not been studied epidemiologically. Certainly there is no evidence of carcinogenicity in test animals, or genotoxicity in vitro studies (Beasley, 1992).

2.3.5 Mutagenicity

Five healthy adult men were exposed to 40 ppm xylene. Three different cytogenetic end-points were evaluated using peripheral blood lymphocytes: number of sister chromatid exchanges (SCEs), cell cycle delay, and cell mortality. Similarly, exposure of human blood lymphocytes in vitro to either toluene (0–2.5 mM) or xylene (0–2 mM) or their mixture for 72 h did not result in any significant cytogenetic effects at lower concentrations, while at higher concentrations, only cell mortality was found to be significantly affected (Richer *et al.*, 1993).

2.3.6 Biological Monitoring of Xylene Exposure

The correlation between low level time-weighted average (TWA) atmospheric xylene exposure (ppm.) and urinary methylhippuric acid (MHA) expressed per gram of creatinine was examined. Subjects were recruited from workplaces that utilized xylene. Ambient monitoring of *o*-, *m*- and *p*-xylene isomers was carried out using passive diffusion vapor monitors. Adjusted (post-shift minus pre-shift) and post-shift urinary levels of xylene metabolites (2-, 3- and 4-MHA) were determined by GC–MS. Twenty subjects were recruited into the study. Total xylene TWA exposures were 3.36 ± 3.63 p.p.m. (mean \pm SD) with a range of 0.03–14.44 p.p.m. The r^2 values for the regression equations between xylene exposure and individual and total adjusted MHA isomers were 0.390, 0.709, 0.677 and 0.631 for *o*-, *m*-, *p*- and total xylenes, respectively, which was greater than the respective

correlations between non-adjusted samples. In conclusion, biological monitoring of occupational xylene exposure at levels <15 ppm. using urinary MHA shows a good correlation with atmospheric levels and is a valid complement to ambient monitoring. Even though occupational xylene exposure in the workplaces studied was generally low, MHA was found in the pre-shift urine of all workers and the use of adjusted values shows modest improvements in correlations. Recent exposure prior to sampling, either from occupational or non-occupational sources, should be considered when biological monitoring of xylene is undertaken. Extrapolation of data from this study predicted a MHA concentration in post-shift urine of 1.3 g/g creatinine after exposure to a TWA of 100 ppm. xylene (Jacobson and McLean, 2003).

2.4 Biodegradation of Xylene

Biodegradation is the process by which organic substances are broken down by other living organisms. The term is often used in relation to ecology, waste management, environmental remediation and to plastic materials, due to their longlife span. Organic material can be degraded aerobically, with oxygen, or anaerobically, without oxygen. A term related to biodegradation is biomineralisation, in which organic matter is converted to into minerals (Wikipedia, 2007c).

BTEX compounds have aerobic pathway which includes degradation to a substituted catechol. Benzene is degraded to catechol. Toluene has many separate biodegradative pathways, some of which include 3-methylcatechol as an intermediate product. Many separate pathways also exist for ethylbenzene, which can be degraded to 3-ethylcatechol. The xylenes are all metabolized to mono-methylated catechols; e.g., m-xylene goes to 3-methylcatechol. In each of these four cases, the aromatic ring of the substituted catechol is later cleaved by a dioxygenase (Stephens, 2006). The biodegradation pathway of BTEX are shown in Figure 2-2 and 2-3 for aerobic and anaerobic degradation respectively.

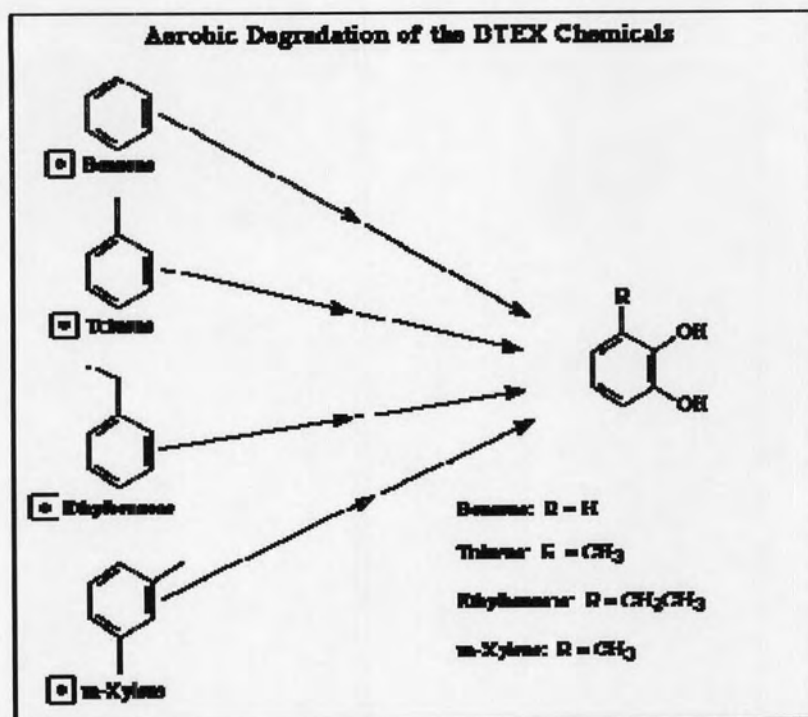


Figure 2-2 Aerobic Degradation of the BTEX Chemicals

Source: Stephens, 2006

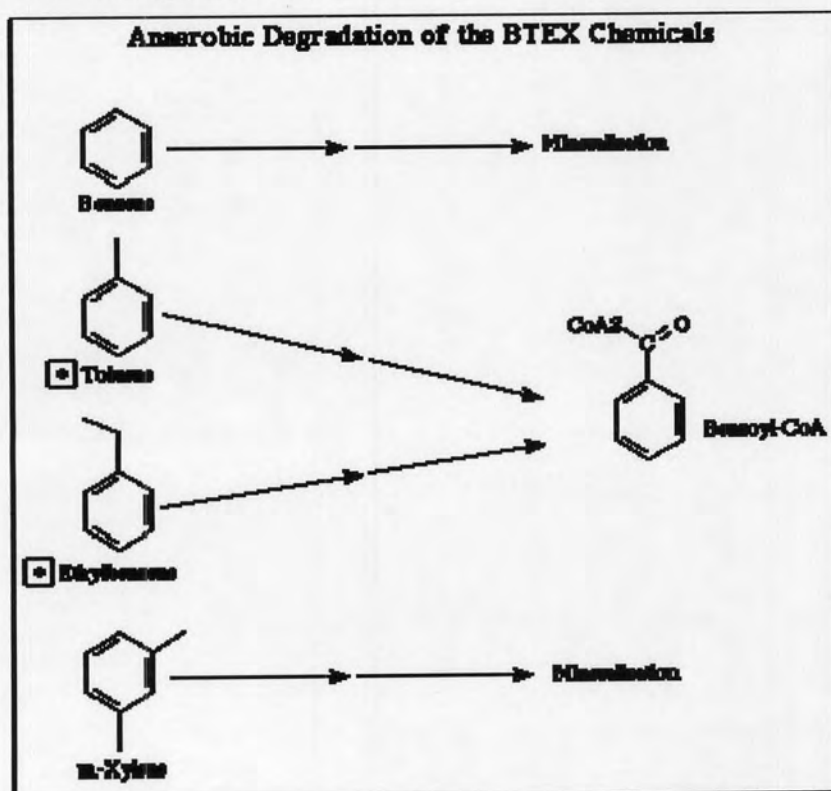


Figure 2-3 Anaerobic Degradation of the BTEX Chemicals

Source: Stephens, 2006

Anaerobic pathways of BTEX biodegradation are important because these compounds are frequently found under conditions where the use of oxygen quickly exceeds the supply (Stephens, 2006). Type of BTEX degrading microorganism, *Dechloromonas* strain RCB has been shown to be capable of both aerobic and anaerobic degradation for benzene. It also can degrade toluene and ethylbenzene with completely process but xylene was not degraded completely (Chakraborty *et al.*, 2005). Many strains of bacteria in mixed culture, *Pseudomonas stutzeri*, *Vibrio mimicus*, *Pseudomonas putida* and *Pseudomonas fluorescens* present as a coculture were studied for their abilities to degrade BTEX compounds (benzene, toluene, ethyl benzene, and o, m, p-xylenes) various growth conditions. The coculture effectively degraded various concentrations of BTEX as sole carbon sources (Babaarslan *et al.*, 2003; Shim *et al.*, 2005).

Xylene and benzene are harder to degrade than toluene and ethylbenzene in biofilter. In the toluene-acclimatized biofilter was also able to degrade all of the other BTEX compounds, even in the absence of toluene. The catalytic efficiency of the reactor for compounds other than toluene was in the order: ethylbenzene > benzene > o-xylene > m-xylene > p-xylene (Plesis *et al.*, 2001). The degradation of BTEX compounds in biofilter was evaluated, percentage removal efficiencies for toluene, ethylbenzene, p-xylene, o-xylene and benzene were 99, 85, 82, 80 and 78, respectively (Mallakin and Ward, 1996). The best performing biofilter, in which bacteria were dominant, showed an elimination capacity of $70 \text{ g TEX m}^{-3} \text{ h}^{-1}$ with a near complete removal of the mixture up to an influent concentration of $1200 \text{ mg TEX m}^{-3}$ at a gas residence time of 57 s. Most of the ingoing carbon was recovered as carbon dioxide in the outgoing gas. In the other biofilters fungi dominated and performance was slightly worse. With single substrates, the elimination capacity was higher for toluene and ethylbenzene than for the TEX mixture, whereas o-xylene removal was slowest in all cases. Also when feeding the mixture to the biofilters, o-xylene was removed most slowly (Kennes *et al.*, 1996). The following are text-format o-,m- and p- pathway map. Organisms that can initiate the pathway are given, but other organisms may also carry out later steps. Follow the links for more information on compounds or reactions.

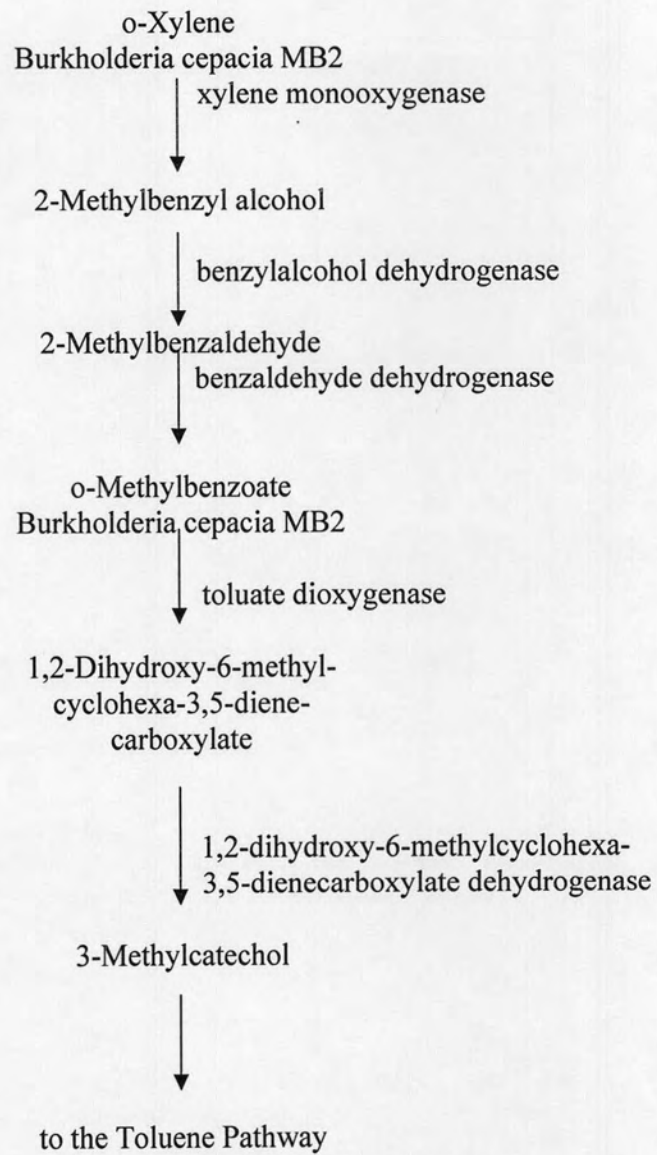


Figure 2-4 o-Xylene Pathway Map
Source : Oh, 2006

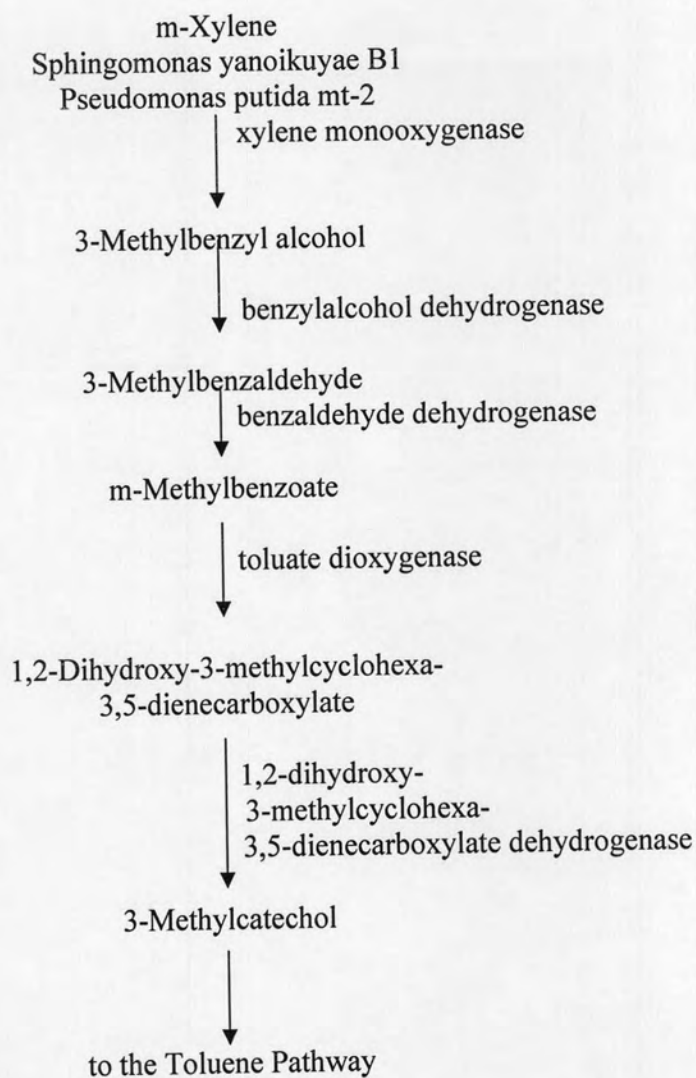
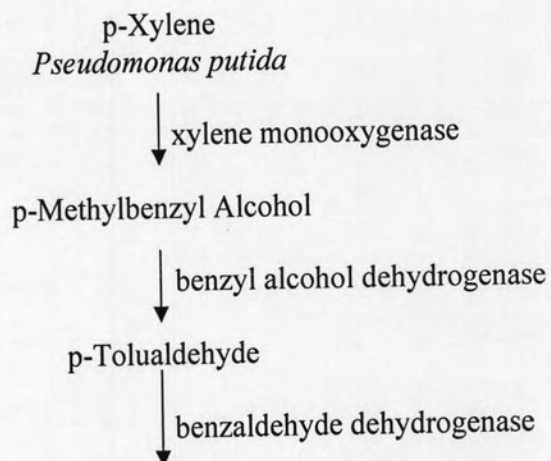


Figure 2-5 m-Xylene Pathway Map
 Source: Hyatt and Oh, 2006



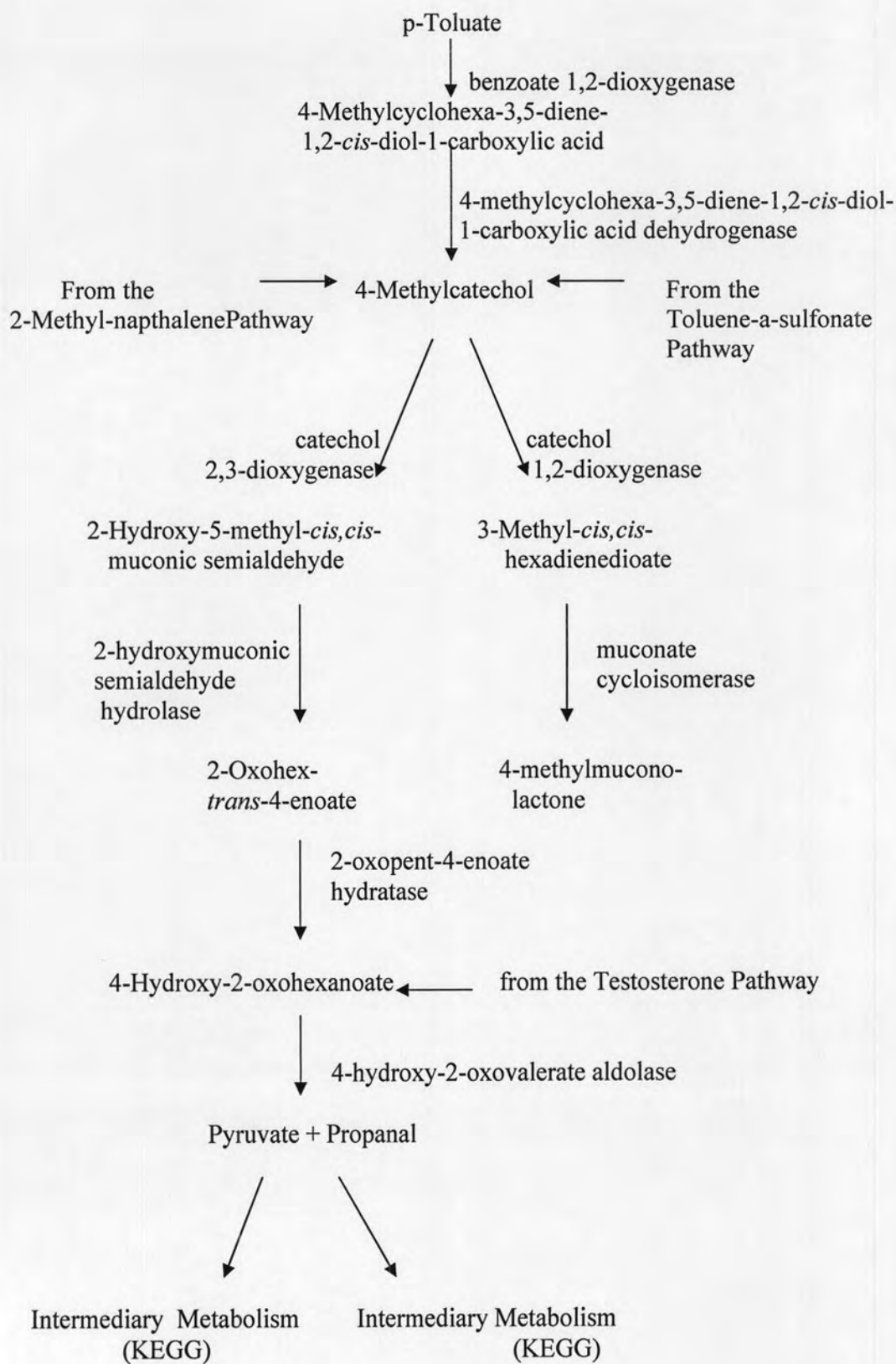


Figure 2-6 p-Xylene Pathway Map
Source: Jeon and Stephens, 2006

2.5 Overview of Biofiltration

Biofilters are air phase bioreactors considered to be one of the most promising technologies for treating waste gases contaminated by VOCs. It is currently the most used biological gas treatment technology. Biofiltration is based on the ability of microorganisms to degrade variety of compounds. Pollutants are oxidised or converted into biomass by the action of microorganisms on the packing material (Malhautier *et al.*, 2005). The carrier provides to the microorganisms a favorable environment in terms of pH, temperature, moisture, nutrients and oxygen supply (Sene *et al.*, 2002; Ramírez-López *et al.*, 2003). The biofiltration is a one promising new technology for removing both NO_x and VOCs from off-gas streams is biofiltration, a simple process whereby contaminated air is passed through a biologically active packed bed (Woertz *et al.*, 2001). The diagram for a biofilter system and inner mechanisms overall system design, porous media reaction zone and a conceptual model of the surface of the biofilm is shown in Figure 2-7.

Compared with other air pollution control technologies, biofiltration is considered economical, cleaner and greener because of low operating costs, low pressure drops, and absence of residuals. Even most of advantage but biofiltration also has some disadvantages such as relatively high area requirements and moderate to high capital costs. In addition, biofiltration can only be applied to deodorize concentrations of relatively soluble and biodegradable compounds (Ergas and Gonzales, 2004).

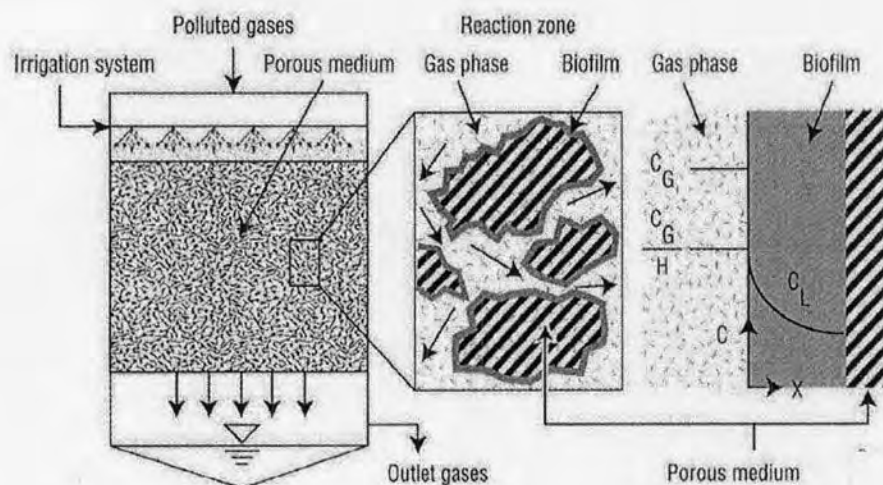


Figure 2-7 Process Diagram for a Biofilter System

Source: Ergas and Gonzales, 2004

Since 1923 the first biological method was used to treat odorous compounds in control of the emissions of H_2S from a wastewater treatment plant. From 1955 to 1960's biological methods were applied to treat odorous emissions in low concentrations in Germany and US. In 1970s, interest on biofilter increased and it was capable of handling larger loads of odors and volatile organic compounds. Biofiltration was a high success in Germany in 1970s. During 1980s and 1990s, biofiltration were used in Europe (especially in Germany and the Netherlands) and in North America (Devinny *et al.*, 1999; Bellis 2007). Since 1990's until the present, there have been more than 500 biofilters operating both in Germany and the Netherlands and it is widely spreading in US. Applications for odor control since 1950 ranged from soil filters to large biological trickling filter plants (Anit and Artuz, n.d.).

The application of biofiltration was widely used in many industries (Table2-2) and used to treat many pollutants (Table 2-3) especially VOCs with low concentrations. Since 1923 the first biological methods was used to treat odorous compounds.

Table 2-2 Industries using Biofiltration.

Types of industries	Types of industries
Chemical operations	Coffee roasting
Composting facilities	Chemical storage
Coca roasting	Landfill gas extraction
Film coating	Fish frying
Slaughter houses	Investment foundries
Flavors and fragrances	Tobacco processing
Paint shops	Pet food manufacturing
Waste oil recycling	Industries and municipal wastewater treatment plants

Source: Leson, 1991; Friedrick *et al.*, 2003 *cited in* Park, 2004

Table 2-3 List of Chemicals Treatable by Biofiltration

Chemicals	Chemicals	Chemicals
Acetate	Dimethyl sulfide	Methyl mercaptan
Acetone	Ethanol	Nitrogen oxide
Ammonia	Ethylbenzene	Nitrogen dioxide
Benzene	2-Ethyl hexanol	Pentane
Butanol	Hexane	Scatole
Butylaldehyde	Hydrogen sulfide	Styrene
Butyl Acetate	Indole	Tetrachloroethane
Carbon monoxide	Iso-propanol	Thiophene
Mono-, Di-, Tri-chloromethane	Methane	Toluene
Diethyl amine	Methanol	Trichloroethane
Dimethyl disulfide	Methyl-ethyl-ketone	Xylene

Source: Park, 2004

2.6 Basic Types of Waste Gas Treatment

Air emissions control involves the reduction of emissions through raw products substitution, reduction, or recycling. The reduction mechanisms are reduce the quality of the products or increase costs (Devinny *et al.*,1999). The biological techniques for gases treatment are developed based on the absorption of volatile contaminants in an aqueous phase or biofilm followed by oxidation by the action of microorganisms (Van Groenestijn and Hesselink, 1993).

The biofilter, bioscrubber and biotrickling filter are used for elimination of contaminants such as odors, ethanol, formaldehyde, methanol, ethyl, amines, and phenol from air and water. Each technology operates under different conditions as summarized briefly in Table 2-4 and the advantage and disadvantage of waste gas treatment are shown in Table 2-5.

Table 2-4 The Technical Characteristics of Bioscrubbers, Biotrickling Filters and Biofilters

Bioprocess	Microorganisms	Liquid phase	Depollution Step
Bioscrubber	Suspended in bioreactor, in aqueous growth medium	Mobile Continuously dispersed Recycled	VOC/ air separation within the absorption column VOC oxidation in the aerated bioreactor
Biotrickling filter	Immobilized on the filtering material	Mobile Continuous tricking over the filter bed Possible recycling	In the filter bed In the biofilm
Biofilter	Immoobilized on the filtering material	Occasional bed irrigation with nutrient solutions	In the filter bed In the biofilm

Source: Delhomenie and Heitz, 2005 *cited in* Park, 2004

Table 2-5 Comparison of Waste Gas Control Technologies

Control Technology	Advantage	Disadvantage
Biofiltration	Low operating and capital costs, Effective removal for compounds, Low pressure drop, No future waste streams produced.	Large require foot print requirement, Medium deterioration will occur, Less suitable for high concentrations, moisture and pH difficult to control, Particulate matter may clog medium.
Biotrickling filter	Medium operating and capital costs, Effective removal for compounds, Treats acid-producing contaminants, Low pressure drop.	Clogging by biomass, More complex to construct and operate, Future waste streams produced.
Wet scrubbing	Low capital costs, Effective removal of odors, No medium disposal required, Can operate with a moist gas stream, Can handle high flow rates, Ability to handle variable loads.	High operating costs, Need for complex chemical feed systems, Does not remove all VOCs, Water softening often required, Nozzle maintenance often required
Carbon adsorption	Short retention time / small unit, Effective removal for compounds, Suitable for low / moderate loads, Consistent, reliable operation.	High operating costs, Moderate capital costs, Carbon life reduced by moist gas stream, creates secondary waste streams.
Incineration	System is simple, Effective removal for compounds, Suitable for very high loads, Performance is uniform and reliable, Small area required.	High operating costs and capital costs, High flow / low concentrations not cost effective, Creates a secondary waste stream, Scrutinized by public.

Source : Webster, 1996 *cited in* Devinnny *et al.*, 1999: 12

2.6.1 Bioscrubber

Bioscrubber technology consists of an activated carbon filter that supports microbial growth. The bioscrubber is used in a treatment train to convert dilute organic contaminants from other soil, water, and air decontamination processes into carbon dioxide, water, and other nonhazardous compounds. The process removes biomass, supplies nutrients, and adds moisture to enhance bioactivity. In addition to efficient degradation, the bioscrubber provides an effective sink to minimize feed fluctuations. The biodegradation keeps the carbon at maximum adsorption capacity, eliminating the need for regeneration and reducing the required bed length and associated cost (EPA, n.d.). Bioscrubber used to remove n-butanol from the gas phase was examined with a mixed culture. The extent of the cell concentration was limited by the supply of n-butanol, phosphate or potassium, and the growth rate was determined by the dilution rate. With n-butanol as the limiting substrate the cellular yield was 0.53 g dry cell weight/g n-butanol. Phosphate limitation decreased this yield to 0.34 g and potassium limitation to 0.31 g dry cell weight/g n-butanol at a dilution rate of 0.1/h. Under these conditions n-butanol was eliminated from the gas phase by 84%-100% (Wübker and Friedrich, 1996).

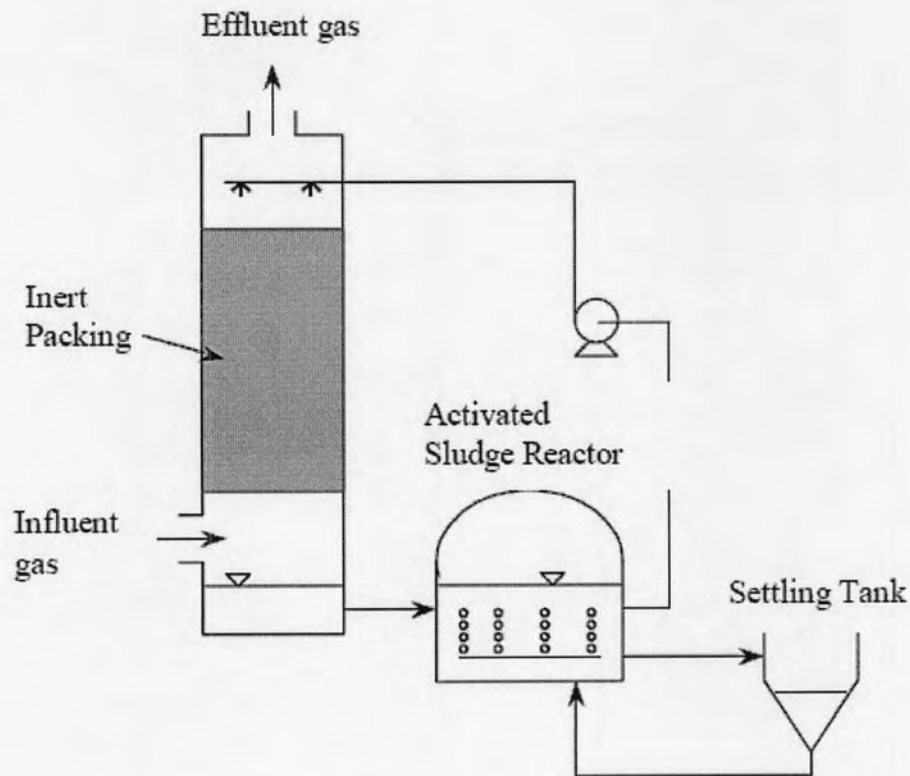


Figure 2-8 Schematic Diagram of a Bioscrubber.

Source: Van Groenestijn and Hesselink 1994 *cited in* Park, 2004

2.6.2 Biotrickling Filter

A biotrickling filter is working in a similar manner to a biofilter, except that an aqueous phase is continuously trickled over the packing, liquid nutrient medium continuously recirculating through the column and the filter bed is made of some synthetic or inert material, like plastic rings, open pore foam, or lava rock. The trickling solution contains essential inorganic nutrients such as nitrogen, phosphorous, and potassium, and is usually recycled (Jin *et al.*, 2007).

They are more recent designs, in which microorganisms form a biofilm on an inert carrier material that is kept moist by circulation of a liquid medium. These

bioreactors provide superior process control, which is an advantage especially for highly concentrated waste streams or waste streams containing acidifying pollutants, like sulfur, chlorine or nitrogen containing compounds (Sercu, *et al.*, 2005). The result from Sercu, *et al.*, 2005 was shown a biotrickling filter removing dimethyl sulfide. The maximal dimethyl sulfide elimination capacity at 90% removal efficiency of biotrickling filter₁ was $7.2 \text{ g m}^{-3} \text{ h}^{-1}$ after 30 days of operation. The elimination capacity decreased, however, when the inlet loading rate exceeded $15 \text{ g m}^{-3} \text{ h}^{-1}$ (200 ppmv inlet concentration). The performance of biotrickling filter₂ was much better, with an elimination capacity of $8.3 \text{ g m}^{-3} \text{ h}^{-1}$ (90% removal efficiency) after 2 days of operation, increasing to a maximum of $57 \text{ g m}^{-3} \text{ h}^{-1}$ at 92% removal efficiency.

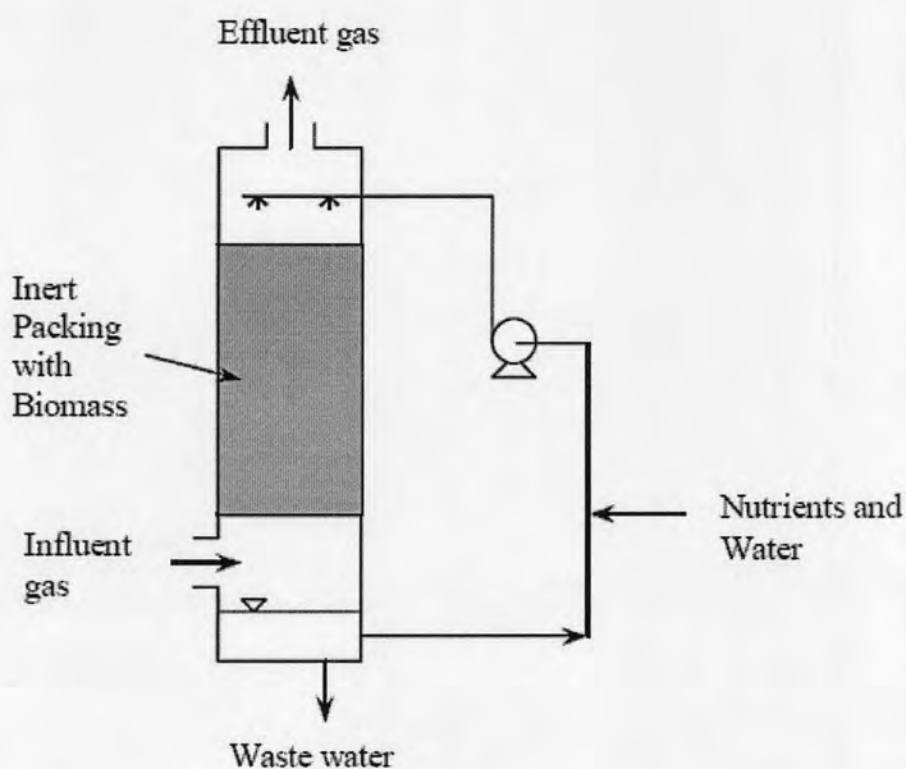


Figure 2-9 Schematic Diagram of a Biotrickling Filter

Source: Van Groenestijn and Hesselink, 1994. *cited in* Park, 2004

2.6.3 Biofilter

Biofiltration has proven to be an effective and economical control technique compared with the other air pollution control techniques such as adsorption, incineration, and absorption in reducing VOC and odiferous emissions. Biofilter is the oldest and simplest method of the three vapor phase bioreactors and involve passing a contaminated air stream through a reactor containing biologically-active packing material

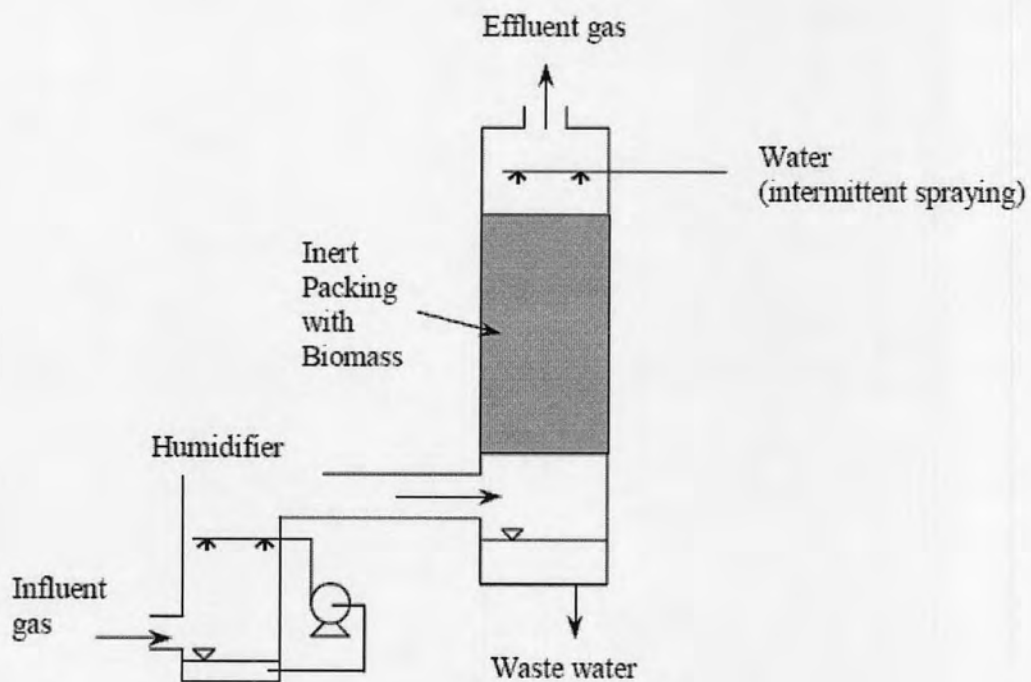


Figure 2-10 Schematic Diagram of a Biofilter

Source: Van Groenestijn and Hesselink, 1994 *cited in* Park, 2004

2.7 Internal Mechanisms in Biofilter

Biofilters are not filtration units as strictly defined. Instead, they are systems that use a combination of basic processes: absorption, adsorption, degradation, and desorption of gas phase contaminants.

The internal mechanisms in a biofilter (Figure 2-11), contaminated air (C_G) passes through the filter bed medium (compost, peat, soil, etc.) with oxygen (O_2) and absorbs into a microbial biofilm/liquid phase attached to their filter medium. Microbes convert the contaminant to carbon dioxide (CO_2) and water (Devinny *et al.*, 1999).

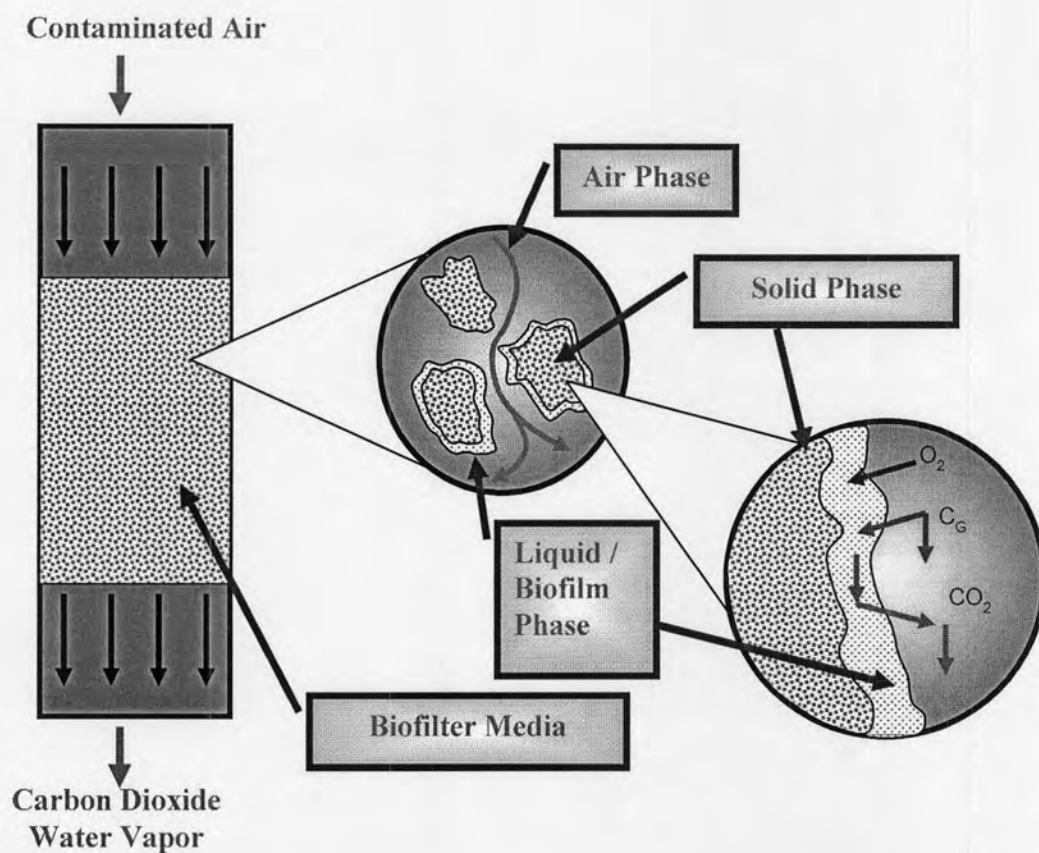


Figure 2-11 Internal Mechanisms of Biofilter

Source: Devinny *et al.*, 1999

2.8 Biofilter Terminology

2.8.1 Empty Bed Residence Time and True Residence Time

The term empty bed residence time (EBRT), empty bed contact time or empty bed detention time relates the flow rate to the size of the biofilter. It is defined as the empty bed filter volume divided by air flow rate (Devinny *et al.*, 1999).

$$\text{EBRT} = \frac{V}{Q}$$

2.8.2 Surface (or Volumetric) and Mass Loading Rate

Surface (or volumetric) and mass loading rate are terms used to define the amount of air or contaminant that is being treated. The mass loading rate is the mass of the contaminant entering the biofilter per unit area or volume of filter material per unit time, often expressed as grams per m² or m³ of filter material per hour (Devinny *et al.*, 1999).

$$\text{Mass Loading (surface)} = \frac{Q \times C_{\text{in}}}{A}$$

$$\text{Mass Loading (surface)} = \frac{Q \times C_{\text{in}}}{V}$$

Where C is Xylene concentration (g m⁻³), Q is the volumetric gas flow rate (m³ h⁻¹), A is the filter area (m²) and V is the volume (m³) of the packing bed considered; Subscripts “in” and “out” are referred to the inlet and outlet of the packing bed considered.

2.9 Operation and Biofiltration Performance

The operational and performance parameters of biofilters were including loading, elimination capacity, removal efficiency, and empty bed retention time. Mass loading rate was defined as the mass of pollutant introduced in a unit volume of

biofilter material per unit time. Empty bed retention time was the time the contaminant spends in the empty volume of column. Elimination capacity is defined as the fraction of the mass-loading rate biodegraded in the biofilter. It differs from removal efficiency, an operational parameter, which is a measure of the effectiveness of the biofilter in degrading a contaminant.

In biofilter for VOCs treatment, the removal efficiencies were influenced from many parameters such as types of filter, bed materials, inlet concentration and flow rate of pollutants. In compost bioreactor, with for inlet concentrations of ≥ 200 ppm of each of the BTEX compounds and a gas loading rate of $17.6 \text{ m}^3 \text{ m}^{-2} \text{ h}^{-1}$, the removal efficiencies of $\geq 90\%$ were achieved (Abumaizar *et al.*, 1998).

Compost biofilter for gasoline treatment at empty bed retention time (EBRT) of 10 min and influent total petroleum hydrocarbon (TPH) and BTEX concentrations of less than 7800 and $1600 \text{ m}^3 \text{ h}^{-1}$, respectively. The biofilter had an overall removal efficiency of 80% for TPH in gasoline vapor and 85% for BTEX in gasoline for an operating period of 4 months. Maximum elimination capacities observed in this research for TPH and BTEX were $40 \text{ g TPH/m}^3/\text{h}$ and $5.3 \text{ g BTEX/m}^3/\text{h}$, respectively. Biodegradation portions of TPH and BTEX were 60 and 64%, respectively. Benzene removal efficiency was the lowest among BTEX. Half of the input TPH were removed in the lower half of the biofilter. When the influent BTEX concentration was less than 720 mg BTEX/m^3 , approximately 80% of BTEX was removed in the lower half of the filter (Namkoong *et al.*, 2003).

Under steady state conditions, observed elimination capacities were 68, and $36 \text{ g m}^{-3} \text{ h}^{-1}$ at inlet concentration ranges of 70 – 550 and 10-400 ppmv for toluene and xylene, respectively. At EBRT value of 60 s and loading rates of 17-135 and 2-105 $\text{g m}^{-3} \text{ h}^{-1}$, maximum elimination capacities achieved were 120 and $100 \text{ g m}^{-3} \text{ h}^{-1}$ for toluene and xylene, respectively. Gas flux through the biofilters was around $72 \text{ m}^3 \text{ m}^{-2} \text{ h}^{-1}$ at which maximum pressure drops that were observed, were 700 and 2800 Pa/m.bed for xylene and toluene, respectively (Torkian and Dehghanzadeh, 2002).

Toluene was found to enhance the catalytic efficiency of the reactor for p-xylene, while catabolism of all the other compounds was inhibited competitively by the presence of toluene. The toluene-acclimatized biofilter was also able to degrade all of the other BTEX compounds, even in the absence of toluene. The catalytic efficiency of the reactor for compounds other than toluene was in the order: ethylbenzene > benzene > o-xylene > m-xylene > p-xylene (du Plessis *et al.*, 2001). The inlet concentration is the one of important parameter with constant xylene inlet concentration of 1.39 g/m^3 . The gas flow rate was varied between 0.4 and $1.1 \text{ m}^3 \text{ h}^{-1}$ corresponding to an EBRT varying between 150 and 56 s , corresponding to inlet loads between 34 and $95 \text{ g m}^{-3} \text{ h}^{-1}$, and the biofilter response to these variations was examined. The results obtained revealed that the removal efficiency of the biofilter regained its high values (above 96%) in less than 24 h following the change to low concentrations and gas flow rate (Elmrini *et al.*, 2004).

The removal of hydrophobic pollutants in biofilters is often limited by gas liquid mass transfer to the biotic aqueous phase where biodegradation occurs. For a hexane inlet load of around $140 \text{ g.m}^{-3}.\text{h}^{-1}$, elimination capacities (EC) of 60 and $100 \text{ g m}^{-3} \text{ h}^{-1}$ were respectively reached with the neutral and acid systems. Increasing the inlet hexane load showed that the maximum EC obtained in the acid biofilter ($150 \text{ g m}^{-3} \text{ h}^{-1}$) was twice greater than in the neutral filter. The biomass in the acid biofilter was 187 mg g^{-1} (dry perlite) without an important pressure drop. Two fungi were isolated from the acid biofilter and were identified as *Cladosporium* and *Fusarium* spp. Hexane EC of $40 \text{ g m}^{-3} \text{ h}^{-1}$ for *Cladosporium* sp. and $50 \text{ g m}^{-3} \text{ h}^{-1}$ for *Fusarium* sp. were obtained in short time experiments in small biofilters (0.230 L). A biomass content around 30 mg g^{-1} (dry perlite) showed the potential for hexane biofiltration of the strains (Arriaga and Revah, 2005a).

A laboratory-scale biofilter employing yard waste compost filter media was successful in reducing the methyl ethyl ketone (MEK) airborne concentrations to levels that consistently exceeded the regulatory performance standards mandated for surface coating air emissions control technologies. During Phase I, the biofilter reduced the influent airborne MEK concentration from 184 ppmv (parts per million –

volume basis) to zero, an operational performance that corresponded to a HAP removal rate of $1,084.2 \text{ g m}^{-3}\text{d}^{-1}$. Similarly, in Phase II, when the steady state influent airborne MEK concentration was increased to 608 ppmv, the biofilter maintained an average effluent MEK concentration of 26.1 ppmv, which reflected a HAP removal rate of $3,429.1 \text{ g m}^{-3}\text{d}^{-1}$ or a 95.7 % control efficiency (McFarland *et al.*, 2003).

2.9.1 Packing Material

The filter bed was an important part because it provides support for microbial growth. The list of characteristics that suitable filtering materials was presented. The following criteria are among the more important of the required specifications: a high specific surface area, which is favorable to microflora establishment and maintenance, and to gas/biofilm exchange; a high porosity to facilitate gas convection and to promote the homogeneous distribution of gases throughout the bed; a good water retention capacity to avoid bed desiccation; the presence and availability of intrinsic nutrients; the presence of a dense and diverse indigenous microflora. A good biofilter medium should support a large diverse microbial population; provide pH buffering capabilities; have the ability to retain microbes; be physically stable; have a low pressure drop; produce clear drainage water (leachate); drain freely, releasing excess moisture; have high bearing-strength (Easter *et al.*, 2005; Bohn, 1996; Delhomenie and Heitz, 2005).

The filter bed or packing material widely used in biofiltration are sugarcane bagasse, glass beads, activated carbon, polystyrene packaging, soil, broken brick, compost, wood mulch, pig manure, sawdust, peanut shells, rice husk, coconut shells, and maize stubble (Sene *et al.*, 2002; Christen *et al.*, 2002; Elias *et al.*, 2002; Ramírez-López *et al.*, 2003; Kim, 2003; Khammar *et al.*, 2004; Savage and Tyrrel, 2005). Peat was as filter bed to remove BTEX compounds in biofilter (Mallakin *et al.*, 1996). Peanut shells constitute a potential alternative to peat in biofiltration application, especially in regions where peat is not available at a low price and in large quantities. They have a regular particle size, a large specific surface area, a low

bulk density, a natural pH, a large number of microorganisms, sufficient for microbial growth (Ramírez-López *et al.*, 2003).

Compost filter bed are common use in many biofilter to treat VOCs such as Abumaizar *et al.*, 1998 used the compost as a mixture of yard waste and sewage sludge at room temperature with moisture content (62.3% on dry weight basis), specific gravity (1.9), and organic content (77.8%). Different amounts of granular activated carbon (GAC) are mixed with the compost in two of the three columns to evaluate the extent to which biofilter performance can be enhanced. Namkoong *et al.*, 2003 used compost as a biofilter media with moisture content of biofilter media was adjusted to 60–80% of the water holding capacity and was approximately 50% on a dry weight basis. Each biofilter reactor was packed with approximately 2.0 l of media with an estimated bulk density of 770 kg/m³.

Bishop and Govind, n.d. used compost and peat biofilters treating slightly soluble iso-pentane at high (360-960 ppmv) concentrations in humidified air were completed using the indigenous microorganisms and nutrients of each media to establish bioactivity. The compost biofilter exhibited substantially higher removal efficiencies at the 360 ppmv iso-pentane concentration than the peat biofilter.

Many agriculture wastes can be used as biofilter bed materials to inoculate with mixed or single culture. The agro waste, yellow-gram (*Cajanus cajan*) stalk also can be used as filter bed for toluene treatment. (Singh *et al.*, 2006) The filter bed in reactors for toluene were compared for determining the suitability of coconut fiber, digested sludge compost from a waste water treatment plant, peat and pine leaves as packing materials. A deep characterization of materials was carried out. Biological activity and packing capabilities related to toluene removal were determined throughout 240 days of operation under different conditions of nutrients addition and watering regime (Maestre *et al.*, 2006).

Peat as a good packing materials were used to treat VOCs such as n-propanol and a mixture of methyl and ethyl alcohols and iso-pentane at high

concentration (Kiared *et al.*, 1997; Bishop and Govind, n.d.) and also were used in biofiltration to remove toluene with toluene inlet load was maintained at constant value throughout the trial. To improve toluene biofiltration, changes in the inoculation of the filter bed have been diversified (Wu *et al.*, 1999). A high mineralized peat extracted from the *Torreblanca* with a diameter less than 3 mm was selected as a filter bed materials to remove ethylbenzene vapours (Álvarez-Hornos *et al.*, 2007). The preparing of filter bed or packing materials in biofiltration, poly(vinyl alcohol)/peat composite bead was prepared as a filter materials. The optimal preparation condition was investigated with the peat size of 16–35 mesh, the ratio of water to peat of 40g water/10 peat and the immersion time in the phosphate solution of 30min. The composite bead prepared by this process is a porous spherical particle with a density of 0.692 g/cm³. The phosphorus and nitrogen nutrient were 2.91mg P/g dry solid and 3.25 mg N/g dry solid, respectively. The diameter of composite bead was between 2.4 and 6.0mm and the average diameter was about 4.0 mm (Chan and Lu, 2005).

The filter bed can made from wood bark (Andreoni *et al.*, 1996) or a mixture of wood chips/municipal compost (80: 20 vol. %) initially acclimated by addition of enriched nutrient and pollutant solution. During the start up of the system at mesophilic conditions, loading rates were gradually increased to evaluate system behavior and determine optimum ranges for different operational variables including moisture content, loading rates, residence time, and inlet concentrations (Torkian and Dehghanzadeh, 2002). Several biofilters and biotrickling filters were used for the treatment of a mixture of formaldehyde and methanol with three different inert filter bed materials (lava rock, perlite, activated carbon) suggested that the packing material had only little influence on the performance (Prado *et al.*, 2004).

The synthetic material also currently used for example, pelletized media was chosen as filter material for their high porosity enough to hold in biofilter for toluene (Kim and Sorial, 2006). The cubed polyurethane foam media was packed to remove pollutants, four-component mixture of *n*-butyl acetate, methyl ethyl ketone, methyl propyl ketone, and toluene at target influent concentrations of 124, 50.5, 174, and 44.6 mg/m³, respectively was operated with an empty bed residence time of 15 s

(Moe and Qi, 2004). A novel trickling fibrous-bed bioreactor was developed for biofiltration to remove pollutants present in contaminated air. Air containing benzene as the sole carbon source was effectively treated with a coculture of *Pseudomonas putida* and *Pseudomonas fluorescens* immobilized in the trickling biofilter, which was wetted with a liquid medium containing only inorganic mineral salts (Zhou *et al.*, 1998). Biofilter containing randomly packed 6-mm R-635 Celite pellets as biological attachment media. The main focus of the study was to expand biofiltration technology to treat high volatile organic compounds (VOC) concentrations while maintaining consistently high removal efficiencies (Sorial *et al.*, 1997 b).

2.9.2 Nutrient

Nutrients are necessary to maintain biofiltration system especially in long term biofilter. Carbon, nitrogen and phosphorus are three important nutrients for microbial growth and metabolism. Carbon can be provided by the VOCs in the air stream, but nitrogen and phosphorus must both be provided by the filter material. Nitrogen can make up approximately 15% of microbial cell dry weight and thus is a major constituent of microorganism proteins and nucleic acids (Carlson and Leiser, 1966 *cite in* Chan and Lin, 2006).

For peat-based biofilter to remove toluene in eighty days, the effects of different inocula and nutrient supplies on the biofiltration efficiency. Four pure microbial strains, *Arthrobacter paraffineus*, were used for the inoculation of the biofilter matrix. To improve toluene biofiltration, changes in the inoculation of the filter bed, supply of nutrients by various aqueous solutions to humidify the filter packing material have been diversified. To evaluate the influence of nutrient supplies, the operating parameter measurements have been monitored on an 80 day cycle. Parameters observed included the filter bed temperature, pressure drop and the toluene concentrations at both the entry and exit of the biofilter, the pH and physiological activities resulting from the various operational conditions (Wu *et al.*, 1999).

Biofiltration using simple packing material was tested for the removal of butanal. Excellent results were obtained when the filters operated at optimal humidity and were supplemented with inorganic nutrients. Without nutrients, butyric acid was detected in the effluent gas, which may explain the lower efficiency of filters without nutrients. Under optimal conditions an elimination of around $90 \text{ g}\cdot\text{m}^{-3}\cdot\text{h}^{-1}$ was reached (Weckhuysen *et al.*, 1992). Biofiltration of a gaseous stream contaminated with benzene, toluene, ethylbenzene, and the three xylene (BTEX) compounds was evaluated. Removal rate constants, and nutrient-phosphorous (nutrient-P) were a limitation as a biomass control (Sorial *et al.*, 1997b).

The nutrient supply is one of an important operational parameters. The experimental results have revealed that greater styrene elimination rates (up to $141 \text{ g}\cdot\text{m}^{-3}\cdot\text{h}^{-1}$) are achieved in the biofilter supplied with ammonia as the major nitrogen source in comparison to the lesser elimination performance (up to $50 \text{ g}\cdot\text{m}^{-3}\cdot\text{h}^{-1}$) obtained with the nitrate provided biofilter. However, in achieving the high styrene removal rates in the ammonia supplied biofilter, the excess of biomass accumulates on the filtering pellets and causes progressive clogging of the filter media (Jorio *et al.*, 2000)

The effect of nutrient limitation was also evaluated in biofilter to treat methyl isoamyl ketone. A gradual decrease of removal capacity was observed under the nutrient-limited environment. When nutrient was provided to the biofilter, the removal capacity increased from 55 to 93% in 3 days. A nutrient ratio of chemical oxygen demand (COD):N:P = 200:4:1 was sufficient for the removal of volatile organic compounds from the polluted air stream (Son *et al.*, 2005).

A process to prepare a synthetic filter material containing nutrients for biofiltration, an optimal process to prepare a synthetic filter material (poly(vinyl alcohol) (PVA)/peat/ KNO_3 composite bead) containing nutrient was developed for biofiltration. The optimal preparation condition for each of the peat and PVA aqueous solutions mixed with 6.4 g KNO_3 , and the minimum nitrogen content in the boric and phosphate aqueous solutions was 3.94 and 1.52 g N/l, respectively. The equilibrium

amount of water-soluble nitrogen dissolved out of the prepared composite bead was between 7.95 and 8.21 mg N/g dry solid, and it could be increased to 20.59 and 20.85 mg N/g dry solid when the composite bead was immersed in 0.896 M KNO₃ aqueous solution (Chan and Lin, 2006). Nutrient addition is necessary to achieve and maintain high levels of α -pinene removal; a biofilter composed of an 80/20 wood chips/compost mixture has insufficient nutrients to sustain microorganisms capable of α -pinene degradation (Dirk-Faitakis and Allen, 2000).

2.9.3 pH

Biofilter pH where the microorganisms are the most efficient is around 7. Thus the pH of the contaminated gas should be maintained at or near neutral to facilitate maximum microbial activity required for maximum odor and air emissions controls. Hydrogen sulfide-degrading compounds can survive at pH levels as low as 2, while biological degradation of other compounds commonly requires a near neutral pH. Therefore, for air emissions removal, monitoring must be conducted to ensure the pH stays in the range of about 6–7.5 (Easter *et al.*, 2005).

The pH was effected on VOCs removal in biofilter indicated that most bacteria in a trickle-bed air biofilter preferred a weak basic environment. In the pH range of 7.5–8, the removal efficiencies of each compound were greater than 80% (Lu *et al.*, 2002). Biodegradation and growth were possible in biofilter treating alkylbenzene vapors, over the pH range of 3.5-7.0 at appreciable rates, both with mixed cultures and with pure bacterial cultures (Veiga *et al.*, 1999).

2.9.4 Moisture Content

The water content of the biofilter bed is one of the most important parameters of biofiltration process. Media that is too dry will not support a diverse and robust microbial community. Media that is too wet can become too dense, resulting in compaction reduced porosity and high back-pressures. Perhaps most important of all is to provide a stable, moist environment (Easter *et al.*, 2005).

The equilibrium moisture content of the bead from adsorption and holding experiments are 50.5 and 66.8% on a wet basis, respectively (Chan and Lu, 2005). Compost biofilter for the removal of toluene and xylene were filled with a mixture of wood chips/municipal compost (80: 20 vol. %) initially acclimated by addition of enriched nutrient and pollutant solution. By remixing of the medium and a combination of lower organic loading and optimum moisture content was in range of 60-70% (Torkian and Dehghanzadeh, 2002).

In compost and perlite (8:2) biofilter for degradation of toluene and xylene, the optimum moisture content of about 70 % was found to be optimal for effective process and plays an important role in reaching high values of removal efficiency (Klapková *et al.*, 2006). Moisture content in biofilter for toluene was various among 30-70% (Sun *et al.*, 2002).

Effects of moisture on the performance of a trickle-bed air biofilter treating benzene, toluene, ethylbenzene and *o*-xylene (BTEX) waste gas were investigated to establish the optimum operating conditions and design criteria. The relative humidity of the first section was equal to 98% and significantly decreased to 71% in the last section. The higher moisture and nutrient contents were present at a higher nutrient feeding rate, which caused an increase in biomass growth and sloughing rates and thus led to an increase in the pressure drop and suspended solid of leachate (Lu *et al.*, 2002). The moisture content vary to type of filter bed , for the peat biofilter, the moisture content was maintained in an average value of 74% by weight and for the soil amendment biofilter, the moisture content was maintained in an average value of 35% by weight (Álvarez-Hornos *et al.*, 2007).

Toluene biofiltration by the fungus *Scedosporium apiospermum* TB1, the initial moisture content of the support of toluene was 70%. Stable operation was maintained for 20 days with a moisture. Under these conditions the average moisture content was 60% and 41 mg biomass/g dry support was produced (Garcia-Pena *et al.*, 2001).

The effect of moisture content of filter packing materials in elimination capacity was investigated in novel batch recycle reactor. Degradation data obtained from bioreactor indicated unique elimination capacity profiles along the wetting and drying curves. Moisture content changes in biofilter media caused elimination capacity changes in the system (Ranasinghe and Gostomski, 2003). The effects of the relative humidity (RH) in fungal biofilter appears to be an effective treatment process for the removal of α -pinene at optimal conditions with relative humidity of the inlet waste gas stream around 85%, and nitrate as nitrogen source (Jin *et al.*, 2006). A gas-phase biofilter inoculated with the fungus *Fusarium solani*, isolated from a consortium grown on hexane vapors, was used to degrade this compound. The biofilter, packed with perlite and operated with an empty bed residence time of 60 s, was supplied with hexane concentrations between 0.5 g m^{-3} and 11 g m^{-3} . Biofilter performance was evaluated over 100 days of operation (Arriaga and Revah, 2005b). The moisture content of the bed and humidity of the inlet waste gas stream are important parameters in biofilter performance. Even after the humidity was restored to the entering waste gas, the biofilters continued to be dry and extra direct water addition to the bed was required before removal efficiencies returned to their previous levels (Dirk-Faitakis and Allen, 2000).

2.9.5 Temperature

Operation of a biofilter or biotower depends on gas and media temperatures. Microorganisms operate efficiently at temperatures ranging from about 15 to 30 °C (Easter *et al.*, 2005). In biofilter with temperature changing can dominate different dominant species microorganisms. For example in the mesophilic reactor fungi became dominant after long-term operation, while bacteria dominated in the thermophilic unit. Microbial acclimation was achieved by exposing the biofilters to initial BTEX loads of 2 to $15 \text{ g m}^{-3} \text{ h}^{-1}$, at an empty bed residence time of 96 s. After adaptation, the elimination capacities ranged from 3 to $188 \text{ g m}^{-3} \text{ h}^{-1}$, depending on the inlet load, for the mesophilic biofilter with removal efficiencies reaching 96% (Mohammad *et al.*, 2007). Similar as the biofilter for toluene the degradation rate was decrease in lower temperature. The degradation of toluene in biofilter during the

thermophilic phase (45 to 55 °C), toluene biodegradation rates reached 110 g toluene.m⁻³.h⁻¹ at an inlet concentration of about 5 g.m⁻³.h⁻¹ and a gas residence time of 90 seconds. Biodegradation rates decreased rapidly (50% in 48h) in the cooling stage (Matteau *et al.*, 2004) at some conditions with lower temperature. But with optimum condition, the degradation process still continue with high removal efficiency. For biofiltration of gasoline vapor by compost media at 20 °C incubator to maintain isothermal condition, the average removal efficiencies of total petroleum hydrocarbon and BTEX were 80 and 85%, respectively. The experiment was preformed during 4 months of stable operation (Namkoong *et al.*, 2003).

In biofiltration of ethylbenzene vapours maintain bed temperature indifferent condition. For moderate inlet loads up to 40 g m⁻³ h⁻¹ corresponding to the first two weeks of operation, the mean temperatures stayed at approximately 24.7 °C (maximum value of 25.5 °C) and 23.3 °C (maximum value of 24.7 °C) for the fibrous peat and the soil amendment materials, respectively. Besides, temperature values of the first two or three days of operation suggested that microbial activity was right developed since the beginning of operation (Álvarez-Hornos *et al.*, 2007).

Effects of temperature change in the range of 15–50°C on the performance of a trickle-bed biofilter for treating benzene, toluene, ethylbenzene and o-xylene (BTEX) vapors in air streams were investigated. In the steady-state condition, the BTEX removal efficiency increased as the operating temperature increased in the range of 15–30°C. However, an opposite trend was observed between 30 and 50°C. The trickle-bed biofilter appears to be an effective treatment process in the temperature range of 25–35°C. The microscopic observations showed that the morphologies of the leading microorganisms within the first-stage biofilm were rod-shaped bacteria in association with filaments, bacilli, and cocci at 15, 30, and 50°C, respectively. A theoretical evaluation on the temperature coefficient (θ) indicated that the temperature effects on the performance of a trickle-bed biofilter are more significant under lower BTEX loading rates. Furthermore, the mean θ value for a trickle-bed biofilter was equal to 1.021, which is in the typical range of some commonly used aerobic processes (1.0–1.10) (Lu *et al.*, 1999).

The effect on performance of temperature was changed in the range of 15-40 °C for α -pinene. The effect of temperature on biodegradation kinetics in continuous reactors was elucidated through equations derived from the Arrhenius formula. Fungal biofilter appears to be an effective treatment process for the removal of α -pinene. The fungal biofilter also showed a good potential to withstand shock loads and recovered rapidly its full performance after a 3-7 days starvation period (Jin *et al.*, 2006).

2.9.6 Microorganisms

Microorganisms was an essential factor to degrade VOCs in biofilter, many researches used mixed culture from waste water treatment plants or identified mixed culture as following.

A mixed culture containing *Pseudomonas maltophilia*, *P. testosteroni* and *P. putida* biotype A exhibited contrasting BTEX degradation patterns. While *P. putida* biotype A degraded all of the BTEX compounds, *P. maltophilia* and *P. testosteroni*, appeared unable to degrade benzene and xylenes, respectively. When the peat, inoculated with the mixed culture, was used as a biofilter for degradation of toluene and ethylbenzene vapours, percentage removal efficiencies were 99 and 85, respectively. When the capacity of the biofilter to degrade a combination of BTEX compounds was evaluated, percentage removal efficiencies for toluene, ethylbenzene, *p*-xylene, *o*-xylene and benzene were 99, 85, 82, 80 and 78, respectively. The importance of using the mixed culture as an inoculum in the biofilter was established and also the relationship between contaminated vapour flow rate and percentage removal efficiency (Mallakin *et al.*, 1996). BTEX substrate interactions for a toluene-acclimatized biofilter consortium were investigated. Benzene, ethylbenzene, *o*-xylene, *m*-xylene and *p*-xylene removal efficiencies were determined at a loading rate of 18.07 g m⁻³ h⁻¹ and retention times of 0.5-3.0 min (du Plessis *et al.*, 2001)

The mixed microbial culture used to inoculate the biofilter was comprised of five species, including: *Sphingobacterium multivorum*, *Comamonas testosterone*, *Pseudomonas putida*, *Pseudomonas fluorescens* and *Chryseobacterium indologenes*. All the bacterial strains were primary toluene and xylene degraders. The inoculation suspension was prepared using three-stage submerged cultivations with toluene vapor as the sole carbon and energy source (Klapková *et al.*, 2006). In other experiment, activated sludge taken from the local wastewater treatment plant was used to remove toluene vapour in agro-waste biofilter (Singh *et al.*, 2006).

The biodegradation of benzene, toluene, ethylbenzene, and *o*-xylene by a coculture of *Pseudomonas putida* and *Pseudomonas fluorescens* immobilized in a fibrous-bed bioreactor. A fibrous-bed bioreactor containing the coculture of *Pseudomonas putida* and *P. fluorescens* immobilized in a fibrous matrix was developed to degrade benzene (B), toluene (T), ethylbenzene (E), and *o*-xylene (X) in synthetic waste streams. The kinetics of BTEX biodegradation by immobilized cells adapted in the fibrous-bed bioreactor and free cells grown in serum bottles were studied. In general, the BTEX biodegradation rate increased with increasing substrate concentration and then decreased after reaching a maximum, showing substrate-inhibition kinetics. Both bacteria and fungi were present in the bioreactor. Five strains were isolated. Two bacteria, *Bacillus* and *Pseudomonas*, were shown to be dominant, as well as a *Trichosporon* strain that could, however, hardly grow on alkylbenzenes in pure culture (Veiga *et al.*, 1999). *Burkholderia (Pseudomonas) cepacia* strain, as an example of the effectiveness of microbial toluene removal was tested in batch culture (Andreoni *et al.*, 1996).

However, for immobilized cells, the degradation rate was much higher than that of free cells. Compared to free cells, immobilized cells in the bioreactor tolerated higher concentrations ($>1000 \text{ mg l}^{-1}$) of benzene and toluene, and gave at least 16-fold higher degradation rates for benzene, ethylbenzene, and *o*-xylene, and a 9-fold higher degradation rate for toluene. Complete and simultaneous degradation of BTEX mixture was achieved in the bioreactor under hypoxic conditions. Cells in the bioreactor were relatively insensitive to benzene toxicity; this insensitivity was

attributed to adaptation of the cells in the bioreactor. Compared to the original seeding culture, the adapted cells from the fibrous-bed bioreactor had higher specific growth rate, benzene degradation rate, and cell yield when the benzene concentration was higher than 100 mg l^{-1} . Cells in the fibrous bed had a long, slim morphology, which is different from the normal short-rod shape found for suspended cells in solution (Shim and Yang, 1999).

The performance of biofilters inoculated with the fungus *Scedosporium apiospermum* to treat toluene was evaluated. The experiments were performed in a 2.9 L reactor packed with vermiculite or with vermiculite-granular activated carbon as packing material. The initial moisture content of the support and the inlet concentration of toluene were 70% and 6 g m^{-3} , respectively (Garcia-Pena *et al.*, 2001).

The fungal biofilter was operated to treat a waste gas comprised of a four-component VOC mixture inoculated with a pure culture of the fungus *Cladosporium sphaerospermum*, was maintained under acidic conditions throughout the duration of the experiments. Although the column was initially inoculated with only *Cladosporium sphaerospermum*, several additional species of fungi tentatively identified as *Penicillium brevicompactum*, *Exophiala jenselmei*, *Fusarium oxysporum*, *Fusarium nygamai*, *Talaromyces flavus*, and *Fonsecaea pedrosi* were found growing by the end of experiment. The fungal biofilters can consistently maintain high removal efficiency for paint VOC mixtures over extended periods of operation (Qi *et al.*, 2005).

Two biofilters fed toluene-polluted air were inoculated with new fungal isolates of either *Exophiala oligosperma* or *Paecilomyces variotii*, while a third bioreactor was inoculated with a defined consortium composed of both fungi and a co-culture of a *Pseudomonas* strain and a *Bacillus* strain. Elimination capacities of $77 \text{ g m}^{-3} \text{ h}^{-1}$ and $55 \text{ g m}^{-3} \text{ h}^{-1}$ were reached in the fungal biofilters (with removal efficiencies exceeding 99%), respectively. In the case of *E. oligosperma* and *Paecilomyces variotii* when feeding air with a relative humidity (RH) of 85%, The

inoculated fungal strains remained the single dominant populations throughout the experiment. Conversely, in the biofilter inoculated with the bacterial–fungal consortium, the bacteria were gradually overgrown by the fungi, reaching a maximum elimination capacity around $77 \text{ g m}^{-3} \text{ h}^{-1}$ (Estévez *et al.*, 2005).

Single culture of fungus, *Aspergillus niger* was successfully applied to remove hexane (a volatile organic compound) from contaminated air streams in biofilter (Spigno *et al.*, 2003). *Paecilomyces variotii* CBS115145 was used to treat toluene-contaminated air and a toluene elimination capacity (EC) was of around $250 \text{ gm}^{-3} \text{ h}^{-1}$, which was higher than the values usually reported for bacteria. *P. variotii* assimilated *m*- and *p*-cresols but not the *o* isomer. Initial toluene hydroxylation occurred both on the methyl group and through the *p*-cresol pathway. These results were corroborated by detecting benzyl alcohol, benzaldehyde, and *p*-cresol as volatile intermediates. In liquid cultures with toluene as a substrate, the activity of toluene oxygenase (TO) was $5.6 \text{ nmol of O}_2/\text{min}/\text{mg}$ of biomass, and that of benzyl alcohol dehydrogenase was $16.2 \text{ nmol of NADH}/\text{min}/\text{mg}$ of protein. Toluene biodegradation determined from the TO activity in the biofilter depended on the biomass distribution and the substrate concentration. The specific enzymatic activity decreased from 6.3 to $1.9 \text{ nmol of O}_2/\text{min}/\text{mg}$ of biomass along the reactor (García-Peña *et al.*, 2005).

Butyl acetate and xylene mixtures are commonly encountered from the manufacture of semi-conductor or opto-electronic apparatuses. Almost complete VOC removal could be attained with influent carbon loadings of butyl acetate and xylene below 40 and $15 \text{ g m}^{-3} \text{ h}^{-1}$, respectively. As the influent carbon loadings of butyl acetate and were increased up to 150 and $110 \text{ g m}^{-3} \text{ h}^{-1}$, removal efficiencies higher than 80% were achieved. Therefore, the trickle-bed air biofilter appeared efficient in the control of emissions containing mixtures of butyl acetate and xylene with low to medium carbon loadings. The removal efficiencies of butyl acetate were higher than those of xylene, indicating that butyl acetate was the substrate preferred in the utilization of butyl acetate and xylene mixtures by the microorganisms. Carbon recoveries of 98 - 101% were achieved, demonstrating the accuracy of results. The carbon mass rate of the liquid effluent was approximately two to three orders of

magnitude less than that of the CO₂ effluent, indicating that the dissolved VOCs and their derivatives in the leachate were present in a negligible amount in the reactor. Applicable operating conditions of the the trickle-bed air biofilter unit for treating Butyl acetate and xylene mixtures were suggested (Lu and Chang, 2005).

2.10 The Relevant Research Studies

The studies of biofiltration and its performance including biofilter media and microorganisms used to inoculate in biofiltration process were reported as the following.

Hu *et al.* (1998) studied on the effects of biodegradable substrates and microbial concentration on the acclimation of microbes to acrylonitrile in aerobic submerged biofilter. The results show that the acclimation of microbial film to acrylonitrile was promoted by a higher microbial concentration in the biofilter and by the coexistence of glucose and peptone in the influent. It was clarified that the upper limit of acrylonitrile loading to the biofilter for the ultimate degradation, i.e., complete mineralization, of the influent acrylonitrile was about 2.0-2.2 kg m⁻³ d⁻¹. In addition, a new microbial quinone profile method was applied for the analysis of the microbial community change in the biofilter. The change in quinone profiles of the microbial film during the acclimation to acrylonitrile suggested that *Brevibacterium* sp., *Pseudomonas aeruginosa* and *Corynebacterium* sp. could contribute to the degradation of acrylonitrile in the aerobic biofilter.

Kleinheinz *et al.* (1999) studied on characterization of alpha-pinene-degrading microorganisms and application to a bench-scale Biofiltration system for VOC degradation. The study revealed that biology system was utilized to identify the bacteria as *Pseudomonas fluorescens* and *Alcaligenes xylosoxidans*. Aerobic growth and biodegradation studies confirmed that rapid growth and biodegradation were being achieved with α -pinene. Complete degradation of α -pinene was achieved in 36 h with a maximum rate of degradation of 3.9 mg/L/h. A nitrogen test was performed and confirmed that the removal of α -pinene was due to biological activity. Given the

ability of these microorganisms to utilize high levels of α -pinene, they will be used in a coupled treatment system using a physical/chemical adsorption/desorption unit coupled to a biofiltration column.

Darlington *et al.* (2000) investigated the application of the biofiltration of air circulated within the space as an alternative approach to maintain indoor air quality. A biofilter with living botanical matter as the packing medium reduced concentrations of toluene, ethylbenzene, and o-xylene concurrently present at parts per billion (volume) in indoor air. The greatest reduction in concentrations per pass was under the slowest influent air flux (0.025 m s^{-1}); however, the maximum amount removed per unit time occurred under the most rapid flux (0.2 m s^{-1}). There was little difference between the different compounds with removal capacities of between 1.3 and $2.4 \mu\text{mol m}^{-3} \text{ biofilter s}^{-1}$ (between 0.5 and $0.9 \text{ g m}^{-3} \text{ biofilter h}^{-1}$) depending on influent flux and temperature. Contrary to biofilters subjected to higher influent concentrations, the optimal temperatures for removal by this biofilter decreased to less than 20°C at the most rapid flux for all three compounds. Microbial activity was decreased at these cooler temperatures suggesting the biofilter was not microbially limited but rather was limited by the availability of substrate. The cooler temperatures allowed greater partitioning of the VOCs into the water column that had a greater impact on removal than its reduction in microbial activity.

Jorio *et al.* (2000) reported effects of gas flow rate and inlet concentration on xylene vapors infiltration performance. The biofiltration of xylene vapors has been investigated on a laboratory scale biofilter packed with a new filter material composed essentially of peat mixed with structuring and conditioning agents and initially inoculated with a microbial consortium. Three various gas flow rates, i.e. 0.4 , 0.7 and $1 \text{ m}^3 \text{ h}^{-1}$, were tested for xylene inlet concentration ranging from 0.2 to 4 g m^{-3} . The biofilter proved to be highly efficient in the removal of xylene at a gas flow rate of $0.4 \text{ m}^3 \text{ h}^{-1}$ corresponding to a gas residence time of 157 s . For all the tested inlet concentrations, both the removal efficiency and the elimination capacity decreased for high gas flow rates. For all the tested gas flow rates, a decrease in the elimination capacity was noticed for high xylene inlet concentration. The follow-up of carbon

dioxide concentration profile through the biofilter revealed that the mass ratio of carbon dioxide produced to the xylene removed was approximately 2.5/1, which confirms complete degradation of xylene if one considers the fraction of the consumed organic carbon used for the microbial growth.

Dhamwichukorn *et al.* (2001) studied on thermophilic biofiltration of methanol and α -pinene and found that biofiltration systems utilizing thermophilic (55°C) bacteria were constructed and tested for the removal of methanol and α -pinene, two important volatile organic compounds in the forest products industry. Thermophilic bacterial mixtures that can degrade both methanol and α -pinene were obtained via enrichment techniques. Two bench-scale thermophilic biofiltration systems (1085 and 1824 cm³) were used to examine compound removals at different residence times, with influent concentrations of 110 ppmv methanol and 15 ppmv α -pinene. At a residence time of 10.85 min, the smaller system had removal efficiencies of >98% for methanol, but only 23% for α -pinene. The larger system was operated with the same parameters to evaluate residence time and surfactant effects on compound removals. At a residence time of 18.24 min, both methanol and α -pinene removal rates were 95%. However, α -pinene removal dropped to 26% at a residence time of 6.08 min; methanol removal was not affected. Subsequent addition of a surfactant mixture increased removal to 94% at the shortest residence time. No residual α -pinene was detected with the support medium Celite R-635, indicating that the surfactant may increase mass transfer of α -pinene

Woertz *et al.* (2001) investigated a fungal vapor-phase bioreactor for the removal of nitric oxide from waste gas streams. Ground-level O₃ formation is becoming a major concern in many cities due to recent tightening of O₃ regulations. To control O₃ formation, more efficient treatment processes for O₃ precursors, such as NO_x and volatile organic compounds, are needed. One promising new technology for removing both NO_x and VOCs from off-gas streams is biofiltration, a simple process whereby contaminated air is passed through a biologically active packed bed. In this study, a toluene-degrading fungal bioreactor was used to treat an aerobic gas stream contaminated with NO. The fungal bioreactor removed 93% of the inlet 250-ppmv

NO at an empty bed contact time (EBCT) of 1 min when supplied with $90 \text{ g m}^{-3} \text{ hr}^{-1}$ toluene. The presence of NH_4^+ concentrations greater than $0.4 \text{ mg NH}_3/\text{g}$ dry packing medium, however, resulted in poor NO removal. The bioreactor achieved a maximum toluene elimination capacity of $270 \text{ g/m}^3/\text{hr}$ and maintained greater than 95% toluene removal efficiencies over the 175-day study period.

Christen *et al.* (2002) reported biofiltration of volatile ethanol using sugar cane bagasse inoculated with *Candida utilis*. Ethanol removal was complete, and 76.3% of the carbon consumed was found in carbon dioxide. At an higher aeration rate (ethanol load= 153.8 g/h m^3), an average removal efficiency of 70%, and an elimination capacity (EC) of 107.7 g/h m^3 . Only 64.4% of the carbon consumed was used for CO_2 production. Acetaldehyde and ethyl acetate in the outlet gas attained 7.86 and 20.4% in terms of carbon balance, respectively. In both cases, the transient phase was less than one day. At a high inlet ethanol concentration (52.4 g/m^3), no steady-state was observed and the process stopped during the third day. In the three cases, final biomass was poor, ranging from 10.5 to 14.8 mg/g dm . Final pH 4.0–4.6, indicated that acidifying non-volatile metabolites, such as acetate, accumulated in the reactor.

Sun *et al.* (2002) reported Toluene vapour degradation and microbial community in biofilter at various moisture content, toluene vapour was degraded in a biofilter packed with various initial moisture contents of packing materials at $650\text{--}1000 \text{ mg (toluene) m}^{-3}$ (gas) and $24.0\text{--}36.8 \text{ g m}^{-3} \text{ h}^{-1}$ load. The results demonstrated that a higher degradation capacity (DC) could be reached within a shorter operation time at a higher initial moisture content. During 144 h operation, the maximal degradation rate (DR) and degradation capacity (DC) were, respectively, 60%, $20 \text{ g m}^{-3} \text{ h}^{-1}$ for 30 and 40% initial moisture content. For 60 and 70% initial moisture content, the DR and DC could be higher at the beginning of operation, which were above 70% and $20 \text{ g m}^{-3} \text{ h}^{-1}$, and reached the maximum of 100% and above $25\text{--}30 \text{ g m}^{-3} \text{ h}^{-1}$ at about 75 h operation. The microbial determination results of packing materials (30, 50 and 70% initial moisture content) in biofilter operating for 144 h showed that the initial moisture content of packing materials would affect the numbers and types of microbial community of packing materials. With the increase in

the initial moisture content, the quantity of moulds and actinomyces would decrease and the number of bacteria would increase. The packing material with 50% initial moisture content was beneficial to the yeast growth.

Aizpuru *et al.* (2003) studied biofiltration of a mixture of volatile organic compounds on granular activated carbon. The performance of a biofilter packed with active carbon(AC) was evaluated. The effluent (alcohol, ketones, esters, aromatic and chlorinated compounds) treated was a representative mixture of most common industrial emissions. To achieve a better knowledge of multicomponent adsorption mechanisms, and to underline the interest of inoculating AC, a control abiotic humidified filter had been operated in the same conditions as the biofilter. For a load of $110 \text{ g VOC m}^{-3} \text{ AC h}^{-1}$, after 55 days of operation, the removal efficiency was higher in the biotic than in the abiotic filter (85% and 55%, respectively). Moreover, in the biofilter, at steady state, the elimination of all compounds was almost complete except for chlorinated compounds and p-xylene (removal efficiency of 25% and 64%, respectively). The microbial colonization of active carbon involved a decrease of the adsorption sites accessibility and enhanced the treatment of volatile organic compounds having a lower affinity for activated carbon. Moreover, while aromatic compounds and Methyl Isobutyl Ketone (MIBK) were eliminated along the overall height of the biofilter, pollutants with reduced affinity for AC, such as methanol, acetone, and halogenated compounds were only treated on the second half of the reactor. Thus, the affinity for activated carbon was an important parameter controlling the biodegradation process. Nevertheless, the use of AC as packing material in biofilters treating complex mixtures of volatile organic compounds is limited. Actually, similar removal efficiency could be reached, in the same conditions, for a biofilter packed with granular peat. Furthermore, for the biofilter packed with AC, the column height necessary to remove biodegradable compounds, with reduced affinity for the support, was important.

Delhomenie *et al.* (2003) investigated on degradation of toluene, xylene, and trimethylbenzene vapors by biofiltration: a comparison. This paper presents a

comparative study of the biodegradation of three aromatic volatile compounds in a compost-based biofilter: toluene, xylene, and 1,2,4-trimethylbenzene, used in the course of this work for the first time in the field of biofiltration. Hence, three identical biofiltration units have been operated at the laboratory scale. During the experiments, nitrogen (as urea) was supplied at various concentrations to each reactor, via irrigated nutrient solutions. A comparative analysis of the results showed that the biodegradability scale followed the degree of substitution around the aromatic ring: toluene > xylene > trimethylbenzene, with 95, 80, and 70% maximum conversions, respectively. In addition, and despite the different removal levels achieved in the three bioreactors, it was established that from a reaction viewpoint, the degradation of the three compounds seemed to follow similar metabolic pathways involving methylcatechol isomers. Finally, by varying the nitrogen input concentrations in the three reactors, three degradation regimes have been highlighted: an N-limitation regime and an N-optimum regime, common to the three solvents, and an N-excess regime, favorable to the colonization of the filter beds by nitrifying species, which particularly affected the xylene and trimethylbenzene biodegradation

Shareefdeen *et al.* (2003) reported the application of biofiltration to eliminate nuisance chemical odors from industrial air streams. Through successful laboratory and pilot research on biofiltration of odorous air-stream constituents, numerous commercial biofilters have been designed and installed across North America. In this paper, case studies related to biofiltration of air emissions from meat rendering plants, municipal wastewater treatment applications, and printed circuit board production are discussed to demonstrate the robustness of this technology in eliminating a wide variety of compounds.

Spigno *et al.* (2003) investigated VOCs removal from waste gases: gas-phase bioreactor for the abatement of hexane by *Aspergillus niger*. A lab-scale bioreactor of $1.77 \times 10^{-3} \text{ m}^3$ was assembled with expanded clay inoculated with the selected strain as the medium. The system proved to be efficient and stable during a 2-month trial. The average elimination capacity was $150 \text{ g m}^{-3} \text{ h}^{-1}$ and it increased with the organic load until a maximum level after a load of $300 \text{ g m}^{-3} \text{ h}^{-1}$. On the opposite, the removal

efficiency was over 70% for the lowest hexane concentrations. Considering the plant as the sum of the two biofiltration columns, the removal efficiency was almost always over 80%. The fungal development onto the support was also monitored in terms of weight increase and visual assessment by SEM observations of expanded clay particles from the biofilters.

Hwang *et al.* (2003) studied biofiltration of waste gases containing both ethyl acetate and toluene using different combinations of bacterial cultures. These strains, namely AC6, TO3 and B5, can degrade different substrates at a different rate. Owing to substrate competition, the toluene degradation efficiency of strain B5 would decrease in the presence of high concentration of ethyl acetate. However, the addition of strain AC6 would alleviate such inhibition because it could remove ethyl acetate rapidly. Microbial community competition from strain AC6 or B5 would impede the toluene degradation efficiency of strain TO3 unless a large amount of strain TO3 was inoculated. In biofiltration, strain B5 would be a better choice for inoculation into biofilters than strains AC6 and TO3, as it would grow rapidly under a low concentration of ethyl acetate.

Elmrini *et al.* (2004) investigated in biofiltration of xylene emissions with variations in the pollutant inlet concentration and gas flow rate. In order to remove xylene vapors from an air stream, an upflow laboratory scale biofilter was operated for a period of 2 months. The experimental study consisted of two different phases: in the first phase, the biofilter was operated at various gas flow rates and the xylene inlet concentration was maintained at 1.39 g m^{-3} . In the second phase, various inlet concentrations of the contaminant were tested at a constant gas flow rate of $0.4 \text{ m}^3 \text{ h}^{-1}$ corresponding to an empty bed residence time of 150 s. The biofilter response to steep and abrupt variations in the xylene inlet concentration and gas flow rate was examined. The results obtained revealed that the removal efficiency of the biofilter regained its high values (above 96%) in less than 24 h following the change to low concentrations and gas flow rate. Temperature measurements showed that the biofilter temperature strongly depends on the intensity of the microbial activity in the filter bed. The experimental mass ratio of carbon dioxide produced to the xylene removed

was equal to 2.72 indicating that the contaminant was eliminated exclusively by aerobic biodegradation. These findings suggest that a follow up of the amount of carbon dioxide produced in the filter bed can be very helpful in monitoring the performance of the biofilter. For relatively small inlet loads of xylene, the contributions of the different sections of the biofilter to the removal efficiency of the contaminant and the carbon dioxide production were unevenly balanced but became more uniformly distributed for relatively high inlet loads.

Namkoong *et al.* (2003) studied biofiltration of gasoline vapor by compost media. The average removal efficiencies of total petroleum hydrocarbon (TPH) and Benzene, toluene, ethylbenzene and xylene (BTEX) were 80 and 85%, respectively, during 4 months of stable operation. Biodegradation portions of the treated TPH and BTEX were 60 and 64%, respectively. When the influent concentration of TPH was less than 7800 mg TPH/m³, approximately 50% of TPH in the gas stream was removed in the lower half of the biofilter. When the influent concentration of BTEX was less than 720 mg BTEX/m³, over 75% of BTEX in the gas stream was removed in the lower half of the biofilter. Benzene removal efficiency was the lowest among BTEX. A pressure drop could not be detected over a 1-m bed height at a gas velocity of 6 m/h after approximately 4 months of operation. Results demonstrated that BTEX in gasoline vapor could be treated effectively using a compost biofilter.

Namkoong *et al.* (2004) studied effect of gas velocity and influent concentration on biofiltration of gasoline off-gas from soil vapor extraction. The inlet concentration of gasoline total petroleum hydrocarbon (TPH) ranged from about 300 to 7000 mg m⁻³ and gas was injected at velocities of 6 and 15 m h⁻¹ (empty bed residence time (EBRT) = 10 and 4 min, respectively). The maximum elimination capacities of TPH at 6 and 15 m h⁻¹ found in this research were over 24 and 19 g m⁻³ of filling material h⁻¹, respectively. TPH removal data was fitted using a first-order kinetic relationship. In the low concentration range of 300–3000 mg m⁻³, the first-order kinetic constants varied between 0.10 and 0.29 min⁻¹ regardless of gas velocities. At TPH concentrations greater than 3000 mg m⁻³, the first-order kinetic constants were about 0.09 and 0.07 min⁻¹ at gas velocities of 6 m h⁻¹ and 15 m h⁻¹,

respectively. To evaluate microbial dynamics, dehydrogenase activity, CO₂ generation and microbial species diversity were analyzed. Dehydrogenase activity could be used as an indicator of microbial activity. TPH removal corresponded well with CO₂ evolution. The average CO₂ recovery efficiency for the entire biofilter ranged between 60% and 70%. When the gas velocity was 6 m h⁻¹, most of the microbial activity and TPH removal occurred in the first quarter of the biofilter. However, when the gas velocity was 15 m h⁻¹, the entire column contributed to removal. Spatial and temporal variations in the biofilter microbial population were also observed. Nearly 60% of the colonies isolated from the compost media prior to biofiltration were *Bacillus*. After 90 days of biofiltration, the predominant species in the lower portion (0–50 cm) of the filter were *Rhodococcus*, while *Pseudomonas* and *Acinetobacter* dominated the upper portion (75–100 cm).

Otten *et al.* (2004) reported biofiltration of odours: laboratory studies using butyric acid. Results indicate that butyric acid can be effectively removed at efficiencies nearing 100% by both compost and compost/perlite filled biofilters at all times during a run period of 2000 h. Bed sterilization, nutrient addition, extraction results and changes in nitrogen composition of the bed indicated that microbial activity was mainly responsible for the removal and conversion of butyric acid.

Moe and Qi (2004) investigated on the performance of a fungal biofilter treating gas-phase solvent mixtures during intermittent loading. This corresponds to a total VOC loading rate of 94.3 g/(m³ h). Biofilter performance was evaluated over a 94-day period for three loading conditions intended to simulate processes generating contaminated gases only during daytime operation, daytime operation with weekend shutdown periods, and with long term (9-day) shutdown. Results indicate that fungal biofilters can be an effective alternative to conventional abatement technologies for treating solvent contaminated off-gases even under discontinuous loading conditions.

Khammar *et al.* (2004) studied the evaluation of dispersion methods for enumeration of microorganisms from peat and activated carbon biofilters treating volatile organic compounds. The comparison between these methods showed that

crushing was the most efficient for the removal of microorganisms from both peat and activated carbon. The comparison between three chemical dispersion agents showed that 1% Na-pyrophosphate was less efficient, compared with 200 mM phosphate buffer or 1% Na-hexametaphosphate. To optimize the cultivation of microorganisms, three different agar media were compared. Tryptic soy agar tenfold diluted (TSA 1/10) was the most suitable medium for the culture of microflora from a peat biofilter. For the activated carbon biofilter, there was no significant difference between Luria Bertoni, TSA 1/10, and plate count agar. The optimized extraction and enumeration protocols were used to perform a quantitative characterization of microbial populations in an operating laboratory activated carbon biofilter and in two parallel peat biofilters.

Hwang *et al.* (2004) studied removal of multiple nitrogenous wastes by *Aspergillus niger* in a continuous fixed-slab reactor. A fungus that was characterized as being able to remediate multiple nitrogenous wastes was identified as *Aspergillus niger* NBG5. The fungus assimilated ammonium, nitrite and protein at rates of 0.247, 0.07 and 0.096 g-N/g-cell/day, respectively, at 22 °C. The remediation rates of ammonium nitrogenous wastes decreased by a factor of eight at 35 °C, while the specific growth rates slightly increased. For nitrogenous wastes, ammonium was a preferred substrate but its rate of consumption declined significantly as temperature increased. The nitrogen consumption rates were inconsistent with the cell yields at high temperature. Further analysis of consumption ratios of C/N revealed that cells grew predominantly from the carbon at high temperature. The *A. niger* NBG5 consumed glucose rapidly at specific rates of 2–2.5 g-C/g-cell/day at 35 °C in the presence of ammonium and nitrite; while sluggish consumption of glucose was observed in the protein substrate. A suitable operational temperature was suggested, depending upon the amount of waste contents of C/N. A high temperature stimulates the use of carbon waste, while a low temperature favors remediation of all nitrogenous wastes.

Iliuta and Larachi (2004) investigated transient biofilter aerodynamics and clogging for VOC degradation. While the existing biofilter models appear to capture

adequately the transport and reaction phenomena at the biofilm scale, they poorly address, or provide little insight about the connection between the aerodynamics, biological filtration (or clogging) and biokinetics at the bioreactor length scale. An attempt has been made with this contribution to fill in this gap by developing a unidirectional dynamic flow model based on the volume-average mass, momentum and species balance equations coupled with conventional diffusion/reaction equations describing apparent kinetics in the biofilm. Toluene biodegradation by biodegrading microbes immobilized on pelletized diatomaceous earth biological support media was chosen as a case study to illustrate the consequences of formation of excessive amounts of biomass. The simulation results were rationalized in terms of biofilm thickness, bed local porosity, gas-phase substrate residual concentration, and pressure drop rise in biological fixed-bed filters.

Dehghanzadeh *et al.* (2005) investigated biodegradation of styrene laden waste gas stream using a compost-based biofilter. The treatment of waste gas styrene vapor was investigated in a three-stage bench-scale biofilter. Biofilter media consisted of yard waste compost mixed with shredded hard plastics in a 25:75 v/v ratio. Microbial acclimation to styrene was achieved by exposing the system to an inlet concentration (C_{in}) of 0.25 g m^{-3} styrene and an empty bed retention time (EBRT) of 360 s for 30 days. Under steady-state conditions, maximum elimination capacity (EC) obtained was $45 \text{ g m}^{-3} \text{ h}^{-1}$ at a loading rate (L) of $60 \text{ g m}^{-3} \text{ h}^{-1}$ (C_{in} of 2 g m^{-3} and EBRT of 120 s). Reduction of retention time adversely impacted the performance resulting in the maximum EC of 39 and $27 \text{ g m}^{-3} \text{ h}^{-1}$ for EBRT of 60 and 30 s, respectively. Evaluation of the concentration profile along the bed height indicated dominance of first-order kinetics at $C_{in} \leq 0.45 \text{ g m}^{-3}$ and zero-order for higher concentrations.

Liu *et al.* (2005) studied the removal of ternary VOCs in air streams at high loads using a compost-based biofilter. The biofilter treated up to $200 \text{ g m}^{-3} \text{ bed h}^{-1}$ of ethyl acetate and $120 \text{ g m}^{-3} \text{ bed h}^{-1}$ of isopropanol with percentage removals of nearly 100% and the empty bed retention time between 45 and 90 s. Toluene removal efficiencies were in the range of 40–100% with the inlet concentration about 0.5 g m^{-3} due to the inhibition of ethyl acetate and isopropanol. During the 3 months

operation, filter media clogging/channeling, pH decrease and nitrogen loss from the media resulted in the deterioration of the biofilter performance. The results demonstrated that under the conditions of pH ranging from 6.4 to 7.4 and the nitrogen content of the media above 0.3 mg g^{-1} , the mixture of ethyl acetate, isopropanol and toluene could be treated effectively using a compost-based biofilter.

Shim *et al.* (2006) evaluated the individual and combined removal capacities of benzene, toluene, and xylene (B, T, and X) in the presence and absence of methyl tert-butyl ether (MTBE) in a polyurethane biofilter inoculated with a BTX-degrading microbial consortium, and further examined their interactive effects in various mixtures. In addition, Polymerase chain reaction-denaturing gradient gel electrophoresis and phylogenetic analysis of 16S rRNA gene sequences were used to compare the microbial community structures found in biofilters exposed to the various gases and gas mixtures. The maximum individual elimination capacities (MECs) of B, T, and X were 200, 238, and $400 \text{ g m}^{-3} \text{ h}^{-1}$, respectively. There was no significant elimination of MTBE alone. Addition of MTBE decreased the MECs of B, T, and X to 75, 100, and $300 \text{ g m}^{-3} \text{ h}^{-1}$, respectively, indicating that benzene was most strongly inhibited by MTBE. When the three gases were mixed (B + T + X), the removal capacities of individual B, T, and X were 50, 90, and $200 \text{ g m}^{-3} \text{ h}^{-1}$, respectively. These capacities decreased to 40, 50, and $100 \text{ g m}^{-3} \text{ h}^{-1}$ when MTBE was added to the mix. The MEC of the three-gas mixture (B + T + X) was $340 \text{ g m}^{-3} \text{ h}^{-1}$, and that of the four-gas mixture was $200 \text{ g m}^{-3} \text{ h}^{-1}$. Although MTBE alone was not degraded by the biofilter, it could be co-metabolically degraded in the presence of toluene, benzene, or xylene with the MECs of 34, 23, and $14 \text{ g m}^{-3} \text{ h}^{-1}$, respectively. The microbial community structure analysis revealed that two large groups could be distinguished based on the presence or absence of MTBE, and many of the dominant bacteria in the consortia were closely related to bacteria isolated from aromatic hydrocarbon-contaminated sites and/or oil wastewaters. These findings provide important new insights into biofiltration and may be used to improve the rational design of biofilters for remediation of petroleum gas-contaminated airstreams according to composition types of mixed gases.

Singh *et al.* (2006) investigated on removal of toluene vapour using agro-waste as biofilter media. Biodegradation of toluene vapour was investigated in a laboratory scale biofilter packed with cylindrical pieces of yellow-gram (*Cajanus cajan*) stalk. Inlet concentrations and volumetric flow rates of toluene were varied from 2.56 to 34.73 g/m³ and 0.18 to 0.24 m³/h, respectively. The steady state was achieved within seven days and the degradation of toluene followed an exponential behaviour with time. Elimination capacity increased and tended towards a constant value but removal efficiency decreased with increase in inlet toluene loading. Depending upon loading rate, the process was either mass transfer or reaction-controlled.

Kim and Sorial (2006) investigated role of biological activity and biomass distribution in air biofilter performance. The effects of temporal and spatial changes in biological activity and biomass amount on biofilter performance were investigated in a lab-scale trickle-bed air biofilter at a toluene loading of 46.9 g m⁻³ h⁻¹ under two different experimental strategies, namely, periodic backwashing at a rate of 1 h once a week and 2 d starvation. Analysis of the overall reaction for toluene metabolism revealed that cell synthesis was relatively favored over toluene oxidation in the inlet section of the biofilter, but over time its oxidation became favored throughout the biofilter bed. Periodic in situ backwashing with media fluidization effectively made even spatial distribution of biomass along the bed media, by which consistent high removal performance in the biofilter has been attained. After 2 d starvation, the ratio of the biofilm EPS to the total biomass increased along the media bed depth, while the total biomass in the media bed subsequently decreased. The presence of sufficient biomass and microbial activity favorably influenced biofilter reacclimation after restart-up following starvation.

Maestre *et al.* (2007) reported fungal biofilters for toluene, the result shown that packing materials play a key role in the performance of bioreactors for waste gas treatment and particularly in biofilter applications. In this work, the performance of four differently packed biofilters operated in parallel for the treatment of relatively high inlet concentration of toluene was studied. The reactors were compared for

determining the suitability of coconut fiber, digested sludge compost from a waste water treatment plant, peat and pine leaves as packing materials for biofiltration of toluene. A deep characterization of materials was carried out. Biological activity and packing capabilities related to toluene removal were determined throughout 240 days of operation under different conditions of nutrients addition and watering regime. Also, biofilters recovering after a short shutdown was investigated. Nutrient addition resulted in improved removal efficiencies (RE) and elimination capacities (EC) of biofilters reaching maximum ECs between 75 and 95 g m⁻³ h⁻¹ of toluene. In the first 80 days, the pH decreased progressively within the reactors, causing a population change from bacteria to fungi, which were the predominant decontaminant microorganisms thereafter. All reactors were found to recover the RE rapidly after a 5 days shutdown and, in a maximum of 7 days, all reactors had been completely recuperated. These results point out that fungal biofilters are a suitable choice to treat high loads of toluene. In general, coconut fiber and compost biofilters exhibited a better performance in terms of elimination capacity and long-term stability.

Mohammad *et al*, 2007 studied mesophilic and thermophilic biotreatment of BTEX-polluted air in reactors, this study compares the removal of a mixture of benzene, toluene, ethylbenzene, all three xylene isomers (BTEX) in mesophilic and thermophilic (50 °C) bioreactors. In the mesophilic reactor fungi became dominant after long-term operation, while bacteria dominated in the thermophilic unit. Microbial acclimation was achieved by exposing the biofilters to initial BTEX loads of 2 to 15 g m⁻³ h⁻¹, at an empty bed residence time of 96 s. After adaptation, the elimination capacities ranged from 3 to 188 g m⁻³ h⁻¹, depending on the inlet load, for the mesophilic biofilter with removal efficiencies reaching 96%. On the other hand, in the thermophilic reactor the average removal efficiency was 83% with a maximum elimination capacity of 218 g m⁻³ h⁻¹. There was a clear positive relationship between temperature gradients as well as CO₂ production and elimination capacities across the biofilters. The gas phase was sampled at different depths along the reactors observing that the percentage pollutant removal in each section was strongly dependant on the load applied. The fate of individual alkylbenzene compounds was checked, showing the unusually high biodegradation rate of benzene at high loads under thermophilic

conditions (100%) compared to its very low removal in the mesophilic reactor at such load (<10%). Such difference was less pronounced for the other pollutants. After 210 days of operation, the dry biomass content for the mesophilic and thermophilic reactors were 0.300 and 0.114 g g⁻¹ (support), respectively, reaching higher removals under thermophilic conditions with a lower biomass accumulation, i.e. lower pressure drop.

There are only few researches on xylene vapor degradation, so the goal of this thesis was to identify microorganisms capable to degrade xylene and verify their efficiencies in biofilter system. The result will benefit further researches and can be applied to VOCs treatment for industries in the future.