การบำบัดอากาศปนเปื้อนด้วยเมทานอลและโทลูอีน โดยการกรองชีวภาพ

(Treatment of Air Contaminated with Methanol and Toluene by Biofiltration)

รายงานฉบับสมบูรณ์

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บทคัดย่อ

ในการศึกษานี้ ได้ทำการวัดประสิทธิภาพของตัวกรองชีวภาพชนิดที่บรรจุด้วยเปลือกถั่วหรือกะลาปาล์มในการบำบัดเมทานอลบริสุทธ์ โทลูอีนบริสุทธ์ หรือสารผสมระหว่างเมทานอลกับโทลูอีน สารเมทานอลนั้นเป็นสารที่มีความสามารถในการละลายน้ำได้ดีจึงถูกนำมาใช้เป็นตัวแทนของสารอินทรีย์ระเหยประเภท hydrophilic ในขณะที่โทลูอีนซึ่งมีความสามารถในการละลายน้ำได้น้อยกว่ามากถูกนำมาเป็นตัวแทนของสารอินทรีย์ระเหยประเภท hydrophobic ถึงแม้ว่าลักษณะเฉพาะตัวของเปลือกถั่วและกะลาปาล์มจะต่างกัน แต่ตัวกรองทั้งคู่มีความเหมาะสมในการใช้เป็นตัวกรองชีวภาพสำหรับการบำบัดอากาศที่ปนเปื้อนด้วยเมทานอลหรือโทลูอีน เนื่องจากค่าความสามารถในการบำบัดสูงสุดที่ได้จากการทดลองนี้มีค่าใกล้เคียงกับค่าที่ได้จากตัวกรองชนิดอื่นๆ ในส่วนของค่าความสามารถในการบำบัดสูงสุดในระบบที่ใช้เปลือกถั่วลิสงเป็นตัวกรอง คือ 198 g methanol/m^3/h และ 141 g toluene/m^3/h และในส่วนของระบบที่ใช้กะลาปาล์มเป็นตัวกรองมีค่าความสามารถในการบำบัดสูงสุด 168 g methanol/m^3/h และ 133 g toluene/m^3/h และในส่วนระบบผสมของสารระเหย มีค่าความสามารถในการบำบัดสูงสุด 215 g methanol/m^3/h และ 6.6 g toluene/m^3/h ในระบบที่ใช้เปลือกถั่วลิสงเป็นตัวกรอง และ 185 g methanol/m^3/h และ 8.8 g toluene/m^3/hในระบบที่ใช้กะลาปาล์มเป็นตัวกรอง จากค่าดังกล่าวพบว่า ค่าความสามารถในการบำบัดสูงสุดของเมทานอลบริสุทธ์สำหรับทั้งสองตัวกรองมีค่าใกล้เคียงกัน แต่ค่าความสามารถในการบำบัดสูงสุดของโทลูอีนในระบบสารผสมมีค่าบ่งชี้ประสิทธิภาพในการบำบัดต่ำกว่าค่าที่ได้จากระบบสารบริสุทธ์สารเดียวมาก ซึ่งอาจเกิดจากการปล่อยโทลูอีนเข้าสู่ระบบซึ่งมีจุลินทรีย์ที่ได้ถูกปรับตัวให้เข้ากับเมทานอลแล้ว จากสิ่งที่ได้เรียนรู้จากการศึกษานี้ พบว่ายังมีองค์ความรู้อีกมากที่ยังต้องทำการศึกษาต่อไปในภายภาคหน้า โดยเฉพาะในหัวข้อเรื่องปฏิสัมพันธ์ระหว่างการตอบสนองของจุลินทรีย์ในการบำบัดสารระเหยที่แตกต่างกัน ซึ่งจะเป็นประโยชน์อย่างมากในการวิจัยต่อไปในอนาคต

เปลือกถั่วมีค่าความสามารถในการบำบัดสูงสุดมากกว่ากะลาปาล์มเล็กน้อย และมีค่าความหนาแน่นรวมต่ำกว่ามากซึ่งทำให้มีความได้เปรียบทางด้านค่าใช้จ่ายเมื่อเทียบกับกะลาปาล์ม อย่างไรก็ตามจากผลของการใช้กะลาปาล์มเป็นตัวกรองพบว่ามันมีโครงสร้างที่มั่นคงกว่าการใช้เปลือกถั่วเป็นตัวกรอง ซึ่งทำให้ระบบที่ใช้เปลือกถั่วเป็นตัวกรองต้องการการเปลี่ยนตัวกรองใหม่บ่อยกว่า ซึ่งหมายความว่าความสะดวกในการหาวัสดุตามท้องถิ่นและราคาของวัสดุนั้นจะต้องถูกนำมาเป็นปัจจัยในการพิจารณาเลือกวัสดุที่จะนำมาใช้เป็นตัวกรอง การใช้เปลือกถั่วหรือกะลาปาล์มถือเป็นประโยชน์อย่างมากต่ออุตสาหกรรมไทยในการที่จะพิจารณาติดตั้งตัวกรองชีวภาพในการ

บำบัดสารระเหย เนื่องจากการใช้วัสดุทั้งสองมาทำเป็นตัวกรองนั้นมีราคาถูกกว่าการนำวัสดุแบบดั้งเดิมมาใช้

ในการสร้างแบบจำลองมหภาคนั้น ค่าความสามารถในการบำบัดถูกใช้เป็นฐาน และถูกเลือกมาสำหรับใช้ในการจำลองประสิทธิภาพตัวกรองชีวภาพ โดยคิดเป็นตัวแปรตามของค่าภาระบรรทุก แบบจำลองนี้มีประโยชน์เพื่อนำไปออกแบบระบบตัวกรองชีวภาพได้ โดยมีสมการความสัมพันธ์ระหว่างค่าประสิทธิภาพการกำจัดกับค่าภาระบรรทุกดังนี้ $EC = aH_{\max}(1-e^{-bIL})$ หลักที่นำมาวางไว้ในแบบจำลองนี้ก็คือกระบวนการการย่อยสลายสารระเหยโดยจุลินทรีย์ดำเนินไปตามกลไกของ Michaelis-Menten ฉะนั้นที่จุดใดๆในระบบตัวกรองชีวภาพ ค่าการย่อยสลายสารอินทรีย์ระเหยสามารถขึ้นไปได้ถึงค่าสูงสุด ในกรณีที่ความเข้มข้นนำเข้าต่ำจะมีความสัมพันธ์แบบลำดับหนึ่ง อย่างไรก็ตามเมื่อความเข้มข้นนำเข้าสูงขึ้น กลไกความสัมพันธ์จะถูกเปลี่ยนไปเป็นลำดับศูนย์ แม้ว่าความสูงของชั้นตัวกรองจะถูกรักษาให้คงที่ระหว่างทำการทดลองแต่ก็ถูกนำมารวมอยู่ในแบบจำลองในฐานะตัวแปรเพื่อที่จะให้แบบจำลองนั้นเป็นประโยชน์ต่อผู้ที่ต้องการออกแบบตัวกรองชีวภาพเพื่อจุดประสงค์แบบอื่น ทั้งนี้แบบจำลองค่าประสิทธิภาพการกำจัดนี้พบว่ามีค่าที่สอดคล้องกับค่าที่ได้จากการทดลองนี้และค่าที่ได้จากผลการทดลองของงานวิจัยอื่นๆ

Abstract

The performances of biofilters packed with palm shells or peanut shells for removal of pure methanol, pure toluene, or a mixture of methanol and toluene were investigated. Methanol, which has a high water solubility was used as a representative of the hydrophilic class of VOCs while toluene, which has a much lower water solubility, was used as the representative hydrophobic solvent. Although the characteristics of peanut shells and palm shells are different they both appear suitable for use as media in biofilters treating air contaminated with methanol or toluene since their maximum elimination capacity (EC_{max}) values are comparable to those obtained using other media. The maximum elimination capacities were 198 g methanol/m^3/h and 141 g toluene/m^3/h for peanut shell systems and 168 g methanol/m^3/h and 133 g toluene/m^3/h for palm shell systems. In the mixed VOCs systems, the maximum elimination capacities were 215 g methanol/m^3/h and 6.6 g toluene/m^3/h for the peanut shell system, and 185 g methanol/m^3/h, and 8.8 g toluene/m^3/h for the palm shell system. It can be seen that the EC values for methanol in the single component systems are very similar, but the EC values obtained for toluene in the mixed system are well below those obtained in the single component systems. This is probably because toluene was only introduced into the biofilter systems after the microorganisms were well acclimatized to methanol. There is evidently much still to be learnt about interactions between microorganisms responsible for degrading different VOCs and this could be a fruitful area for further research. The EC_{max} values for peanut shells are slightly higher than those for palm shells, and the peanut shells have a much lower bulk density, which would certainly have cost advantages. However, the results also show that palm shells could retain their structural integrity better than peanut shells and so require replacing less frequently. This means that local availability and costs of the two materials are likely to determine which should be selected. Use of peanut shells or palm shells should be of considerable benefit to Thai industries considering installing biofilters to remove VOCs as it makes the cost of bed packing materials much more affordable than if more conventional packing materials had to be used.

A macrokinetic model based on elimination capacity was chosen for modeling biofilter performance as a function of inlet load. Such a model would be decidedly useful to anyone setting

out to design a biofilter. The equation of elimination capacity vs. the load curve is $EC = aH_{max}(1 - e^{-bIL})$. The underlying basis of this model is that microbially mediated VOC degradation processes follow Michaelis-Menten kinetics, so that in any given biofilter there is a maximum VOC degradation rate that can be achieved. At low inlet loads it would be expected that a first order relationship would exist; however, as the inlet load increases, the relationship moves progressively towards a zero-order relationship. Even though the bed height was kept constant during the present project it has been included as a variable in this model so as to enhance the model's usefulness to those wishing to design biofilters for other purposes. The above elimination capacity model fitted well both our experimental results and those of other studies.

กิตติกรรมประกาศ

ขอขอบคุณเจ้าหน้าที่ภาควิชาวิศวกรรมเคมีที่ช่วยอำนวยความสะดวกทั้งในงานปฏิบัติการและการติดต่อประสานงานกับหน่วยงานต่างๆ ขอขอบคุณคุณญาดา นิติภาวะชน ผู้ช่วยวิจัย และขอขอบคุณภาควิชาวิศวกรรมเคมีที่เอื้อเฟื้อสถานที่และอุปกรณ์ในการทำวิจัย และสุดท้ายขอขอบคุณมหาวิทยาลัยสงขลานครินทร์และสำนักงานคณะกรรมการวิจัยแห่งชาติในการสนับสนุนทุนวิจัยในครั้งนี้

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ผู้จัดทำ

สารบัญ

Chapter 1

Introduction

1.1 Background

Volatile organic compounds (VOCs), such as toluene, benzene, acetone, methanol and ethanol, are organic compounds that evaporate easily at room temperature. Large amounts of VOCs are emitted from many industrial operations. Many VOCs have an adverse impact on the environment and on living organisms, especially humans. Once VOCs enter the atmosphere and are inhaled or ingested by living organisms, it can endanger their health. To set limitations on the quantities of VOC emissions has been a concern in more developed countries, such as the USA, for several decades. In the USA, a major impetus was given to removal of VOCs from contaminated air streams by passing the 1990 Clean Air Act Amendments (CAAA).

Current technologies used for controlling of VOCs (e.g. thermal incineration, wet scrubbing, and adsorption onto activated carbon) are costly, especially in cases where there are low concentrations of the pollutants (Mohseni and Allen, 2000). Moreover, these treatments are unsuitable for treating high volume air flows with fluctuating VOC concentrations. One technology that is well suited for removal of VOCs from contaminated air streams with low and/or fluctuating VOC concentrations is biofiltration.

Biofiltration involves passing an air stream contaminated with VOCs through a bed packed with a solid medium and letting a microbiological process oxidize the volatile organic compounds on the surface of the packing, where a biofilm is formed. Innocuous products such as carbon dioxide and water are the end products from this process. Biofiltration is inexpensive compared with the techniques mentioned earlier and very effective for treating large volumes (up to 10^5 m^3/h) of moist air streams with low concentrations (less than 5 g/m^3) of the biodegradable pollutants (Devinny et al., 1999). Furthermore, the treatment is environmentally friendly, as the treatment can be performed at ambient temperature and it does not generate nitrogen oxides or secondary waste streams. Pollutants are generally converted to carbon dioxide under the action of growing or resting microorganisms (Deshusses, 1997).

Biofiltration is a very complex process affected by several factors including biodegradation kinetics, oxygen availability in the biofilms, microbial ecology and spatial distribution of biofilms, moisture content of the packing material, pH, temperature, and flow characteristics through porous media (Baltzis et al., 1997). Due to the complexity of the physical, chemical and biological processes involved in biofiltration, and because VOCs can have widely varying chemical and physical characteristics, fundamental as well as applied investigations on biofiltration are required for better understanding and design of a biofilter. Currently available data on elimination rates of mixtures of VOCs, especially mixtures of hydrophilic and hydrophobic VOCs, for various filter media are insufficient. Methanol and toluene, which were used in this study, are two examples of VOCs.

One of the main industries in Thailand that generates VOCs is the printing industry and its output of VOCs is likely to be expanding; for example, the number of labels printed in Thailand rose from 9.26×10^8 pieces in 2000 to 15.9×10^8 pieces in 2008 (The office of industrial economics, 2009). This industry employs solvents such as ethanol, ethyl acetate, methyl ethyl ketone, n-propyl acetate, toluene, icinol and acetone (Campbell and Connor, 1997) and emits them to the atmosphere. These VOCs evaporate rapidly during the printing process because of the relatively high process temperatures, such as 60°C in the oven at a local printing plant (My Jet: Digital Ink Jet Printer, China), or 80 °C in the oven at the Conoflex Packaging Plant in Australia (Campbell and Connor, 1997). VOC concentrations in ventilation air from printing works can be significant; Liu et al. (2002) measured toluene concentrations ranging from 0.021 to 0.323 g/m^3, in gases discharged from color printing works in China.

In Thailand, especially less developed parts like southern Thailand, concern about industrial VOC emissions is still limited. However, it is expected that as global and national concerns about the environment increase, pressure to limit the quantities of VOCs emitted by industries such as the printing industry in Thailand will intensify. Biofiltration is a VOC removal technology that could be potentially of interest to particular local industries. It will encourage local industries to pay more attention to using biofiltration for VOC removal if inexpensive bed media and knowledge about effectively designing biofilter systems are available. Since the conventional biofilter bed media are expensive in Thailand, preliminary work suggested that peanut shells and palm shells, agricultural waste products that are readily and cheaply available in various parts of

Thailand, could be suitable for use as biofilter bed media. Although a large body of empirical data has been published, the fundamental knowledge necessary for biofilter design based on theoretical concepts or on mathematical models is still missing. The elimination process of VOCs from industrial waste streams using biofilter with local agricultural waste as packing media have potential value to Thai industries. Thus, this work is aimed at studying the performance of experimental biofilters using peanut shells and palm shells as packing media, characterizing the performance of these biofilters when treating gases containing methanol and toluene (two commonly used VOCs), and generating macrokinetic model to predict VOC elimination rates in the system.

1.2 Literature Review

1.2.1 Volatile Organic Compounds

It may be stated, as an approximate rule, that VOCs are those organic liquids or solids whose room temperature vapor pressures are greater than about 0.0007 atm and whose atmospheric boiling points are up to about 260°C, which means most organic compounds with less than about 12 carbon atoms (Nevers, 2000). VOCs include a variety of carbon-containing chemicals, but not carbon monoxide, carbon dioxide, carbonic acid, and metallic carbides, since those compounds are inorganic. Most VOCs have an adverse effect on air quality and are classed as air pollutants. VOCs form the bulk of the 189 hazardous substances listed by the Clean Air Act of 1990 (Prado et al., 2005). Most VOCs have short- and long-term adverse health effects. VOCs are emitted from many products, such as paints and lacquers, paint strippers, cleaning supplies, pesticides, building materials and furnishings. In addition, a large quantity of VOCs is released from various industrial sources, e.g. petrochemical, printing industries, coating facilities, and hazardous waste sites. When humans are exposed to VOCs, they can cause eye, nose, and throat irritation; headaches, loss of coordination, nausea; damage to liver, kidney, and central nervous system. Some VOCs can cause cancer in animals; some are suspected or known to cause cancer in humans. The ability of organic compounds to cause health effects varies greatly, from VOCs that are highly toxic to those with no known health effect. Similar to other pollutants, the extent and nature of the health effect will depend on many factors including level of exposure and length of

time exposed. Concentrations of many VOCs are consistently higher indoors (up to ten times higher) than outdoors (Spicer et al., 2002; EPA, 2009).

1.2.2 Selection of Experimental VOCs

The solubility of VOCs in water was an important factor in choosing the substances investigated in this study, since the solubility of a VOC affects the rate at which it diffuses from air into the biofilm layer. VOCs vary markedly in their solubility in water; aliphatic compounds are usually quite soluble whereas aromatic compounds are relatively insoluble. In order to make the results of this experiment widely applicable, the study was conducted by using peanut shells and palm shells as packing media in biofilters together with a hydrophilic VOC and a hydrophobic VOC, as well as a mixture of the two. In previous studies, ethanol (Christen et al., 2002; Xiao, 2002; Dastous et al., 2007) and methanol (Mohseni and Allen, 2000; Torkian et al., 2003; Sologar et al., 2004; Prado et al., 2005; Chetpattananondh et al., 2005; Dastous et al., 2007) have been widely used as representatives of soluble VOCs, hence in this study, methanol was chosen as hydrophilic VOCs representative. Methanol is a hydrophilic substance which can easily dissolve in water (with a water solubility of 1,000 g/l at 25°C). On the other hand, toluene appears to have been among the most extensively studied example of a poorly soluble VOC (Delhoménie et al., 2002a; Torkian et al., 2003; Rene et al., 2005; Wright et al., 2005; Vergara-Fernández et al., 2007), hence in this study, toluene was chosen as hydrophobic VOCs representative. Toluene is a hydrophobic substance which is relatively insoluble in water (with a water solubility of 0.53 g/l at 25°C). Therefore, methanol and toluene are used as representatives of VOCs in this study; both are commonly used in chemical industries, furniture industries, etc. They are among the hazardous air pollutants (HAPs) listed in Title III of the 1990 Clean Air Act Amendments (CAAA90) proposed by the US Environmental Protection Agency (EPA). The physical properties of toluene and methanol are presented in Table 1-1.

Table 1-1 Physical properties of studied VOCs (Spicer et al., 2002).

Properties	Methanol	Toluene
Vapor pressure (mmHg, 25°C)	118	28.6
Polarizability (cm^3/mole)	8.2	31
Water solubility (g/l, 25°C)	1000	0.53
Other	Polar	Non polar
Chemical formula/structure	CH_3OH	C_7H_8
Molecular weight	32	92.1
Boiling point (°C)	65	111

1.2.2.1 Methanol

Methanol (methyl alcohol) is a hydrophilic substance with a simple structure. It is a clear, colorless and volatile liquid at ambient temperatures and is registered as CAS#67-56-1 (Spicer et al., 2002). Common sources of methanol toxicity are found in antifreeze, perfumes, paint solvents, beverages, photocopying fluid, and shellac (Askar and Al-Suwaida, 2007). About 40% of methanol is converted into formaldehyde and then used in paint production (Methanol (1), 2008). In addition, methanol is a feedstock in the production of acetic acid; methyl tert-butyl ether (MTBE) and oxinol, which are used to improve gasoline octane; and other chemical intermediates. Methanol is also used as a solvent and in the production of single-cell protein, which is used as animal-feed additives replacing such supplements as powdered milk, soybean meal, and fishmeal (Methanol (2), 2006). Council of the Paper Industry for Air and Stream Improvement (NCASI) methanol sampling method were conducted at two pulp and paper mills. Sampling and analysis procedures followed EPA Method 301 requirements. The sampling location for the first field test was the inlet vent to a softwood bleach plant scrubber, where the methanol concentration was approximately 30 ppm. A second field test was conducted at a vent from a black liquor oxidation tank where the methanol concentration was approximately 350 ppm (Peterson et al., 1995).

Methanol can cause permanent blindness when breathed, ingested, or passed through the skin. Exposure to high concentrations can cause death. Because of the slowness of its elimination by the human body, methanol should be regarded as an accumulative poison. Exposure can cause headaches, cardiac depression, nausea, vomiting, blurred vision, dizziness, a

feeling of intoxication, and irritations of the eyes, nose, mouth, and throat. Repeated or prolonged contact can cause liver, kidney and heart damage, and possible death (Methanol (3), 2001).

1.2.2.2 Toluene

Toluene (methylbenzene, phenyl methane) is a hydrophobic substance with a more complex structure because of the benzene ring. It is an aromatic hydrocarbon (C_7H_8) and is registered as CAS#108-88-3 (Spicer et al., 2002). At room temperature, toluene is a colorless, sweet-smelling, and volatile liquid (Toluene (1), 2000). Toluene is commonly used in the manufacturing processes for varnishes, lacquers, paint thinners (Acuña *et al.*, 1999), adhesives (glues), and rubber. In addition, toluene is applied as a solvent for dissolving printing ink and cleaning the nozzles of printers (Toluene (2), 2008).

Toxicity can occur from accidental or deliberate inhalation of fumes, ingestion, or absorption through the skin. Toluene is commonly abused by saturating or soaking a sock or rag with spray paint, placing it over the nose and mouth, and inhaling to get a sensation of euphoria, buzz, or high. When humans have contact with toluene, skin-irritation, nausea, headache, dizziness, and unconsciousness may occur. In the long term of exposure, cardiac sensitization, severe heart abnormalities, and liver and kidney damage may be fatal (Toluene (1), 2000).

The Occupational Safety and Health Administration (OSHA) has determined the acceptable level of occupational exposure to toluene for people in the workplace as shown in Table 1-2.

1.2.3 Technology Applications for Treatment of Contaminated Air Emissions

There are many techniques to remove VOCs from contaminated air. There are 3 main approaches used in extracting these substances; chemical change, where VOCs are chemically altered to more innocuous products in the gas phase (e.g. incineration); physical transfer of the VOCs out of the gas phase (e.g. condensation, and adsorption); physical transfer of the VOCs out of the gas phase coupled with microbial conversion into less harmful compounds (e.g. biofiltration). In considering which approach is appropriate, many related factors should be incorporated into the determination. These factors include, for example, VOC concentrations in the air, the purpose of recovery (e.g. reuse), the required removal efficiency, and air flow rates. In Figure 1.1 it is shown how the factors of VOC concentration, and air flow rate affect the choice of removal technology.

Table 1-2 Toxic effects of inhaling toluene (Rafson, 1998).

Inhalation Concentration (ppm)	Exposure time	Health effects
10-40	Continuous	No symptoms
80-300	Years	No abnormal liver tests
100	6 h	Eye/nose irritation, headache, dizziness, "high" feeling, normal neurobehavioral tests
117 (average)	Years	No neurologic abnormalities
200	8 h	Mild fatigue, weakness, confusion, skin tingling
600	8 h	Euphoria, headache, dizziness, nausea, pupil dilation
800	8 h	Above symptoms but more pronounced and persisting for days, muscle fatigue, nervousness, insomnia
Glue sniffer	3 yr	Reversible lung, kidney, liver function tests

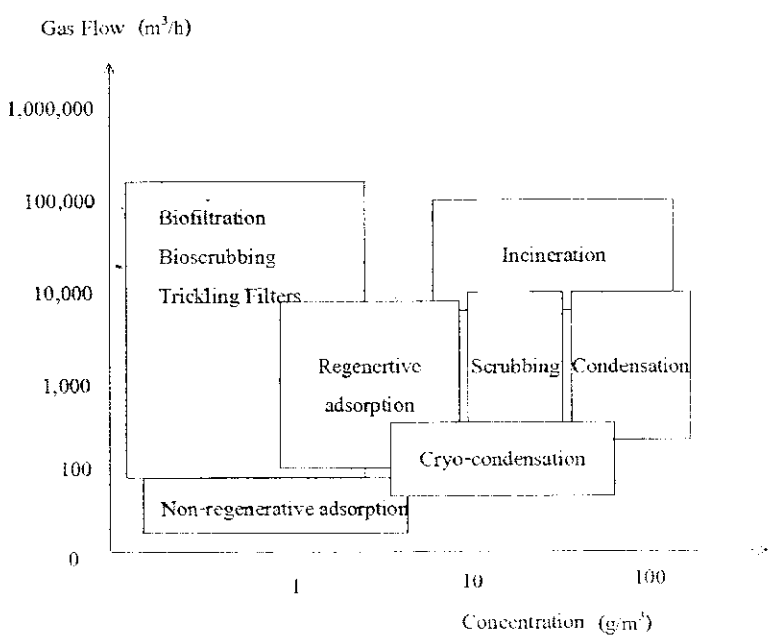


Figure 1-1 Applicability of various air pollution control technologies based on air flow rates and concentrations to be treated. (Devinny et al., 1999).

The more important methods of VOC removal, including incineration, condensation, adsorption, and biological treatment are described below (Devinny et al., 1999).

1.2.3.1 Incineration

Thermal and catalytic incinerations are widely used as effective treatment processes for waste gases. In a thermal incineration, contaminated air stream is combusted at temperature of 700-1400°C. Secondary treatment is necessary because of the formation of nitrogen oxides (NO_x), which harm the environment (smog, acid rain, etc.).

1.2.3.2 Condensation

Condensation is a technique in which gaseous VOCs are changed to liquids. A contaminated air stream is cooled and compressed till a substantial fraction of the VOCs have liquefied. This technique is only economical for concentrated vapors where there is some recycle or recovery value.

1.2.3.3 Adsorption

Adsorption is always applied with low concentration gas. Activated carbon or other porous materials are the main adsorbents used in this technique. Saturated adsorbents are harmful wastes. To avoid loss of adsorbed VOCs back to the atmosphere they need to be converted to more innocuous compounds by another process, such as incineration.

1.2.3.4 Membrane Systems

This method involves compressing waste air streams to enhance the pressure differential between the air-feed side and the permeate side of a membrane (to approximately 310 to 1400 kPa); the pressure gradient causes VOCs to diffuse across the membrane, thus achieving the desired separation. Only a portion of the organic vapors is recovered in the condenser downstream of the membrane; to remove residual VOCs requires another process.

1.2.3.5 Biological Treatment

Biological treatment is effective and economical for low concentrations of contaminants in large quantities of air. Biological processes are widely used in various industrial and residential wastewater treatments to remove VOCs of low molecular weight and highly soluble organic compounds with simple bond structures, such as alcohols, aldehydes, ketones, and some aromatics. Compounds with complex bond structures generally require more energy to be

degraded, such as phenols, chlorinated hydrocarbons, polyaromatic hydrocarbons, and highly halogenated hydrocarbons. Inorganic compounds such as hydrogen sulfide and ammonia are also well biodegraded (Devinny et al., 1999).

VOCs are main sources of carbon and energy input for the metabolism of aerobic bacteria (Delhoménie et al., 2002a). Contaminated air streams that contain biodegradable compounds that are non-toxic to microorganisms have been widely studied (Lee et al., 1996; Auria et al., 2000; Mohseni and Allen, 2000; Zilli et al., 2001; Delhoménie et al., 2002a). Microbial populations may be dominated by one particular microbial species or numerous species (Devinny et al., 1999).

The major air-phase biological reactors are biofilters, biotrickling filters, and bioscrubbers. In biotrickling filters, microorganisms are fixed on inorganic materials and suspended in the water phase. Contaminated air and a mixture of water, buffer, and nutrient are passed continuously over the immobilized microorganisms, whether co-currently or counter-currently depends on the specific operation. In bioscrubbers, microorganisms, nutrient, buffer, and water are mixed and aerated before contaminated air enters counter-currently into the bioscrubbers (Devinny et al., 1999).

Biofiltration uses microorganisms fixed on packing media to break down pollutants present in an air stream. A humid, contaminated air stream is passed through immobile packing media, and contaminants are degraded by oxidation reactions carried out by microorganisms attached to the media. In general, this technique operates at room temperature, hence it can decrease the capital cost by obviating the use of heating or cooling equipment. Products from the reaction are carbon dioxide, water and biomass. In this study, biofiltration was applied and the information is shown below.

Contaminated air treatment technologies often depend on flow rates and concentrations, as was shown earlier in Figure 1-1. These technologies have different advantages and disadvantages, which are shown in Table 1-3.

1.2.3.6 Comparison of VOC Treatment Processes

Two key factors that largely determine which VOC treatment technology is chosen for a particular application are the air flow rate and the VOC concentration. The combinations of these two factors for which different technologies are recommended were shown

in Figure 1-1. A more detailed comparison of the advantages and disadvantages of each process type is given in Table 1-3.

Table 1-3 Comparison of contaminated air control technologies (Devinny et al., 1999).

Control technology	Advantages	Disadvantages
Biofiltration	1. Low operating and capital cost 2. Effective removal of low concentration compounds 4. Minimal waste streams produced	1. Large footprint requirement 2. Medium deterioration will occur 3. Less suitable for high concentration 4. Moisture and pH difficult to control 5. Particulate matter may clog medium 6. Poorly degradable high concentration compounds 7. Microorganisms' sensitivity to loading fluctuations, moisture, temperature, and pH conditions
Biotrickling filters	1. Medium operating and capital costs 2. Effective removal of compounds 3. Treats acid-producing - contaminants	1. Clogging by biomass 2. More complex to construct and operate 3. Further waste streams produced
Wet scrubbing	1. Low capital costs 2. Effective removal of odors 3. No medium disposal required 4. Can operate with a moist gas stream 5. Can handle high flow rates	1. High operating costs 2. Need for complex chemical feed systems 3. Does not remove all VOCs 4. Water softening often required 5. Nozzle maintenance often

Control technology	Advantages	Disadvantages
	6. Ability to handle variable loads 7. Can use with corrosive gases	required 6. High chemical cost in wastewater treatment
Carbon adsorption	1. Short retention time / small unit 2. Effective removal of low organic compounds 3. Suitable for low / moderate loads 4. Consistent, reliable operation	1. High operating costs 2. Moderate capital costs 3. Carbon life reduced by moist gas stream 4. Creates secondary waste streams (transfer waste air to solid)
Incineration	1. System is simple 2. Effective removal of high concentration compounds 3. Suitable for very high loads 4. Performance is uniform and reliable 5. Small area required	1. High operating and capital costs 2. High flow / low concentration not cost effective since required large fuel inputs 3. Creates a secondary waste stream (NO_x) 4. Scrutinized by public

1.2.4 Biofiltration

1.2.4.1 Introduction

As previously indicated, many VOC problems in industrial operations can be effectively solved by using biofilters for organic compounds removal. Biofiltration is a technology to control both VOCs and odor. It depends on good VOC transfer between the gaseous phase containing the contaminant and the active degrading microorganisms retained on a suitable solid support. Biofiltration is an environmentally friendly process as the contaminants are completely converted at room temperature into non-hazardous final products (Mohseni and Allen, 2000; Zilli et al., 2001; Yoon and Park, 2002). In addition, the operating cost of the biofiltration technology is 10-20% lower than that of other treatment technologies (Xiao, 2002). The cited results from

previous studies indicated that biofiltration is the most relevant VOCs treatment technology. Figure 1-2 shows a flowsheet of a typical industrial biofilter.

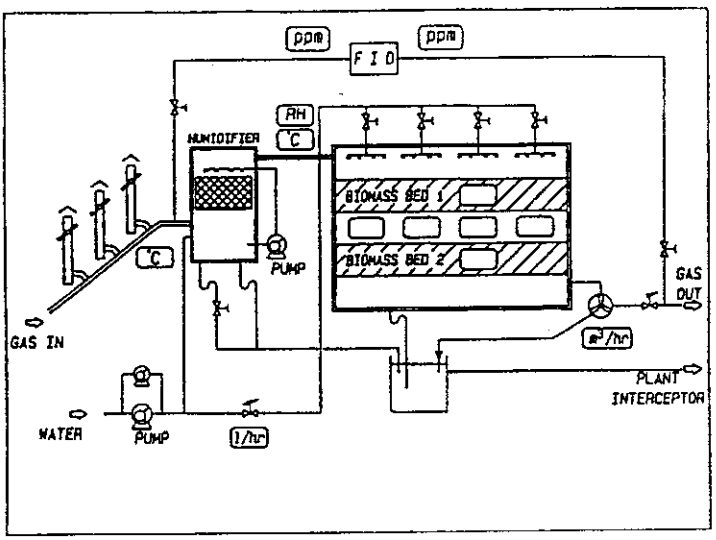


Figure 1-2 The biofilter installation at the Conoflex Packing Plant (Campbell and Connor, 1997).

The equipment illustrated above includes a humidifier tower which is used to humidify the exhaust air from a printing plant. The air is forced up the tower through the packing against a descending water stream. Water recirculation through the tower is achieved by means of a pump. The humidified air passes through two layers of packing beds containing biomass media, where solvent vapors are removed. When contaminated air passes through media, the contaminants can be adsorbed and biodegraded at the same time. After the filter material is saturated with contaminant, biological processes dominate in removing the VOCs (Devinny et al., 1999). The microorganisms growing in a biofilm on the surface of a packing medium or suspending in the water phase surrounding will degrade contaminants by oxidation reactions. They utilize the solvents as a source of energy and as a source of organic carbon for cell synthesis. They convert the contaminants into carbon dioxide, water and biomass. When the moisture content in the filter bed decreases, the overhead sprays can be activated to add water by an algorithm in the computer control system (Campbell and Connor, 1997). Pressure transducers were located at each level within the biofilter to monitor conditions and alert the operator if things go wrong. An exhaust stack 7 m in height was required to disperse residual VOCs in the exhaust air into the atmosphere (Campbell and Connor, 1997).

Campbell and Connor (1997) describe practical experience with a printing plant industrial biofilter in Australia. This used a filter bed medium containing mushroom compost to provide porous structure and microbial nutrients, activated carbon to capture high peak pollutant loads, polystyrene beads to assist in maintaining aeration and gas flow through the beds, and lime to act as a buffering substance. The biofilter contained two filter bed units mounted one above the other in a 10m x 17.5m x 5m insulated box (Figure 1-2). Each bed was packed to a depth of 1 meter with the mixture of bed materials. Gases containing VOCs in a solvent concentration range of 10-1500 mg/m^3, with temperatures of 10-40 °C and initial relative humidities of 10-20% were treated in this biofilter unit. Table 1-4 shows typical biofilter operating conditions for waste air treatment.

Table 1-4 Typical biofilter operating conditions for waste air treatment (Devinny et al., 1999).

Parameter	Typical value
Biofilter layer height	1-1.5 m
Biofilter area	1-3000 m^2
Waste air flow	50-300,000 m^3/h
Biofilter surface loading	5-500 m^3/m^2/h
Biofilter volumetric loading	5-500 m^3/m^3/h
Bed void volume	50%
Mean effective gas residence time	15-60 s
Pressure drop per meter of bed height	0.2-1.0 cm water gauge (max.10 cm)
Inlet pollutant and/or odor concentration	0.01-5 g/m^3
Operating temperature	15-30°C
Inlet air relative humidity*	40-60%
Water content of the support material	60% by mass
pH of the support material	pH 6-8
Typical removal efficiencies	60-100%
Typical elimination capacity	10-300 g/m^3/h

* Campbell and Connor (1997)

1.2.4.2 Flow Direction

Biofilters can be operated in down flow (Krailas and Pham, 2002; Xiao, 2002; Prado et al., 2005; Streese and Stegmann, 2003; Streese et al., 2005; Dorado et al., 2008; Mathur and Majumder, 2008) or up flow (Delhoménie et al., 2002a; Singh et al., 2006; Vergara-Fernández et al., 2007; Dumont et al., 2008); which is used depends on the application. Prado et al. (2005) showed a slight difference in performance between downflow and upflow biofilters. They suggested that the downflow operation could achieve better moisture distribution than upflow operation (Prado et al., 2005). However, in practice, most biofilters employ upflow.

1.2.4.3 Packing Materials

Packing materials play a key role in the performance of bioreactors for waste gas treatment and particularly in biofilter applications (Maestre et al., 2007). Their most obvious functions are as a support structure for an internal and/or external biomass film. Desirable features include a large surface area, a low bulk density, and a high void ratio to help reduce biomass clogging (Kennes and Thalasso, 1998). In addition, a suitable particle size and specific surface area, high moisture retention capacity, and a high buffering capacity (to prevent large pH fluctuations) are necessary to the biofilter (Dumont et al., 2008). Packing materials should have a large surface area for both microbial immobilization and pollutant mass transfer. Hence, bed particles should be relatively small (diameter of 1 to 5 cm) (Devinny et al., 1999). Commonly used packing materials include peat (Yoon and Park, 2002), soil (Delhoménie et al., 2002a), peanut shells (Ramírez-López et al., 2003), compost (Torkian et al., 2003; Rene et al., 2005), and activated carbon (Aizpuru et al., 2003a). The characteristics of these packing materials are described below (Devinny et al., 1999).

1.2.4.3.1 Peat

Peat is naturally acidic and hydrophobic. It does not naturally contain a large population of microorganisms. Peat requires inoculation, e.g. with activated sludge, and nutrient additions. It has a very low-pressure drop, but it does not endure, and it is difficult to control moisture levels.

1.2.4.3.2 Soil

Soil is inexpensive and plentiful. Moreover, it has a large indigenous microbial population, but it has a high pressure drop. Because its permeability remains low, it is necessary to employ large gas residence times and larger reactors.

1.2.4.3.3 Peanut shell

Peanut shells are better suited than other agricultural by-products, such as rice husk, coconut shells, cane bagasse, and maize stubble, to be used as biofilter media, since they have a regular particle size, a large specific surface area (268±6 m^2/m^3), a low bulk density (0.052±0.012), a neutral pH (6.8±0.04), a large number of water holding capacity (85%), sufficient nutrients for microbial growth, no significant clogging risk, and they showed limited pressure drops (Ramírez-López et al., 2003).

1.2.4.3.4 Compost

Compost has good water retention properties, neutral pH and suitable organic content. Composts from sources such as sewage sludge, yard waste and manure composts have been studied. If packing media consist only of compost, there will be a high pressure drop. So it should be mixed with various proportions (20-80%) of bulking agents (wood chips, perlite, etc.).

1.2.4.3.5 Granular activated carbon

Granular activated carbon (GAC) can be used either alone or as a bulking agent. It can be provided in any desired particle size. Typically, coconut shell carbon has 0.3 cm of cylinder height and 0.5 cm of diameter. GAC has excellent structural properties, uniform particle size, and good resistance to crushing. It has substantial water-holding capacity and a good surface for microbial attachment. GAC has no nutrients and no natural microbial population; therefore, it must be inoculated with microorganisms and provided with a nutrient supplement before being used.

Other packing media that have been used in biofilters include natural materials such as: bark (Dumont et al., 2008), rice husk, cane bagasse (Ramírez-López et al., 2003), pig manure and sawdust (Barona et al., 2004), and also synthetics such as: ceramics (Rene et al., 2005; Park and Jung, 2006), glass beads and polyurethane foam. Advantages of inorganic materials are their longer life time and ease of regeneration (Dumont et al., 2008). However, to

reduce the waste from agriculture and the packing material cost, use of agricultural by-products from the local area is preferred.

1.2.4.4 Bed Thickness

Increases in bed thickness cause increases in pressure drop and require the structure supporting the bed to be strengthened. High pressures towards the base of the bed increase the likelihood that structurally weak particles will collapse and that voids between particles at the base of the bed will close up, further increasing the pressure drop. From an industrial perspective the pressure drop through the bed has to be kept fairly low or the cost of moving air through the bed becomes unacceptably high.

1.2.4.5 Microbial Degradation Processes

1.2.4.5.1 The Microorganism Community

Generally the microbial community in biofilters is made up of a wide variety of species. This is to be expected as during its start-up period the biofilter is usually inoculated with activated sludge (Krailas and Pham, 2002; Ng et al., 2004; Prado et al., 2005) or compost (Campbell and Connor, 1997; Delhoménie et al., 2002a; Liu et al., 2002; Torkian et al., 2003) both of which contain a wide variety of aerobic microorganisms. However, in some laboratory studies, pure microbial cultures, or mixtures of a few known species have been used. Some researchers selected specific microorganisms from the laboratory for treating toluene, for instance Kiared (1997) used *Pseudomonas putida*, *Rhodococus* sp., and *Arthrobacter paraffineus*, Zilli et al. (2002) used *Acinetobacter* sp., Park and Jung (2006) used *P.putida*, and García-Peña (2008) used *P.variotii* in their respective biofilters.

During the start-up phase of biofilter operation the composition of the microbial community alters until the relative proportions of the bacterial species present stabilize at those best suited for the physical conditions (such as temperature) and for degrading the particular VOC or VOCs being treated. This process is known as acclimatization. The time taken to achieve an acclimatized microbial community is also affected by the time it takes for VOC levels in the biofilm to stabilize

Since it is very hard to determine the composition of microbial communities quickly and accurately, deciding when a microbial community has become fully

acclimatized has to be done indirectly. Usually it is assumed that an acclimatized community has developed once VOC removal levels have stabilized but this is not necessarily true.

One complicating factor is that slow growing fungal species are often a component of microbial communities in biofilters. For example, Dorado et al. (2008) isolated and identified *Aureobasidium* sp. and *Clonostachys* sp. in a biofilter treating air containing toluene. They concluded that these fungi played an important role in toluene removal. The removal efficiencies were higher when the fungal organisms appeared.

Uncertainties such as those described above may account for the fact that reported acclimatization times for biofilters vary widely. For example, <5 days at an inlet concentration of 0.75 g/m^3 and an empty bed residence time of 60 s (Torkian et al., 2003), 18 days at an inlet concentration of 0.30 g/m^3 and an empty bed residence time of 71 s (Chetpattananondh et al., 2005), and 25 days at an inlet concentration of 2.8 g/m^3 and an empty bed residence time of 150 s (Pineda et al., 2000) for biofilters treating air contaminated with toluene. Hence, we can infer that the microorganisms in each situation have different acclimatization times because of the differences in experimental and climatic conditions.

1.2.4.5.2 Biofilm

Microorganisms form a thin layer or biofilm on the surfaces of the packing material in the biofilter bed. This biofilm divides the packing media from the gas phase. Many processes occur there: mass transfer of contaminants and degradation products, degradation of VOCs by microorganisms, and microbial respiration and growth. Bacteria exist within a matrix of extracellular material (Acuña et al., 1999) such as exopolysaccharide gel (Devinny et al., 1999) or organic polymer gel. Since the biofilm is composed largely of water (90-99%) (Xiao, 2002; Morales et al., 2003), many of its physical properties, such as thermal conductivity, are similar to those of water. However, because of its gel like nature, properties like viscosity can differ considerably from those for pure water.

The bacteria present are immobilized in an aqueous biofilm attached to the packing material. The biofilm is often considered to consist of two compartments: the base film and the surface film. The base film tends to have quite well-defined structure and within it molecular (diffusive) transport is the dominant transport process. The surface film is a region of irregular thickness because outgrowths are filaments, giving a very rough surface with marked

irregularities in the transitional zone between the base film and the surrounding liquid (Xiao, 2002).

1.2.4.6 Transport Processes

Before the bacteria in the biofilm can degrade the VOCs these have to be transported to and absorbed into the biofilm. Mass transfer of VOC from air to the water phase has commonly been modeled in three steps (Figure 1-3). The bulk of the airflow is turbulent, and here the contaminant moves by convection. Near the air-water interface, the airflow becomes laminar, so that molecular diffusion becomes the only transport mechanism (Devinny et al., 1999). And then contaminants are transferred by diffusion from regions of high concentration at the air/water interface to regions of low concentration deeper into the biofilm/water phase.

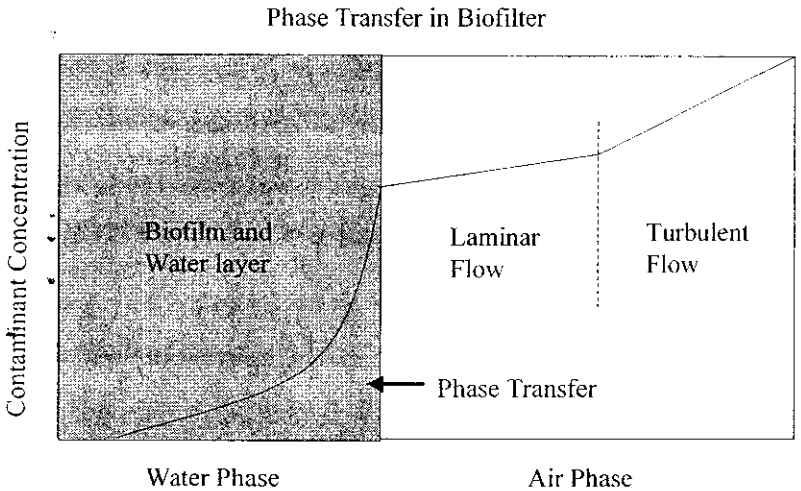


Figure 1-3 Phase transfer in biofilter (Devinny et al., 1999).

Within the biofilm, a number of processes occur simultaneously, including diffusion, adsorption, biodegradation and metabolic activities of the microorganisms. Contaminant molecules may be simply dissolved in the water, but they may also be adsorbed on the surface of water, biofilm, or the medium. For highly soluble contaminants such as methanol, methyl ethyl ketone, and acetone, the dissolved form may be dominant, and the volume of the water phase will have a considerable influence on the amount transferred from the air. For more hydrophobic contaminants, such as p-xylene, ethylbenzene, and toluene, the packing materials may be important adsorbers of contaminants (Devinny et al., 1999; Aizpuru et al., 2003a). In addition,

contaminants may also be taken up by living cells, or adsorbed on the surface of biofilm or organic matters (Figure 1-4) (Devinny et al., 1999). For all of the packing materials, biofilm exopolysaccharides and other biofilm compounds may compete for adsorption sites, reducing adsorption of the contaminant. Finally, adsorption has no effect on steady state conditions: the adsorbed material is simply an inactive reservoir that has no influence on treatment efficiency (Devinny and Ramesh, 2005).

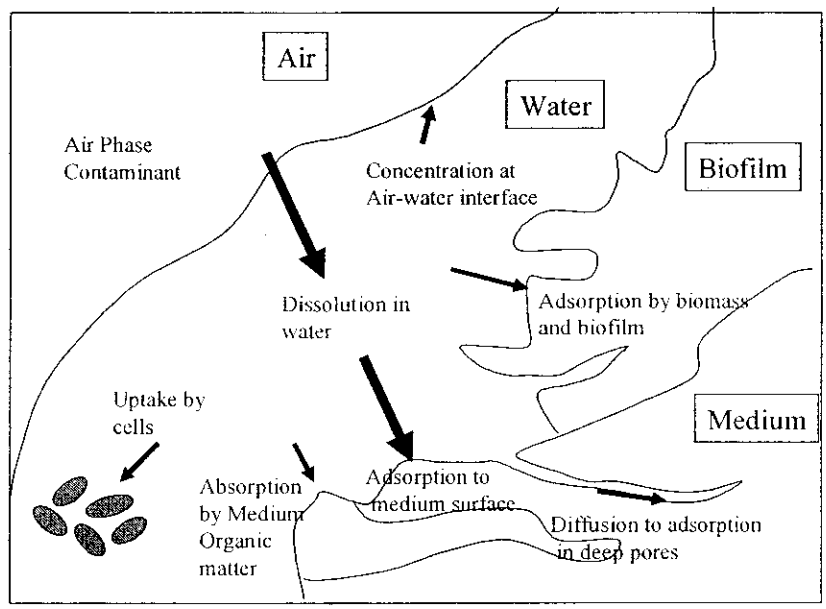


Figure 1-4 Adsorption in biofilters (Devinny et al., 1999).

1.2.4.7 Biodegradation Reactions

Microorganisms degrade VOCs by a sequence of oxidation reactions. The overall biodegradation reaction for VOCs can be represented as follows:

$$VOCs + O_2 \rightarrow CO_2 + H_2O + Biomass \qquad (1.1)$$

In practice, however, for all but the simplest compounds, the process involves the formation of a series of intermediate compounds. Contaminants in air may be energy-rich volatile organics or simpler inorganic compounds such as hydrogen sulfide or ammonia. These may be converted directly to end-products such as carbon dioxide, water, sulfate and nitrate by a single

organism. Or these compounds can be converted to an intermediate product and passed to another organism for further degradation. A complex or difficult-to-degrade compound may undergo several different transformations in several microbial species before it is eliminated (Devinny et al., 1999).

Equation 1.2 shows the overall degradation pathway for organic carbon compounds under aerobic conditions in a biofilm (Xiao, 2002).

$$Organic\ carbon\ compounds + O_2 \rightarrow CH_{1.4}O_{0.4}N_{0.2}(biomass) + CO_2 + H_2O \quad \textbf{(1.2)}$$

Other researchers have developed other formulas involving, for example, the main nutrient-containing substances in the reaction. Delhoménie et al. (2002b), for instance, preferred to represent the overall degradation reaction using the following (non-stoichiometric) expression:

$$C_7H_8 + O_2 + CO(NH_2)_2 \rightarrow CH_{1.8}O_{0.2}N_{0.5}(biomass) + CO_2 + H_2O \quad \textbf{(1.3)}$$

Equations 1.2 and 1.3 employ different empirical formulae for biomass. Yet others have been suggested; for example, Ramirez et al. (2008) used $CH_{1.99}O_{0.64}N_{0.11}$ for biofilm in a biofilter degrading methanol, and $CH_{1.98}O_{0.44}N_{0.18}$ for biofilm in the case where toluene was being biodegraded.

Since the biodegradation reactions are thermodynamically inefficient, significant amounts of energy are released in the biofilter in the form of heat. Much of this is taken up as latent heat of vaporization by water evaporating from the biofilter (Xiao, 2002). If this did not occur, temperatures in the biofilter would rise rapidly to levels that would inhibit bacterial activity.

1.2.5 Factors affecting Biofilter Performance

Many parameters affect the performance of biofiltration, such as solubility of the VOC in the liquid phase, biofilter water content (Auria et al., 2000; Devinny et al., 1999), temperature, pH, type of VOC (Mohseni, 1998) and VOC loading.

1.2.5.2 Water Content

The moisture content of the filter bed needs to be maintained at around 60% (Campbell and Connor, 1997). If the bed moisture content is too high, oxygen will be unable to

penetrate to all parts of the bed and sections of the bed will become anaerobic, reducing the amounts of VOC degraded and causing odour formation. Too low a moisture content results in sections of the biofilm drying out, with a corresponding reduction in biofilter performance. Maintaining an appropriate bed moisture content is difficult, especially in regions of the bed close to the biofilter inlet because biodegradation activity tends to be concentrated in such regions and the heat generated during biodegradation reactions leads to an increase in local water evaporation rates

Two approaches are used to maintain bed moisture content. The first is to ensure that the air entering the filter bed has as high a relative humidity as possible. It is for this reason that air is generally passed through humidifiers, such as that shown in Figure 1-2, before it enters the biofilter bed. The second is to spray water intermittently onto the filter bed surface (Ikemoto et al., 2006). As indicated by Prado et al. (2005) this is most effective in the case of downflow systems. The main difficulty with this approach is that there is no direct way of determining either the amount of water that should be added or how often additions should be made. As indicated above, adding too much water can lead to the development of anaerobic regions in the bed: also, excess water collecting beneath the filter bed may well need treating before it can be released, increasing plant capital and operating costs significantly.

1.2.5.3 Temperature

Operating temperatures also affect biofilters, influencing both reaction rates and the composition of the microbial community. 15-30°C is the range recommended by Devinny et al. (1999). Acuña et al. (1999) showed optimum temperature for toluene degradation is 30°C. In a given system the operating temperature will be determined by a range of factors such as VOC concentration, air flow rates and the amounts of water added. For instance, VOC degradation was inhibited at temperature above 40°C (Lu et al., 1999); however a biofilter may be operated at a temperature higher than 40°C if the incoming VOC concentration is maintained at a low level (Yoon and Park, 2002).

1.2.5.4 pH

Metabolite formation is possible when biodegradation occurs. Metabolites will undergo the same simultaneous diffusion/ biodegradation/ sorption processes as the original VOC. Acidic metabolites may need to be neutralized, and this is usually done by mixing limestone or

other pH buffer agents with the support material prior to the packing of the biofilter (Deshusses, 1997). One acidic metabolite is benzoic acid, which forms during toluene degradation (Xiao, 2002; Dorado et al., 2008). The importance of preventing a pH decrease is well illustrated by the work of Acuña et al. (1999) who found that the toluene consumption rate was greatest at pH 7-7.5, with the removal efficiency decreasing by about 70% when the pH was reduced to 5.6.

Carbon dioxide formed during biodegradation may also affect pH levels. Most diffuses back to the air/water interface and is transferred to the gas phase. However, some of it can also accumulate as carbonate (Deshusses, 1997; Dorado et al., 2008).

1.2.5.5 Type of VOC

Organic compounds such as alcohols, aldehydes, ketones, and some simple aromatics demonstrate excellent biodegradability. Some compounds that show moderate to slow degradation include phenols, chlorinated hydrocarbons, polyaromatic hydrocarbons, and highly halogenated hydrocarbons. Inorganic compounds such as hydrogen sulfide and ammonia are also biodegraded well (Devinny *et al.*, 1999). Many industries produce air streams contaminated with mixtures of VOCs. Biofiltration has been successfully applied to treat mixtures of hydrophilic and hydrophobic compounds (Zarook et al., 1997; Mohseni and Allen, 2000; Yoon and Park, 2002; Torkian et al., 2003; Singh et al., 2006). However, in some cases biodegradation rates of particular VOCs in mixtures can be much lower than rates achievable when the VOC concerned is the only one present. For example, both toluene and chlorobenzene are easily degraded individually, but in mixtures toluene degradation is inhibited if chlorobenzene is degraded by the same organism (Aizpuru et al., 2003a). Hydrophilic methanol exerts a similar impact on the metabolism of hydrophobic alpha-pinene (Mohseni and Allen, 2000). The removal of toluene was inhibited by the presence of ethyl acetate (Liu, 2002).

1.2.5.6 Loading

The performance of a biofilter is impacted on by both the air flow rate and the VOC concentration. Air flow rate affects processes in the biofilter in a number of ways. Higher air flow rates and higher bed pressure drops lead to higher air blower costs. Also higher air flow rates and lower residence times of the air in the biofilter potentially decrease opportunities for VOC transfer to the biofilm. However, higher flow rates potentially increase mass transfer rates across the air/biofilm interface.

VOC concentration also affects processes. For a biofilter of a given bed volume, the VOC inlet load, in $g/m^3/h$, is determined by the product of air flow rate and VOC concentration and has an important influence on the performance of the biofilter. It also influences rates of microbial acclimatization. At low loadings the biofilter has the capacity to absorb and degrade most of the VOC entering the biofilter but as the inlet load increases the capacity of the biofilter to degrade the incoming VOC decreases, leading to a fall off in biofilter performance. Fluctuations in VOC concentration also affect the efficiency of a biofilter.

Fluctuations in air flow rates and VOC concentrations occur frequently in industrial plants, particularly in those such as printing works that employ batch processes (Campbell and Connor, 1997). Such fluctuations, which can often be quite rapid, can have quite an impact on microbial communities in biofilters and hence on biofilter performance. Hence experimental studies often include components where shock loads are applied to biofilters to determine how resilient they are and how rapidly they adapt to changes in operating conditions.

Practical problems associated with intermittent operation and sudden fluctuations in the inlet concentration and the air flow rate are discussed by Rene et al. (2005). An industrial biofilter needs to be able to handle such adverse situations in order to provide maximum removal of the target contaminant. How well it does this, however, depends on the stability and distribution of the biomass in the biofilter. Rene et al. (2005) studied the impact of shock loads on a biofilter treating air containing toluene. When they changed the concentration from 0.09 to 1.4 g toluene/m^3 at an air flow rate of 0.06 m^3/h, the removal efficiency reduced from 92% to 63%. The results of their study indicate that although removal efficiencies fell, EC values increased. Hence the biofilter was able to maintain a good performance even though experiencing such a large jump in concentration.

Not dissimilar results are reported by Kim et al. (2007) who studied the removal of NH_3 in a biofilter using synthetic materials as packing media..The stability and response of the microorganisms to sudden changes in biofilter conditions was investigated. When the inlet load of NH_3 was increased from 0.05 to 6 g $NH_3/m^3/h$, a decrease in the removal efficiency from 100% to about 60% resulted (but as in the previous case EC values would have risen).

1.2.5.7 Excess Biomass

Biodegradation reactions lead to the creation of substantial amounts of new cell biomass. In activated sludge, where aerobic biodegradation reactions not dissimilar to those in biofilters occur, around half of the carbon in the degraded organic compounds ends up in new cell biomass (Banerji, 2005; Hyperion Treatment Plant, 2005).

This biomass tends to gradually fill the voids in the biofilter bed, increasing the pressure drop and decreasing the surface area of biofilm in contact with the air. Initially the biomass growth has only a small effect on biofilter performance but a point is eventually reached where the pressure drop rises steeply and biofilter performance deteriorates (Xi et al., 2006; Dorado et al., 2008).

Once such a condition occurs excess biomass needs to be removed from the biofilter. There are two approaches that can be used to do this, bed stirring and bed washing, which permit the removal of parts of the excess biofilm without affecting the performance (removal efficiency more than 80%) (Delhoménie et al., 2003).

1.2.5.8 Nutrient Levels

If biomass growth is not to be limited, adequate supplies of nutrients need to be available to the microorganisms in the biofilm. Recognising this, Maestre et al. (2007) suggested that phosphate and ammonium additions, as nutrients in the liquid added to the biofilter to keep the bed materials moist, also lead to an improved performance in the biofilter.

1.2.6 Biofiltration Terminology

To describe the performance of biofiltration clearly, general terminology pertinent to the field should be well defined. Important design or operating characteristics in biofiltration are the Inlet Load (IL) and Empty Bed Residence Time (EBRT) while the pollutant degradation performance of the biofilter can be expressed in terms of the pollutant Removal Efficiency (RE) and the Elimination Capacity (EC).

1.2.6.1 Empty Bed Residence Time

EBRT relates the flow rate to the size of the biofilter. It is defined as the empty bed filter volume divided by the air flow rate:

$$EBRT = \frac{V_f}{Q} \qquad (1.4)$$

2.4 Nutrient Solution

Nutrient solution was periodically distributed over the bed upper-surface to maintain bed moisture content at a suitable level and to provide those nutrients necessary for the growth of microorganisms present in the biofilter. The composition of the nutrient solution is shown in Table 2-1 (Aizpuru et al., 2003b; Auria et al., 2000; Kim et al., 2007).

Table 2-1 Composition of one liter of the nutrient solution.

Compounds	Amount
KH_2PO_4	0.91 g
$Na_2HPO_4.12H_2O$	2.39 g
KNO_3	2.96 g
$(NH_4)_2SO_4$	1.97 g
$NaHCO_3$	1.5 g
$FeSO_4.7H_2O$	0.2 mg
$MgSO_4.7H_2O$	2 mg
$MnSO_4.H_2O$	0.88 mg
$Na_2MoO_4.2H_2O$	1 mg
$CaCl_2$	3 mg

where V_f= filter bed volume (m^3), Q= the air flow rate (m^3/h)

The empty bed residence time overestimates the actual treatment time. The medium occupies a substantial fraction of the biofilter, reducing the volume within which the air flows and shortening the contact time. Even so, it is a commonly used parameter because it is easily calculated (Devinny et al., 1999).

1.2.6.2 Mass Loading Rate (volumetric)

The mass loading rate (either surface of volumetric) is the mass of the contaminant entering the biofilter per unit area or volume of filter material per unit time, often expressed as g/m^3 of filter material/h. Because flow remains constant through a filter bed, the mass loading along the length of the biofilter bed will decline as the contaminant is removed. The mass loading rate for a system is defined below (Devinny et al., 1999).

$$mass.loading.(volumetric) = \frac{Q \times C_{in}}{V_f} \qquad (1.5)$$

where C_{in} = inlet concentration (g/m^3).

1.2.6.3 Removal Efficiency

RE is often used to describe the performance of a biofilter. It is the fraction of the contaminant in the inlet air that is removed by the biofilter, expressed as a percentage:

$$RE = \frac{C_{in} - C_{out}}{C_{in}} \times 100 \qquad (1.6)$$

where C_{ini} = inlet concentration (g/m^3); C_{out} = outlet concentration (g/m^3).

RE is an incomplete descriptor of biofilter performance because it varies with contaminant concentration, airflow, and the biofilter size and only reflects the specific conditions under which it is measured. The elimination capacity (EC) (see below) allows for direct comparison of the results of two different biofilter systems because the volume and flow are normalized by definition: however, EC is also a function of input concentrations. Effluent concentration (or %removed) is still commonly used as the goal of regulatory compliance (Devinny et al., 1999).

1.2.6.4 Elimination Capacity

EC is the mass of contaminant degraded per unit volume of filter material per unit time. A typical unit for EC is g/m^{3}of filter material/h. The overall elimination capacity is generally defined as in Equation 1.5 (Devinny et al., 1999).

$$EC = \frac{(C_{in} - C_{out}) \times Q}{V_f} \qquad (1.7)$$

Elimination capacity can only be equal to or less than the mass-loading rate. When the elimination capacity equals the loading rate, the biofilter is removing 100% of the contaminant load in the air (i.e. RE = 100%). This tends to happen only under low loading rate conditions. As loading rate is increased, the elimination capacity/loading rate ratio begins to decrease, i.e the RE value falls below 100 %. On a plot of elimination capacity versus loading rate, the point at which the EC graph separates from the RE = 100 % line is called the critical load or critical elimination capacity. As the loading rate is further increased continuously, EC values plateau at a maximum overall elimination capacity (EC_{max}). According to Devinny et al. (1999) EC has some dependence on contaminant concentrations in the inlet air and on gas residence time in the biofilter.

1.2.7 Previous Investigations

1.2.7.1 Methanol

Experimental studies dealing with the removal of pure methanol from air are given in Table 1-5.

Table 1-5. Comparison of methanol treatment results.

Researchers	C_{in} (g/m^3)	Q (m^3/h)	RE_{max} (%)
Krailas and Pham (2002)	0.46-8.41	0.06-0.17	>90
Prado et al. (2005)	2.43-2.78	0.13-0.26	>99

Researchers	C_{in} (g/m^3)	Q (m^3/h)	RE_{max} (%)
Ramirez et al. (2008)	0.8-4.3	0.25-3.00	N/A

N/A data is not available

In the first of these investigations, the packing materials were sterilized mushroom compost, pall rings, and activated sludge. These enabled a high removal efficiency (>90%) to be attained in the downward flow biofilter used in this study (Krailas and Pham, 2002).

In the second investigation the packing materials were lava rock and activated sludge. Inlet loads were 120-280 $g/m^3/h$, with inlet methanol concentrations of 2-6 g/m^3; loadings were increased stepwise during the experimental period with the EBRT being progressively reduced from 91s to 48s. Operating the biofilter in downflow gave slightly better results than running it in upflow. The removal efficiencies were 92.3±19.4% at inlet load of 102.4±18.6 $g/m^3/h$ for downflow mode and 80.8±16.6% at inlet load of 105.1±27.4 $g/m^3/h$ for upflow mode (Prado et al., 2005). They also showed that no significant adsorption occurred on the support, proving that the elimination was due to the action of the microbes and suggested that use of insufficient inoculum lengthened the biofilter start up period considerably. They tried using various biomass concentrations (3.5, 0.35, and 0.035 g VSS/liter) in the inoculum added to the biofilter. The inlet methanol concentration was 2.6 g/m^3. Their results show that the concentration of biomass in the inoculum and the extent of its adaptation to the pollutant may dramatically affect the performance and start-up of a biofilter packed with an inert filter bed. High biomass concentrations and an adaptation step of the inoculum reduce the start-up period and improve biofilter performance during operation.

1.2.7.2 Toluene

A considerably larger number of experimental studies dealing with the removal of toluene from air streams were located, such as Acuña et al. (1999), Singh et al. (2006), Xi et al. (2006), Vergara-Fernández et al. (2007), and Dorado et al. (2008). In these studies a wide range of packing materials was used, e.g. peat moss by Acuña et al. (1999), yellow-gram stalk by Singh et al. (2006), compost, wood chip, propylene spheres and activated sludge by Xi et al. (2006), sea shells, sewage sludge and compost by Vergara-Fernández et al. (2007) coconut fiber or pine leaves by Dorado et al. (2008).

Of particular interest to this investigation were the studies using plant-derived packings such as yellow-gram stalk, coconut fiber and pine leaves; in their study using yellow-gram stalk, Singh et al. (2006) noted that it had a lower stability than more conventional packing materials and that the bed height dropped by 8 cm out of a total bed height of 0.7 m when run with an air flow rate of 0.24 m^3/h over an operating period of 50 days. The ranges of inlet concentrations, the maximum removal efficiencies and the air flow rates for each of the studies are shown in Table 1-6. The magnitudes of the inlet concentration and the air flow rate had a considerable effect on the removal efficiency. The removal efficiency in cases where biofilters were operated in the low concentration ranges, and at low air flow rates, was high. The highest toluene loading of 1 $g/m^3/h$ was used by Vergara-Fernández et al. (2007); here a 98% removal efficiency was achieved at the air flow rate of 0.12 m^3/h. They used sea shells as a packing media, mixed with compost and sewage treatment plant sludge. The toluene inlet load was 32–95 $g/m^3/h$ while the elimination capacity for toluene showed a linear variation with respect to inlet load over the range of 32–85 $g/m^3/h$. pH values were higher than 7 most of the time. It was observed that in the first few days the pH was over 8.0; this was ascribed to the basic nature of the sea shells and the low level of biological activity during the start-up of the system. The maximum pressure drop was 204 mmH_2O/m of the biofilter. This value exceeded the suggested value of 60 mmH_2O. There were no compaction problems in the operation of the system. In this case, the increase in the values of the pressure drop coincided with the addition of nutrients to the system, indicating that the pressure differences were produced in part by the clogging of the support material due to an increase in its moisture content.

Table 1-6 Comparison of toluene treatment results.

Researchers	C_{in} (g/m^3)	Q (m^3/h)	RE (%)
Delhoménie et. al. (2002a)	0.6-2.6	0.4-1.0	20-99
Rene et al. (2005)	0.5-2.3	0.024-1.144	60-90
Xi et al. (2006)	0.2-2.0	0.27-0.54	30-99
Vergara-Fernández et. al. (2007)	1-3.2	0.12-0.73	93-98
Ramirez et al. (2008)	0.4-3.5	1.00	N/A

N/A: data is not available

Not only did Ramirez et al. (2008) study methanol but they also studied toluene. The biofilters were packed with clay spheres. The ranges of inlet concentrations and air flow rates were 0.8-4.3 g methanol/m^3 and 0.25-3 m^3/h for removal of methanol and 0.4-3.5 g toluene/m^3 and 1 m^3/h for removal of toluene. Their biofilters performed best when supplementary nitrogen was added; the maximum elimination capacities were 80 g methanol/m^3/h and 65 g toluene/m^3/h.

Two effects observed in biofilters treating gases containing toluene are falls in pH and high pressure drops (Dorado et al., 2008; Xi et al., 2006). Dorado et al. (2008) observed a fall in pH to around 3 and attributed this to the presence of benzoic acid, which as discussed earlier, is one of the intermediates in the toluene decomposition pathway. Their reactors packed with coconut fiber or pine leaves were initially inoculated with activated sludge from a municipal wastewater treatment plant. The average inlet load was 77 g/m^3/h and the biofilter was operated at an EBRT of 60 s. Xi et al. (2006) studied the effect of operating conditions on the long-term performance of a biofilter treating gaseous toluene. Their biofilter bed was composed of wood chips (1-4 cm in length and 0.01-0.03 cm in width), propylene spheres (2.5 cm in diameter), and activated sludge. The pressure drop at the inlet section was higher than that at the outlet section. Both an increase in the pressure drop and a decrease in toluene removal capacity occurred simultaneously during the operating period, which indicated that an increase in the pressure drop was being induced by excess biomass accumulation. Up until day 50, the pressure drop was very low, between 5 and 7.2 mmH_2O/m of biofilter height, and stable. Then, it rose quickly and reached about 67 mmH_2O/m by day 65. The excess biomass accumulation was controlled by reducing the inlet concentration. A 90% removal efficiency was then obtained. After day 100, the pressure drop rose again and reached more than 206 mmH_2O/m. Subsequently, the excess biomass was removed.

As was also discussed earlier, fungal activity was important in the biofilter operated by Dorado et al. (2008). They demonstrated the presence in the biofilter of *Aureobasidium* sp. and *Clonostachys* sp. and, based on specific growth rate considerations, showed that removal efficiencies were higher when the fungal organisms appeared. Before fungal appearance, the average volumetric maximum growth rate (calculated assuming Monod-type kinetics) was 815 g/m^3/h. Then the volumetric maximum growth rate went up to 5000 g/m^3/h, indicating that the fungal organisms had a significantly better capacity to biodegrade toluene than

bacteria. This is reflected by the change in kinetic parameters following the evolution from bacterial to fungal operation. Estimates of the half-saturation constant (K_m) yielded a low value of 0.21 g/m^3 during the period of fungal appearance while, K_m in the period of bacterial dominance was much higher, at 5.01 g/m^3. These results demonstrated a higher affinity between toluene and fungi than between toluene and bacteria.

1.2.7.3 Methanol/Toluene Mixtures

The treatment of mixtures of methanol and toluene has not previously been studied. However there have been several investigations where mixtures of methanol or toluene with another VOC have been studied. Information on these studies is provided in Table 1-7. Mohseni and Allen (2000) showed that the presence of methanol, a hydrophilic and easily biodegradable compound, suppressed the growth of the α-pinene degrading microbial community, thereby reducing the α-pinene removal capacity of their biofilters. However, methanol was not affected by the presence of α-pinene and its removal rate from the air stream remained unchanged under different α-pinene loading rates. Jin et al. (2007) showed that pH had little effect on methanol removal when treating a mixture of methanol and hydrogen sulfide. The research of Zhang et al. (2007) also showed effective elimination of methanol in a mixed VOCs system. Liu et al. (2002) studied a mixed VOCs system comprising toluene and ethyl acetate. In this case toluene could be treated more effectively than the ethyl acetate.

Table 1-7 Comparison of mixed VOCs treatment results.

Researchers	Mixed VOCs system					
	1st VOC			2nd VOC		
	Substance	IL_{max}	EC_{max}	Substance	IL_{max}	EC_{max}
Mohseni and Allen (2000)	Methanol	280	250	α-pinene	90	45
Jin et al. (2007)	Methanol	N/A	236	Hydrogen sulfide	23.8	6.4
Zhang et al. (2007)	Methanol	67	43	Dimethyl sulfide	5.9*	1.8*
Liu et al. (2002)	Toluene	60	50	Ethyl acetate	250*	150*

*estimated from graph

N/A data is not available

1.3 Objectives

On the basis of the overall project aim, coupled with the information obtained from a review of existing literature, the following specific objectives were decided on for the project:

1.3.1 To set up three sets of biofilter systems, each comprising one biofilter packed with peanut shells and one packed with palm shells.

1.3.2 To study the performance of the three biofilter systems when used to remove pure toluene, pure methanol and mixtures of toluene and methanol from air under a range of conditions. A separate biofilter system was to be used for each VOC/VOC mixture.

1.3.3 To study the impact on VOC removal efficiency of the three biofilter systems during shock loading conditions.

1.3.4 To develop and validate a macrokinetic model predicting VOC elimination rate in the biofiltration system.

1.4 Research Benefits

1.4.1 Facilitating the use of low-value agricultural by-products such as peanut shells and palm shells as packing material for biofilters could help decrease agricultural waste problems, increase their market value and ultimately benefit agricultural by-product producers.

1.4.2 Acquisition of data on elimination rates of toluene, methanol and methanol/toluene mixtures in peanut shell- and palm shell-packed biofilters.

1.4.3 Development of knowledge in the field of waste air treatment by biofiltration, especially the knowledge necessary for biofilter design based on theoretical concepts and on mathematical models.

1.4.4 Acquisition of basic information and knowledge necessary for biofilter design that can be applied on an industrial scale; this could help stimulate public awareness of and interest in using this environmentally friendly waste air treatment technique.

1.5 Research Scope

1.5.1 The biofilter media to be studied are agricultural by-products, peanut shells and palm shells mixed with the activated sludge from a wastewater treatment plant.

1.5.2 The VOCs to be studied are methanol and toluene as they are the most commonly used VOCs. Methanol is a hydrophilic VOC while toluene is a hydrophobic VOC. The biofilter systems are used for study of removal of pure toluene, pure methanol and mixtures of toluene and methanol.

Chapter 2

Materials and Methods

2.1 VOCs

As explained in the previous chapter, the VOCs selected for study in this project are methanol and toluene. These are commonly produced VOCs in many industries and processes. Methanol is used as a representative of hydrophilic VOCs while toluene is a representative of hydrophobic VOCs. Analytical reagent grade methanol and toluene, obtained from Lab-Scan, Ireland, were used in this project.

2.2 Packing Media

As discussed in the previous chapter, peanut shells and palm shells were selected as the packing media for use in this study. This was in part because Ramírez-López et al. (2003) had suggested that the peanut shells were a good packing media. Peanut shells are readily available in Thailand; in 2008, the peanut-growing area was 390 km^2 (Office of Agricultural Economics, 2008) and the average production was $1.66*10^5$ kg/km^2 (Department of Agricultural Extension, 2009) over the period 2003-2007. Thus, the annual domestic production of peanuts is estimated to be $6.47*10^4$ ton (Office of Agricultural Economics, 2008; Department of Agricultural Extension, 2009). The shells have to be removed prior to further processing them into finished goods, hence large amounts of peanut shells as agricultural wastes are available. Prices vary from one area to the next; in 2009 the local price of peanut shells was 6 baht/kg for assorted sizes. To obtain the peanut shells used in the present study, raw peanuts were bought in the fresh produce market in Songkhla province, the mud was rinsed off using tap water, and the nuts were manually shelled to get the peanut shells.

In 2008, palm oil plantations in Thailand covered an area of 5797 km^2 (Office of Agricultural Economics, 2008) and produced, on average, $1.17*10^7$ ton (Suratthani Oil Palm Research Center, 2009). The cost of palm shells varies from place to place but is generally around 1.5-2 baht/kg for assorted sizes.

The costs of peanut shells and palm shells are much less than those for more conventional packing media such as suitably sized granular activated carbon, which costs up to 70 baht/kg in Thailand. In biofilters, the cost of bed media is a major component of the overall capital cost; therefore the low prices of peanut and palm shells make them much more attractive as packing media than activated carbon. It should be noted that, although peanut shells and palm shells are both locally available materials, their centers of production are different. Peanut shells are most easily available in the north and northeast of Thailand while the palm shells are found only in the south. Hence the location of VOC-producing industries will also affect decisions on which of the above wastes will be preferred as packing media.

2.3 Biofilter Apparatus

Six separate identical bench-scale biofilters made of acrylic were used to treat air contaminated with methanol, toluene, or mixtures of both. Each biofilter column had an internal diameter of 0.08 m and a height of 1.2 m. As shown in Figures 2-1 and 2-2, each biofilter consisted of 5 flanged sections connected in series, namely the column base, three identical segments (with a height of 0.29 m) packed with media and microorganisms, and a top section. Adjacent sections were separated by a sieve plate with a diameter of 8.0 cm and a hole diameter of 0.5 cm fixed by 8 screws. O-rings were used to prevent air leaks through the flanged joints. The structure of the biofilter is described in Figure 2-1 and the function of each component is given in Figure 2-2. The base of the column served as a reservoir for water, nutrients and biomass; it was also where VOC laden air was introduced. A peristaltic pump (Masterflex console drive No.7520-47, Cole-Parmer Instrument Company, USA) was used to eliminate liquid from this section all the time. The second, third and fourth sections were packed with media to a height of 0.22 m; it was here that biodegradation of the VOCs took place. Each biodegradation section had 4 ports for: gas and media sampling to investigate the physical characteristics of media; measurement of pH, temperature, relative humidity and VOC concentration; and also for addition of water to prevent drying out of the packing media. The top section, with a height of 0.11 m, was used primarily for nutrient and water addition. This top section was provided with a buffer layer of packing material with a height of 0.050 m to slow down the water flow rate into section 4 and to achieve better water distribution across the column cross-section.

2.4 Nutrient Solution

Nutrient solution was periodically distributed over the bed upper-surface to maintain bed moisture content at a suitable level and to provide those nutrients necessary for the growth of microorganisms present in the biofilter. The composition of the nutrient solution is shown in Table 2-1 (Aizpuru et al., 2003b; Auria et al., 2000; Kim et al., 2007).

Table 2-1 Composition of one liter of the nutrient solution.

Compounds	Amount
KH_2PO_4	0.91 g
$Na_2HPO_4.12H_2O$	2.39 g
KNO_3	2.96 g
$(NH_4)_2SO_4$	1.97 g
$NaHCO_3$	1.5 g
$FeSO_4.7H_2O$	0.2 mg
$MgSO_4.7H_2O$	2 mg
$MnSO_4.H_2O$	0.88 mg
$Na_2MoO_4.2H_2O$	1 mg
$CaCl_2$	3 mg

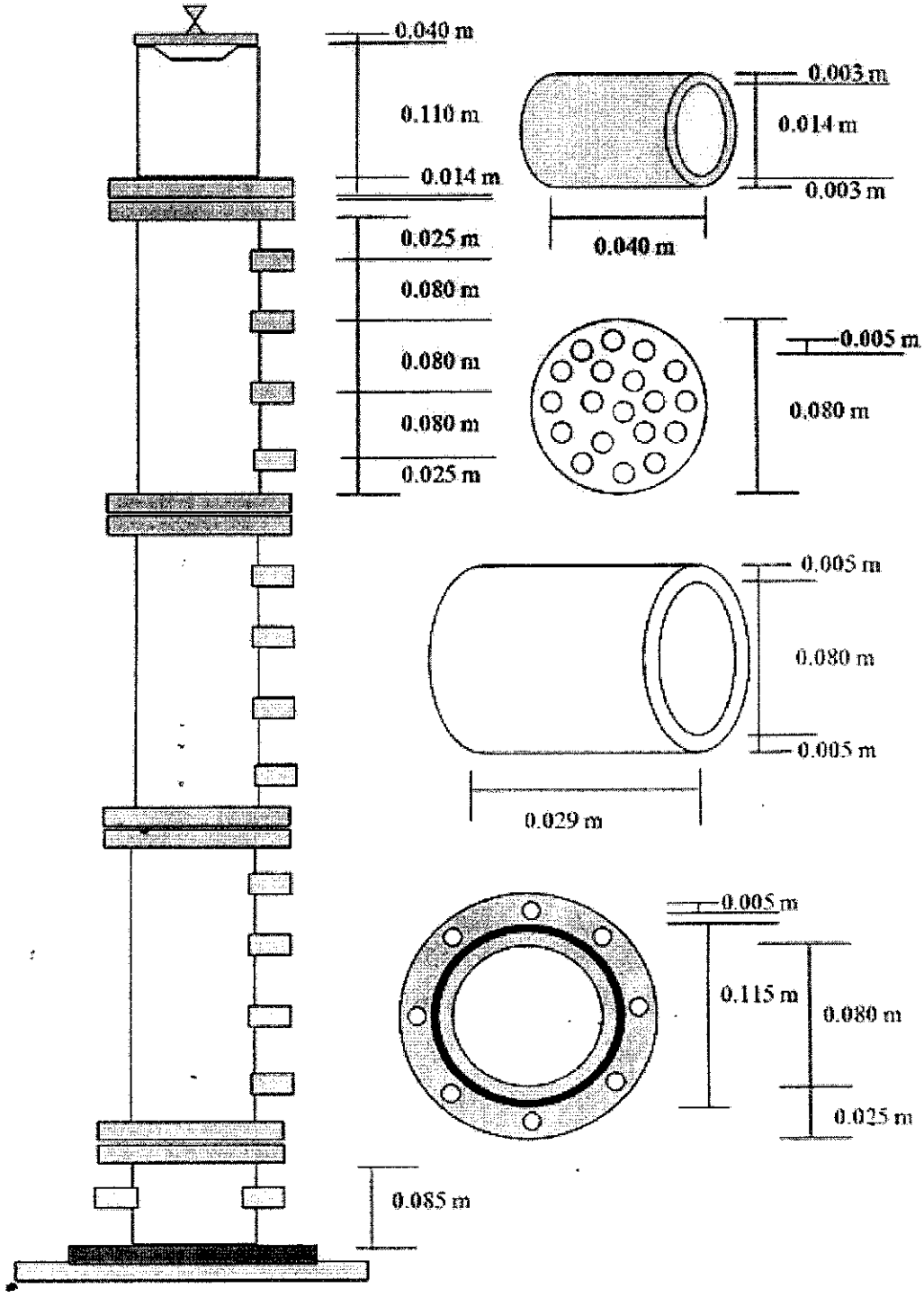


Figure 2-1 The structure of the biofilter column.

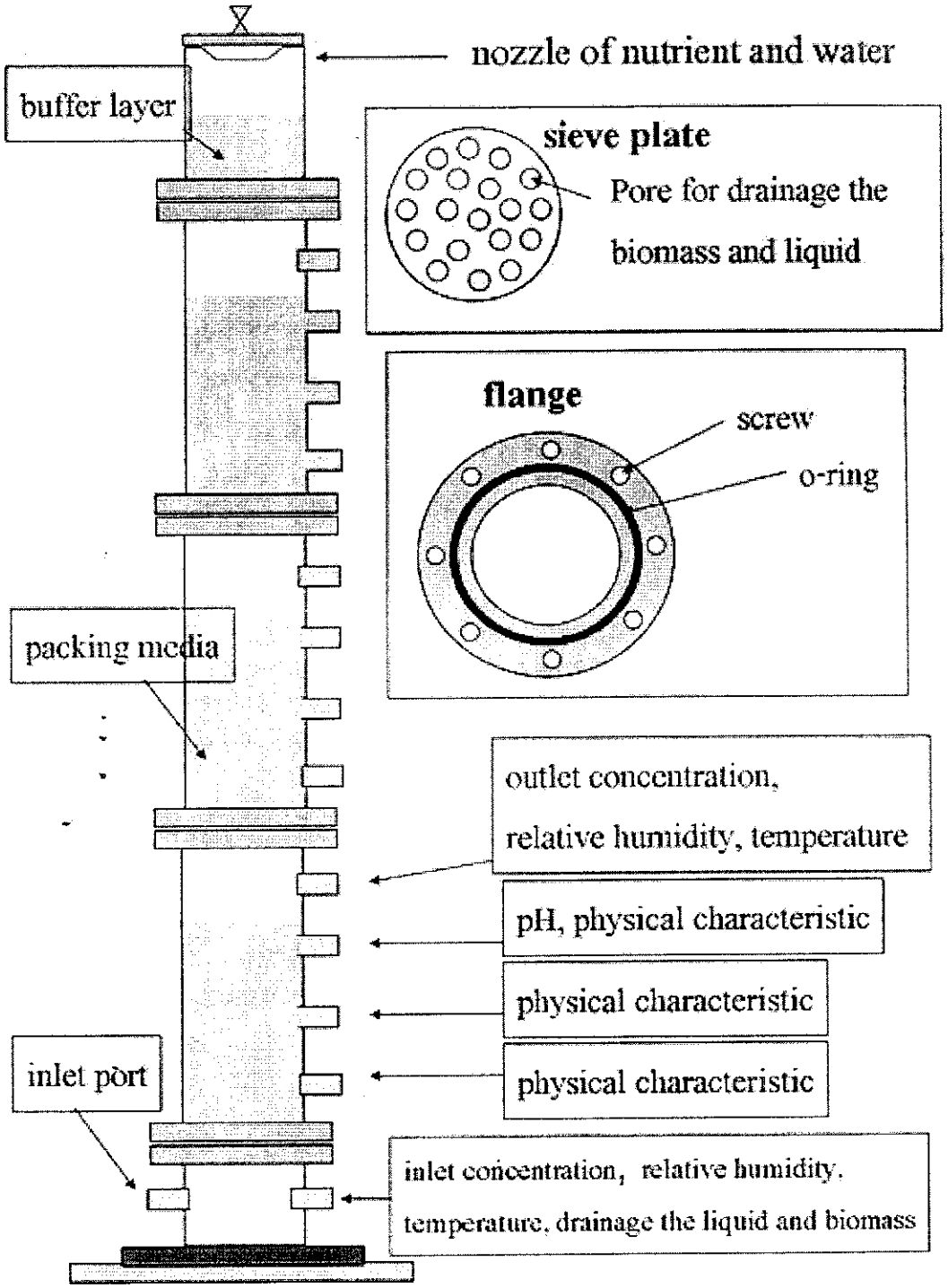


Figure 2-2 The function of each part in the biofilter column.

2.5 Methodology

2.5.1 Preparation of Packing Media

Activated sludge was obtained from Man A Frozen Food Co., Ltd., which is a sea food manufacturing plant in Songkhla province. It was fed with the relevant VOC for 3 days in the ratio of VOC/nutrients/activated sludge 0.001/0.2/6.5 v/v/v. The peanut shells or palm shells, in the size range of 0.5-1 cm, were immersed in activated sludge in a ratio of 1:2 v/v (Aizpuru et al., 2002) for 24 hours to become saturated, so that further particle swelling in the biofilter was avoided (Delhoménie et al., 2002a). After that, these packing media were shaken to remove excess activated sludge and then transferred into the relevant column(s). The excess water was eliminated using the peristaltic pump.

Initially, the packing media just looked wet. However, the biofilm gradually developed and after 2 or 3 weeks the packing media looked more like jelly, as shown in Figure 2-3.

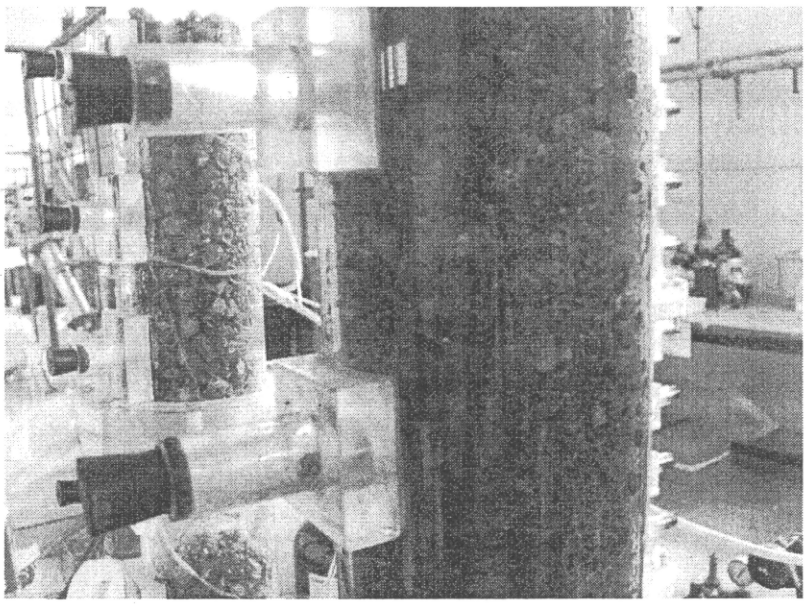


Figure 2-3 Packing media, peanut shells (left) and palm shells (right) in the biofilter column.

2.5.2 Control of VOC Concentration and Humidity

Figure 2-4 shows a diagram of the experimental set up. The synthetic VOC- containing waste gas stream fed to the biofilter was produced by mixing two different air streams from a compressor, one passing through 4 humidifiers in series to raise the relative humidity above 90%

(Prado et al., 2005) and the other passing through an impinger bottle containing pure VOC (Figure 2-5a). Each humidifier was made of a PVC pipe with an internal diameter of 0.037 m and a height of 0.540 m. The humidifiers were filled with water to a height of 0.450 m. The impinger bottle had an internal diameter of 0.053 m and a height of 0.2 m (VN Labglass, Thailand). The impinger bottle was filled with VOC to a height of 0.010 m.The concentration of VOC in the air entering the biofilter was varied by using rotameters (Cole-Parmer Instrument Company, USA or Omega Engineering, Inc.) to modify the flow rates of air passing through the humidifiers and the impinger bottle. In the case where a mixture of VOCs was used, 2 impinger bottles were employed, one containing methanol and the other containing toluene (Figure 2-5b). The air streams were mixed using a three-way mixing valve (Figure 2-6) before being introduced into a biofilter.

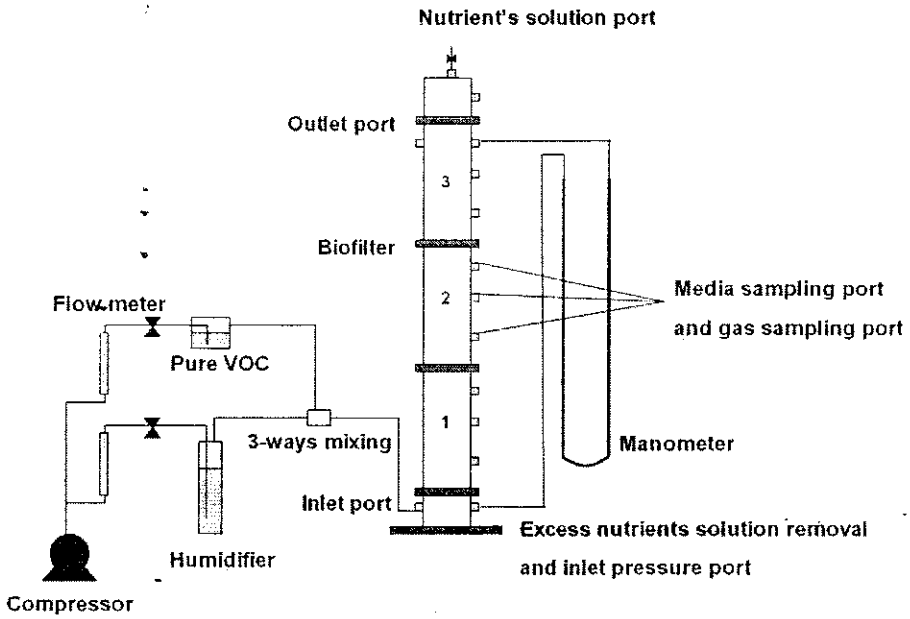
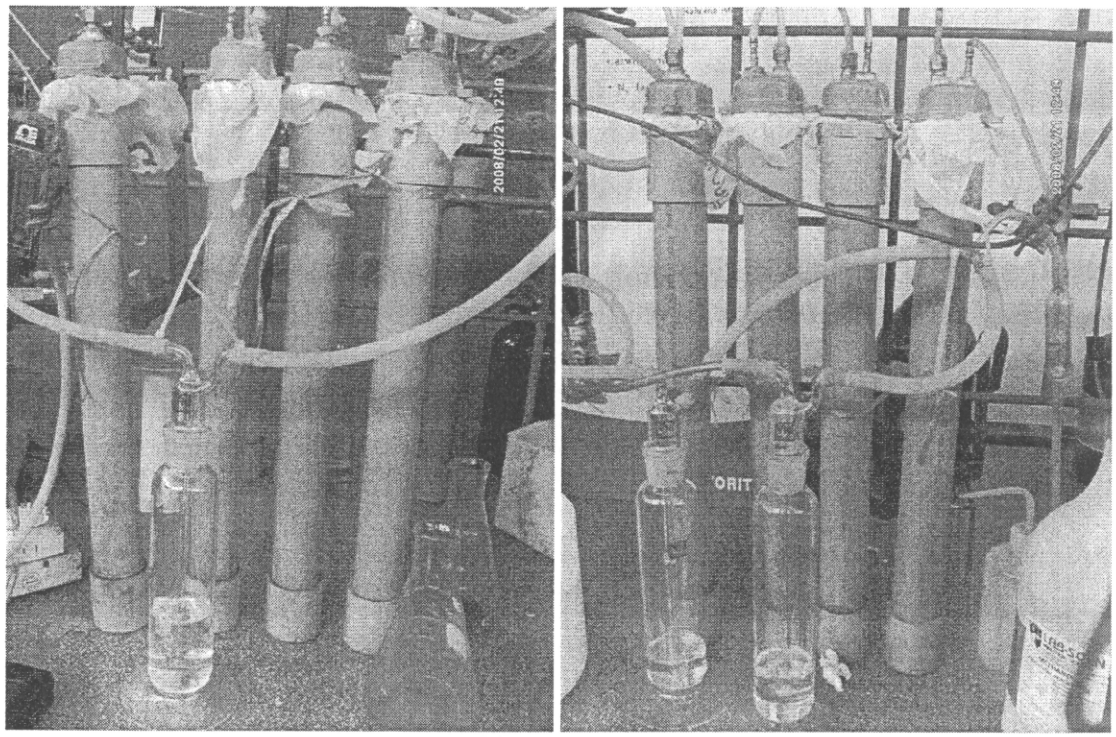


Figure 2-4 Experimental set up.



(a) (b)

Figure 2-5 Humidifiers and impinger bottles used in pure VOC system (a) and mixed VOCs system (b).

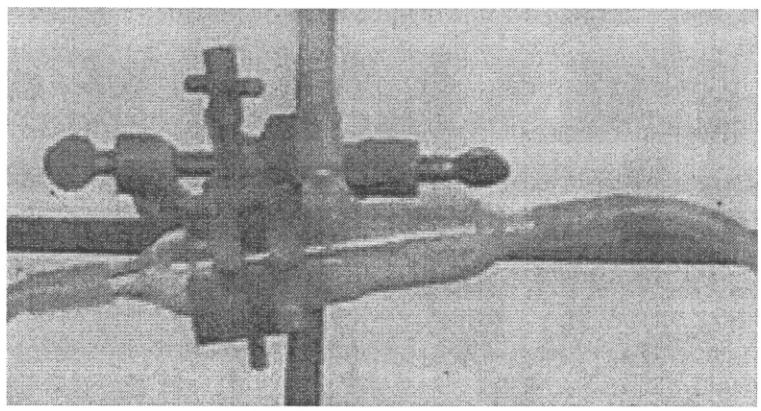


Figure 2-6 Three-way mixing.

2.5.3 Biofilter Operating Conditions

The synthetic waste air stream was introduced at the base of the biofilter and flowed upwards, leaving at the top. Figure 2-7 shows the mixed VOCs biofilter system. The biofilters were operated continuously for 267 days for pure methanol systems and mixed systems, and for

214 days for pure toluene systems. During experiments the biofilters were subjected to a series of step load changes. The VOC concentrations and contaminated air feed rates were increased stepwise, so that the mass loading changed proportionally.

The experimental programs were split into 9 successive stages, A to I; the operating conditions during these stages are summarized in Table 3-2. Stage A was a start up period, during which microorganisms adapted themselves to the conditions in the biofilter systems. After reaching steady state, indicated by the VOC removal efficiencies reaching a constant value, the impact of changes in VOC concentrations and air flow rates on removal efficiency and elimination capacity was investigated in stages B (flow rate 0.1 m^3/h), C (flow rate 0.2 m^3/h) and D (flow rate 0.3 m^3/h). However, it was observed that the microorganisms still needed more time for their adaptation. This became apparent from the removal efficiencies, which were showing no dependence on inlet VOC concentrations, and the appearance of the biofilm, which looked very dry. Therefore, stage E (Initial), with a lower air flow rate of 0.06 m^3/h, was operated as a reacclimation period. After that, the air flow rates were gradually increased from stages E (flow rate 0.06 m^3/h), F (flow rate 0.1 m^3/h), G (flow rate 0.15 m^3/h), H (flow rate 0.2 m^3/h) to I (flow rate 0.3 m^3/h). In each stage, the VOC concentrations were varied from 1 to 9 g/m^3. At the end of the experiment, the impact of a series of shock loadings was also studied.

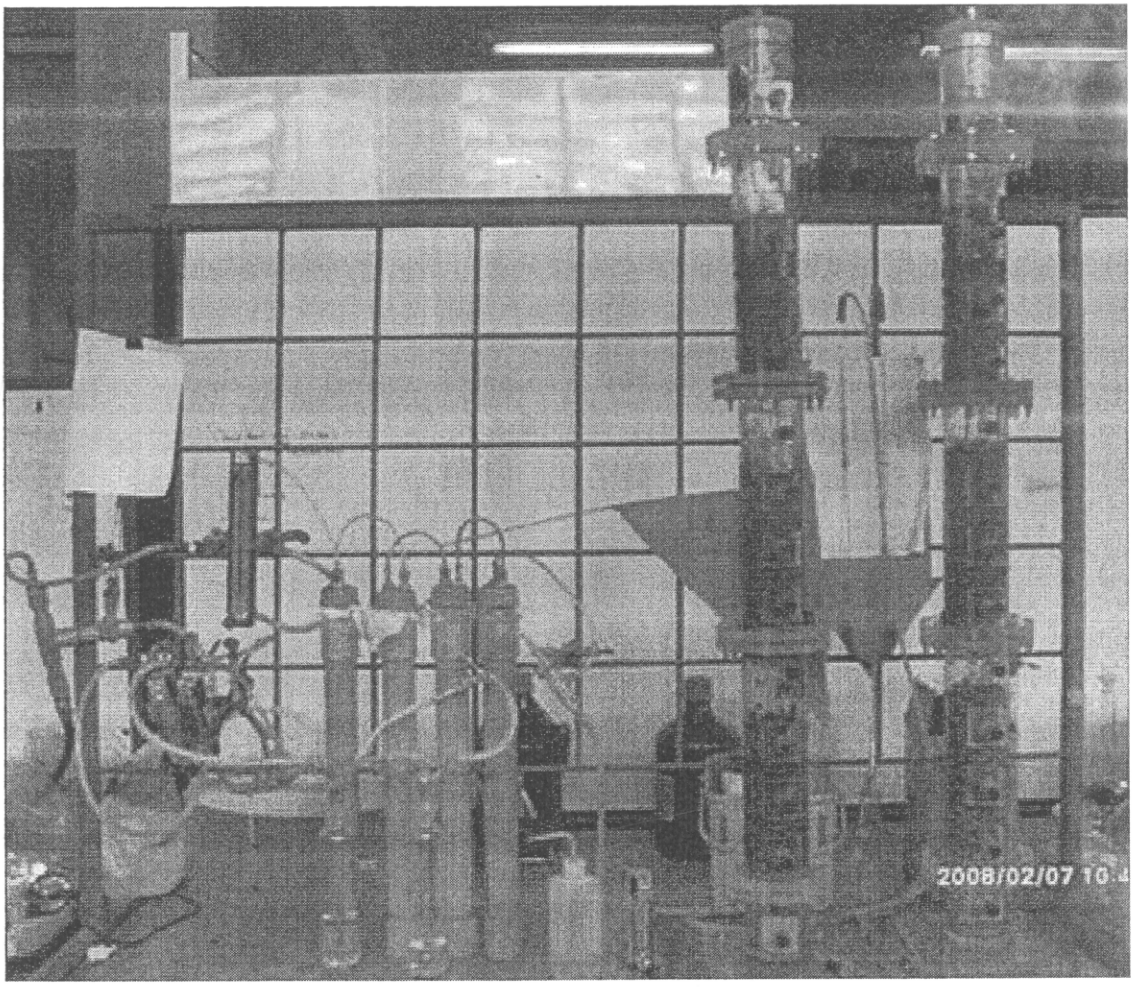


Figure 2-7 The mixed VOCs biofilter system.

Table 2-2 Summary of operating conditions for the biofilter systems.

Experiments	Purpose	Conditions
A	Start up period	C_{in} = 1 g/m^3 Q = 0.1 m^3/h IL = 23.82 g/m^3/h Operation time = until steady EBRT = 151 S

Experiments	Purpose	Conditions
B	Response to increasing contaminant loading rate	C_{in}= 1-9 g/m^3* Q = 0.1 m^3/h IL = 23.82-214.35 g/m^3/h Operation time = until steady EBRT = 151 S
C	Response to increasing contaminant loading rate	C_{in}= 1-9 g/m^3* Q = 0.2 m^3/h IL = 47.63-428.70 g/m^3/h Operation time = until steady EBRT = 76 S
D	Response to increasing contaminant loading rate	C_{in}= 1-9 g/m^3* Q = 0.3 m^3/h IL = 71.45-643.10 g/m^3/h Operation time = until steady EBRT = 50.4 S
E (Initial)	Reacclimation	C_{in}= 1 g/m^3 Q = 0.06 m^3/h IL = 14.29 g/m^3/h Operation time = 4-14 days until steady EBRT = 252 S
E	Response to increasing contaminant loading rate	C_{in}= 1-9 g/m^3* Q = 0.06 m^3/h IL = 14.29-128.61 g/m^3/h Operation time = 20 days EBRT = 252 S

Experiments	Purpose	Conditions
F	Response to increasing contaminant loading rate	C_{in}= 1-9 g/m^3* Q = 0.1 m^3/h IL = 23.82-214.35 g/m^3/h Operation time = 20 days EBRT = 151 S
G	Response to increasing contaminant loading rate	C_{in}= 1-9 g/m^3* Q = 0.15 m^3/h IL = 35.73-321.52 g/m^3/h Operation time = 20 days EBRT = 101 S
H	Response to increasing contaminant loading rate	C_{in}= 1-9 g/m^3* Q = 0.2 m^3/h IL = 47.63-428.70 g/m^3/h Operation time = 20 days EBRT = 76 S
I	Response to increasing contaminant loading rate	C_{in}= 1-9 g/m^3* Q = 0.3 m^3/h IL = 71.45-643.1 g/m^3/h Operation time = 20 days EBRT = 50 S
Shock loading	Response to increasing contaminant loading rate and air flow rate in the period of shock loading (random)	C_{in}= 1-10 g/m^3* Q = 0.06-0.3 m^3/h IL = 14.29-643.1 g/m^3/h Operation time = 30 days EBRT = 252-50 S

* 3 increasing steps: 1-3, 3-6, and 6-9 g/m^3 for methanol

0.1-2, 2-4, and 4-6 g/m^3 for toluene

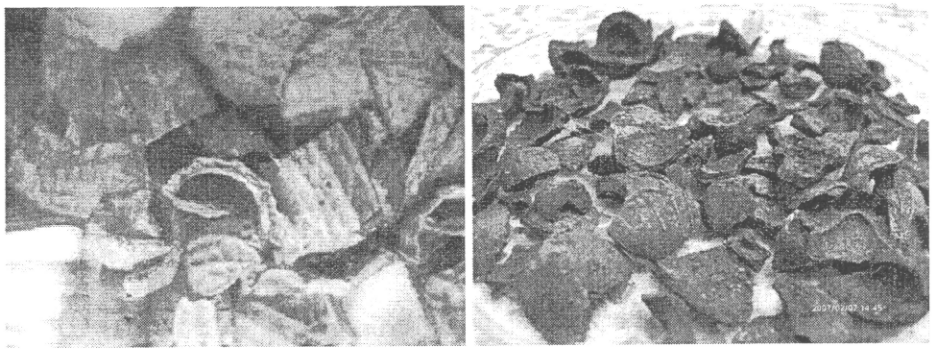
2.5.4 Analytical Methods

2.5.4.1 Packing Material

The following physico-chemical characteristics of packing media were measured: particle size, bulk density, specific surface area, void fraction, and pH.

2.5.4.1.1 Particle Size

The raw peanut shells were cut to the size of 0.5-1 cm (Figure 2-8a) using scissors. The purchased raw palm shells were sorted manually to obtain a selection in the size range of 0.5-1 cm (Figure 2-8b).



(a) (b)

Figure 2-8 The raw peanut shells (a) and the raw palm shells (b): size range: 0.5-1 cm.

2.5.4.1.2 Packing Density

Bulk density is calculated by determining the weight of peanut shells or palm shells occupying a known volume. In this project peanut shells or palm shells were packed into a 250 ml flask, and the weight of the shells determined (Ramírez-López et al., 2003).

2.5.4.1.3 Void Fraction

Samples of peanut shells or palm shells (raw or taken from the biofilter columns) were packed in a graduated cylinder up to the 500 ml mark, and then water was added until the top of the packing material was just covered. The volume of added water was measured. Void fraction was calculated from Equation 2.1 (Ramírez-López et al., 2003).

$$\% \text{ Void fraction} = \frac{\text{Volume of added water}}{\text{Volume occupied by peanut shells}} \qquad (2.1)$$

2.5.4.1.4 BET Surface Area and BJH Pore Size Distribution

Ng et al. (2004) observed a decrease in the BET surface area of activated carbon in a biofilter used to remove hydrogen sulfide (H_2S). They concluded that the biofilm formed on the external surface of the carbon blocked many of the micropores, resulting in a decrease in the specific surface area of the carbon and in the H_2S removal efficiency. Maestre et al. (2007) also used BET surface areas to determine packing material porosity and specific surface area. Therefore in this project the specific surface area of the packing media was determined to obtain information on the density of microorganisms and the stability of the packing media. It was analyzed by BET (Brunauer, Emmet and Teller) surface area and BJH pore size distribution (Barrett, Joyner, and Halenda) methods using the differential pressure principle. Dried peanut shells or palm shells (1x1mm), after drying at 100°C and 12 hours, were degassed at 120°C. Then they were analyzed using a COULTER SA3100 surface area analyzer. This equipment measures the extent to which nitrogen is adsorbed on the sample of packing material. The transfer of nitrogen from the gas phase to the liquid phase during adsorption creates a pressure differential in the sampling tube.

2.5.4.1.5 pH

The pH value was measured by AOAC method 973.04 (Helrich, 1990a). 3 g of peanut shells or palm shells were placed in a 100 ml beaker. 50 ml H_2O was added and the shells allowed to soak for 30 min, with stirring. The pH of the mixture was then determined using a pH meter (Russel RL150).

2.5.4.1.6 Nutrients in Packing Material

The organic carbon content was calculated using the relationship given in Equation 2.2. The sample ash content was obtained by subjecting the sample to a temperature of 600°C for 5 hours by method AOAC 967.04 (Helrich, 1990a). Moisture content was obtained by drying the sample at 105°C for 5 hours by method AOAC 930.15 (Helrich, 1990b).

$$Organic\_carbon = (100 - \%ashcontent - \%moisture) \times 58\% \qquad (2.2)$$

Total nitrogen was obtained using the Jedalth method in AOAC 954.01, 70 (Helrich, 1990b). Total phosphorus was determined by the spectrophotometric method ($HNO_3/HClO_4$ digestion) in

AOAC957.02 Be & 958.01, 12 (Helrich, 1990c). Both analyses were carried out by an external laboratory (Central Analytical Laboratory, Faculty of Natural Resources, Prince of Songkla University).

2.5.4.1.7 SEM

A scanning electron microscope (SEM) can be used to learn about the physical characteristics of microorganisms. Even though biofilms seem to consist of a homogeneous layer, there is a considerable non-uniformity within them. Several groups of microorganisms are involved in the degradation of air pollutants in biofilters, including bacteria, actinomycetes, and fungi (Mathur and Majumder, 2008). The surface area characteristics of a peanut shell and a palm shell and the characteristics of microorganisms on the packing media were observed using a scanning electron microscope (JSM-5800L V, JEOL). In this study, the SEM studies of samples of packing media were carried out by an external laboratory (Scientific Equipment Center, Prince of Songkla University).

2.5.4.2 Internal Biofilter

2.5.4.2.1 Concentration

Gas samples were collected at the inlet and outlet ports of each biofilter. The samples were collected in 0.01 l evacuated glass sample bottles sealed with an aluminum cover (Figure 2-9). When a sample was taken the sample bottle was connected to the inlet or outlet port for 5 minutes via a hypodermic needle installed at the sampling port, as shown in Figure 2-10.

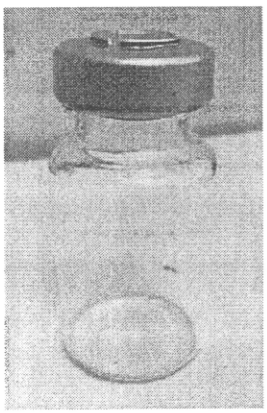


Figure 2-9 A sealed and evacuated glass sample bottle.

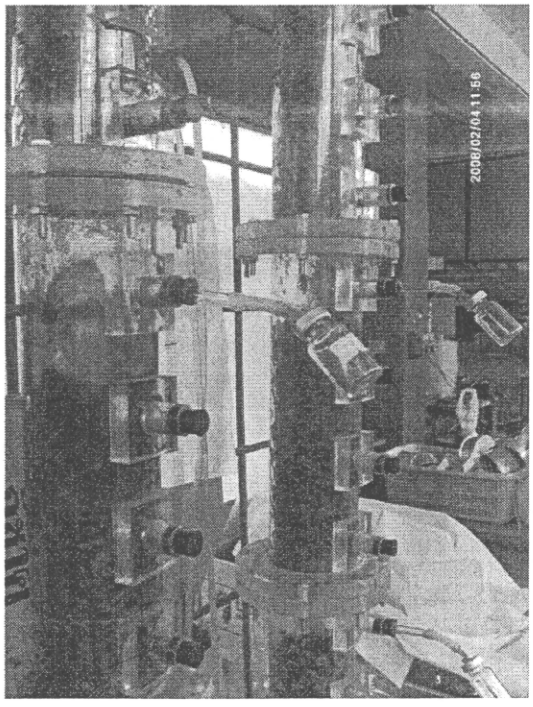


Figure 2-10 Collecting the gas sample.

Toluene and methanol concentrations in the gas samples were analyzed by a gas chromatography unit (HP 6890, Hewlett Packard) equipped with a flame ionization detector (FID) using a 30 meter capillary column (HP-1, crosslinked methyl siloxane). The temperatures of the injection port, the oven, and the detector were maintained at 180, 50, and 200°C, respectively. Three samples of 1 ml each were taken from each sample bottle (Sun et al., 2002) using a gas tight syringe and injected into the gas chromatograph. The calibration of methanol and toluene concentrations can be found in Appendix A.

2.5.4.2.2 Temperature

All biofilters were operated at ambient temperature, which ranged from 25-29°C. Bed temperature and ambient temperature were monitored via AP-104 (Sila Research Co., Ltd., Thailand). This equipment can measure temperature in the range of -40 through 120 °C with a response time of 4 seconds and resolution 0.1 °C. The temperature port is shown in Figure 2-2.

2.5.4.2.3 Pressure Drop

Pressure drop was measured by a U type manometer connected between the inlet port at the base of column and the outlet port at the top of the column. As discussed later, at one stage in the experimental run the pressure drop across the filter bed became very high due to excess biomass accumulation. To remove the excess biomass, the packing media in the filter bed was taken out and put in a basin, and then, after excess biomass was adsorbed by a cotton cloth, the packing was put back into the biofilter (Xi et al., 2006).

2.5.4.2.4 Relative Humidity

Relative humidity was monitored via an AP-104 (Sila Research Co., Ltd., Thailand) which can measure relative humidity over a range of 10-90% with a response time of 4 seconds and resolution 1%. The relative humidity port is shown in Figure 2-2. Relative humidities in this study were in the range of 89-91% for the inlet air contaminated with methanol or toluene. Water (100-200 ml) was occasionally sprayed into the top of the biofilter, through the nutrient solution port, to control the bed moisture content and air relative humidity. At times during the experimental runs, the packing media in the lowest section became dry at the axis of the column and it proved hard to raise the moisture content of these packing media to desired levels. 100-200 ml of water from the system, with added nutrients, was introduced into this section at the gas sampling port (see Figure 2-2). This water was added not just to prevent the bed drying out but also to wash away excess biomass.

2.5.4.2.5 pH

For the greatest spectrum of bacterial activity, a near-neutral pH is required. The usual pH value for packing materials is 6 to 8, although in some cases, as when treating reduced sulfur compounds, a pH as low as 2 to 4 has been observed without important loss of pollutant removal performance (Devinny et al., 1999). The pH test paper (DF Universal test paper, pH 1-14) was used for checking acidity and alkalinity in the biofilter column. The pH port is shown in Figure 2-2.

Chapter 3

Results and Discussions

This chapter presents and discusses the performance of the experimental biofilters under a range of operating conditions. Pressure drop variations across the biofilters, the characteristics of the packing media, and changes in the appearance of the biofilter columns are also discussed. The attempt to develop macrokinetic models of the biofilters is described at the end of this chapter.

3.1 The Overall Performance

The experiments were run continuously, with a series of successive step changes in inlet loading, over 267 days for pure methanol systems and mixed systems, and 214 days for pure toluene systems.

3.1.1 Start-Up Period

Six biofilter units were set up for the experimental component of the project. Each of the six biofilters was filled with packing material that had previously been exposed to activated sludge which was already partly acclimatized to the particular VOC to be studied. Biofilters M1 and M2 were filled with peanut shells and palm shells respectively; throughout the operating period these received gas streams containing only methanol. Biofilters T1 and T2 were filled with peanut shells and palm shells respectively; throughout the operating period, these received gas streams containing only toluene. Biofilters X1 and X2 were filled with peanut shells and palm shells respectively; during the initial part of the operating period these received gas streams containing only methanol but after 54 days they started receiving gas streams containing a mixture of methanol and toluene. A start-up period was allowed for each biofilter in order to enable the microorganisms to become well established on the biofilter packings, to develop biofilm communities adapted to efficiently adsorb the supplied VOC from the gas passing through the biofilter, and to biodegrade the VOCs. Since the biofilm continues to grow throughout the operation of a biofilter, no true steady state is ever achieved. Hence deciding when the biofilters were ready to be subjected to a preplanned sequence of changes in gas flow rate and VOC concentration was, to some degree, an arbitrary decision. For M1, M2, X1, and X2, the biofilters

receiving methanol, the start-up period was terminated after 23, 22, 20, and 22 days respectively. For T1 and T2, the biofilters receiving toluene, the start-up period was terminated after 40 and 26 days respectively.

3.1.2 Main Experimental Program

3.1.2.1 Biofilters Treating a Single VOC Component

For biofilters M1, M2, T1, and T2, the first segment of the main experimental program comprised three stages, denoted stages B, C and D, during which the gas flows to the biofilters were successively increased from 0.1 m^3/h (stage B) to 0.2 m^3/h (stage C) to 0.3 m^3/h (stage D). Empty bed residence times (EBRT) for each of these stages were 151, 76, and 50 seconds respectively. Several step changes in VOC concentration were made during each of the previous stages. Typical concentration ranges used were: 1-3, 3-6, and 6-9 g/m^3 for methanol and 0.1-2, 2-4, and 4-6 g/m^3 for toluene. It was originally intended to increase concentrations progressively so as to determine the limits of biofilter performance. However, measured removal efficiencies and calculated elimination capacities often fluctuated unpredictably and it was sometimes necessary to reduce VOC concentrations in the incoming gas. During stages C and D pressure drops through the biofilters began to increase and reached levels many times those measured at the start of the experiments. These pressure drop changes appeared to be contributing to the erratic performance of the biofilters. Therefore, stage D was terminated early and the biofilter columns were washed down with water to remove excess biomass. This took place on day 163 for M1 and M2 and on day 114 for T1 and T2.

The biofilters were restarted with the gas flow rate at a very low level (0.06 m^3/h) (stage E) and the VOC concentration also at a low level (1 g/m^3). The biofilters then performed much better and their performance was monitored during a sequence of successive increases in gas flow rate to 0.1 m^3/h (stage F), 0.15 m^3/h (stage G), 0.2 m^3/h (stage H), and 0.3 m^3/h (stage I). EBRTs for each of these stages were 151, 101, 76, and 50 seconds respectively. Stage I was terminated on day 267 in the case of M1 and M2 and on day 214 in the case of T1 and T2. These observations are in good accord with those of Barona et al. (2004) who found that the performance of microbial communities in biofilters soon recovered after brief periods of starvation. During each of the above stages, the VOC concentration was raised stepwise several

times, as was done in earlier stages. The biofilters were then subjected to a series of random shocks involving stepwise increases and decreases in inlet VOC loading.

Details of inlet VOC concentrations, air flow rates and inlet loadings (IL = air flow × VOC concentration /biofilter volume), together with calculated elimination capacities (EC) and VOC removal efficiencies (RE) are presented for each of the above four biofilters in Figures 3-1 to 3-8. The EC values provide important information on the capacity the biofilter had at any particular time to degrade the VOC being treated. The RE values provide a good indication of the proportion of incoming VOC which is being removed at any given period of time. In each biofilter the removal efficiency immediately after the start-up period began was close to 100%, but it rapidly dropped to much lower levels. This can be explained as follows. At the start of each experimental run it would be expected that concentrations of VOC in the biofilm would be very low. Hence the concentration difference driving VOC adsorption from the gas phase to the liquid phase would be large, and most (but not all) of the VOC entering the biofilter would be taken up into the biofilm. At this stage the microbial community in the biofilm would increase rapidly. As the VOC levels in the biofilm increased the rates of VOC adsorption into the biofilm could be expected to diminish sharply, with the result that much of the VOC would pass through the biofilter without being removed, and removal efficiency values would therefore drop markedly.

In the case of M1 (Figures 3-1 and 3-2), the peanut shell filled biofilter treating a gas stream containing methanol, the elimination capacity increased in line with the inlet loading for the first half of stage B. The effectiveness of the biofilter microbial community at this time is well illustrated by the RE values of close to 100% that were achieved over this period. Midway through stage B, however, the EC value stabilized and a limiting value appeared to have been reached; this is well demonstrated by the decrease in RE values as the inlet loading was increased above the limiting EC value. In stage C the EC values behaved quite strangely, fluctuating for a long time about a mean value somewhat less than that observed in stage B before showing an abrupt increase followed by a massive drop and then a further sharp increase. Not dissimilar behavior was observed in stage D, at which point the pressure drop in the biofilter increased markedly (see section 3.61) and the biofilter had to be washed down to remove excess biomass. Once this had been done the performance of the biofilter was much more consistent.

Through stages E to G, EC values increased as inlet loads were increased, until a maximum (limiting) value was reached, and until this limiting value was reached removal efficiencies were high. A fairly similar pattern was followed in stages H and I, although the EC values fluctuated a little more and the limiting EC value appeared to have fallen slightly. This may well be attributable to the fact that the pressure drop increased markedly during these two stages.

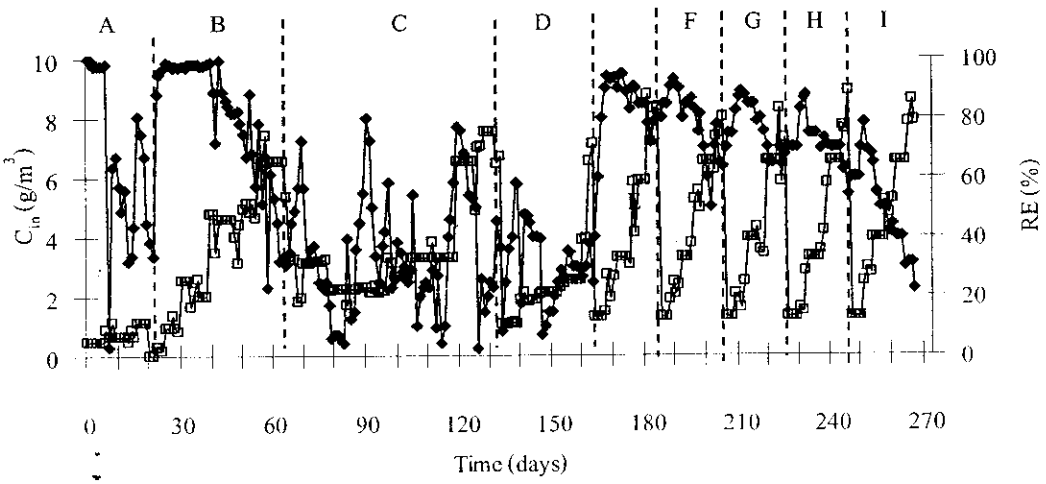


Figure 3-1 The overall performance in terms of removal efficiency for removal of pure methanol in the biofilter packed with peanut shells (M1): (◆) the removal efficiency, and (□) the inlet concentration.

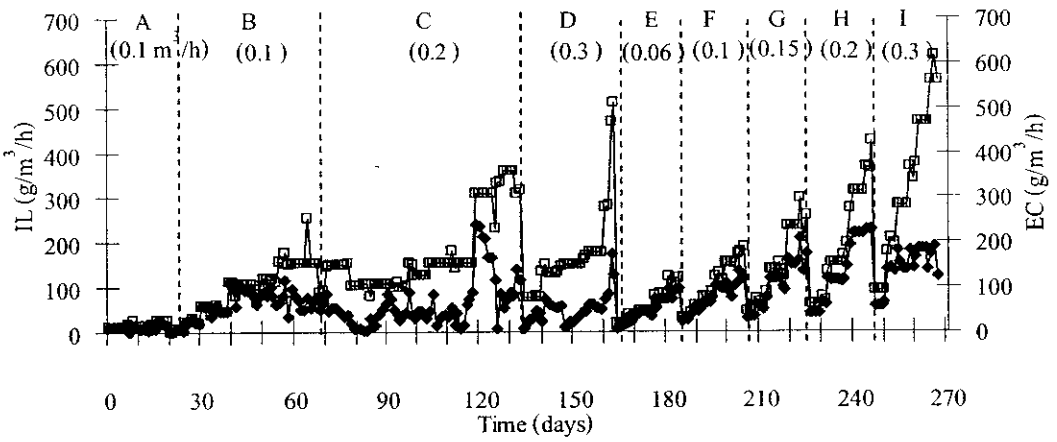


Figure 3-2 The overall performance in terms of elimination capacity for removal of pure methanol in the biofilter packed with peanut shells (M1): (□) the inlet load, and (♦) the elimination capacity.

In the case of M2 (Figures 3-3 and 3-4), the palm shell filled biofilter treating a gas stream containing methanol, the elimination capacity increased in line with the inlet loading for the first half of stages B and C. The effectiveness of the biofilter microbial community at this time is well illustrated by the RE values of close to 100% that were achieved at the start of stage B. Both figures show well the decrease in RE values that occurred as the inlet loading was increased above the limiting EC value. This system was washed down to remove excess biomass in stage D because the RE values had dropped to below 40% and EC values were also declining. After excess biomass removal the performance of the biofilter was much more consistent. Through stage E to midway through stage G, EC values increased as inlet loads were increased, until a maximum value was reached; and until this limiting value was reached, removal efficiencies were high. A fairly similar pattern was followed in stages H and I though the EC values fluctuated a little more and the maximum EC value attained in each stage appeared to fall in each successive stage. Again this was attributed to pressure drop increases (see section 3.61).

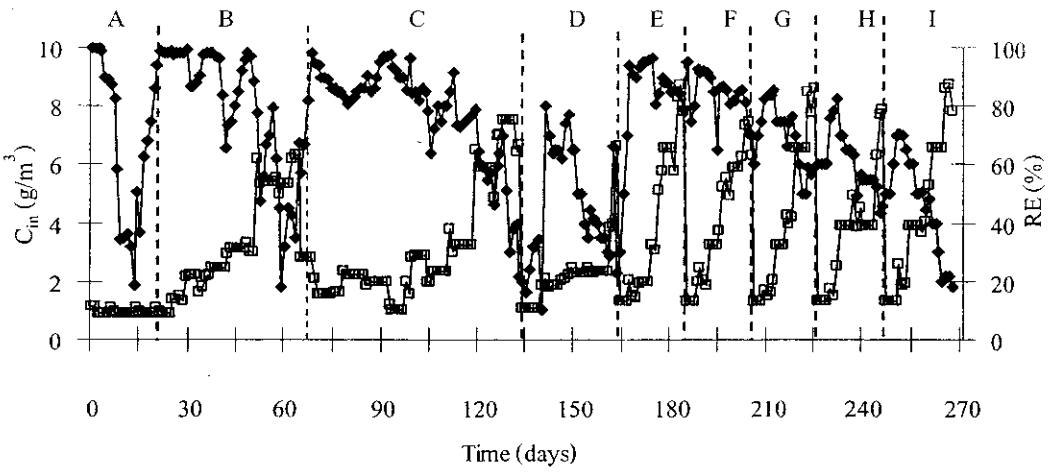


Figure 3-3 The overall performance in terms of removal efficiency for removal of pure methanol in the biofilter packed with palm shells (M2): (◆) the removal efficiency, and (□) the inlet concentration.

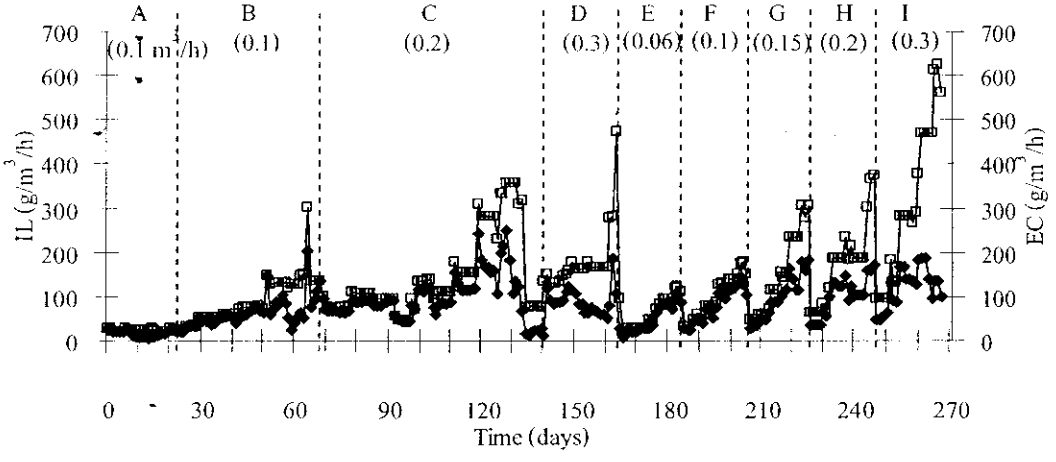


Figure 3-4 The overall performance in terms of elimination capacity for removal of pure methanol in the biofilter packed with palm shells (M2): (□) the inlet load, and (◆) the elimination capacity.

In the case of T1 (Figures 3-5 and 3-6), the peanut shell filled biofilter treating a gas stream containing toluene, removal efficiencies stayed at around 80% and EC values increased steadily during much of stage A. This suggests that the microbial community was adapting well to the toluene. In the latter part of stage A the removal efficiencies fell sharply and the EC values also dropped substantially. Why this occurred is not known. When, at the start of stage B, the inlet

load was cut back, the biofilter performance stabilized and shortly afterwards EC values returned to the maximum level attained in stage A and fluctuated about this value for the remainder of stage B. However, RE values fell away as inlet loads were increased. With the marked reduction in inlet load at the start of stage C, some improvement in RE values occurred but this was less than might have been expected. EC values increased as inlet loads were gradually increased but they stabilized at a level well below that achieved in stage B. As in biofilters M1 and M2, there was a pressure drop problem (see section 3.61) and excess biomass was washed out of the column at the end of stage C. This did not completely overcome the pressure drop problem; the pressure drop after washing did not fall to its original low level but it did stay reasonably stable at between 1 and 5 mmH_2O for the remainder of the experimental period (stages E to I). During these 5 stages biofilter performance was very consistent and EC values tended to increase in line with increases in inlet load until a maximum value was reached. The maximum EC value reached increased slightly from stage E to stage G and then stabilized.

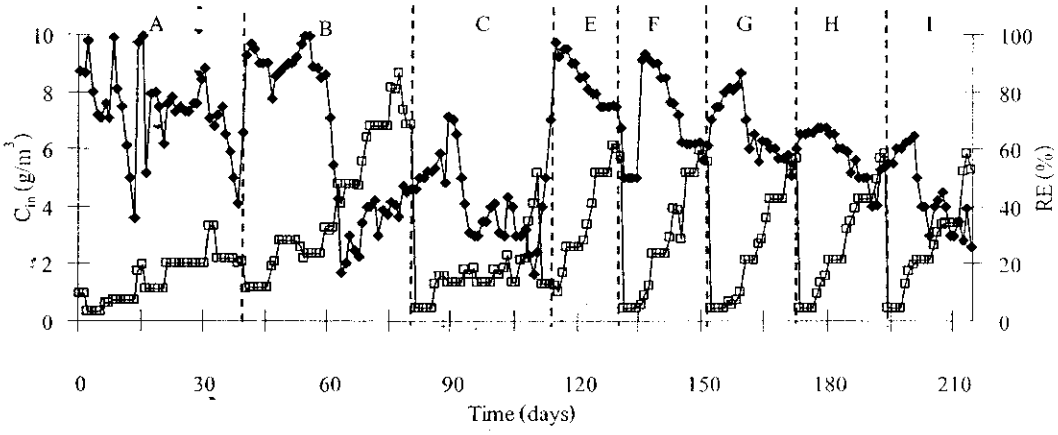


Figure 3-5 The overall performance in terms of removal efficiency for removal of toluene in the biofilter packed with peanut shells (T1): (◆) the removal efficiency, and (□) the inlet concentration.

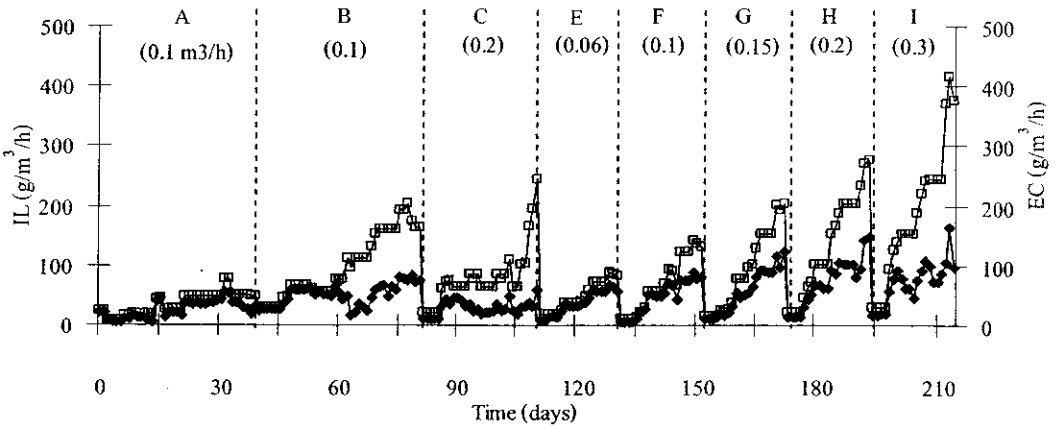


Figure 3-6 The overall performance in terms of elimination capacity for removal of toluene in the biofilter packed with peanut shells (T1): (□) the inlet load, and (◆) the elimination capacity.

In the case of T2 (Figures 3-7 and 3-8), the palm shell filled biofilter treating a gas stream containing toluene, the pressure drop stayed low well into stage C and so no washing out of biomass was done (see section 3.61). Over this period this biofilter's performance was similar to but rather better than that of T1. Beginning in stage C, and continuing through the remaining stages, there was a trend of increasing pressure drop, which reached a very high value of 230 mmH_2O at the end of the experimental period. Despite the big differences between the pressure drops in this biofilter and T1, the performance of the two biofilters was nevertheless very similar.

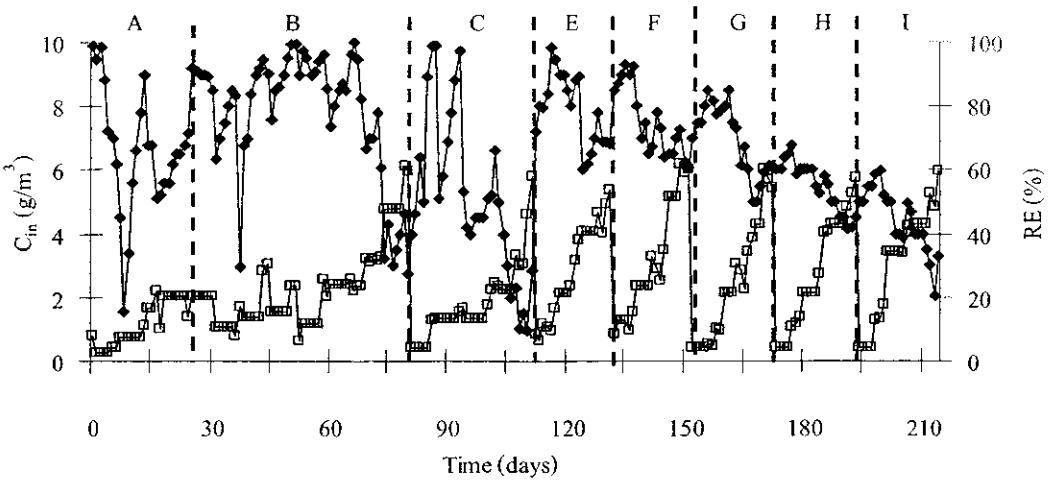


Figure 3-7 The overall performance in terms of removal efficiency for removal of pure toluene in the biofilter packed with palm shells (T2): (◆) the removal efficiency, and (□) the inlet concentration.

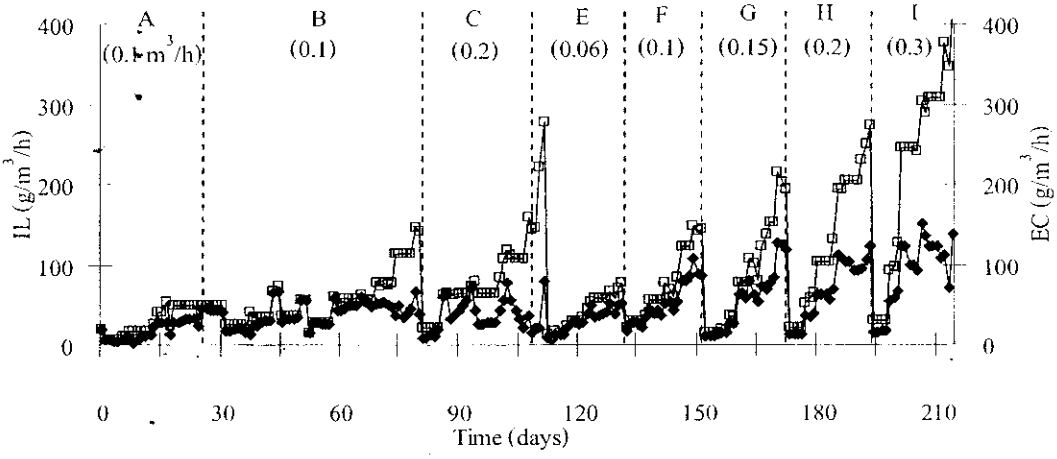


Figure 3-8 The overall performance in terms of elimination capacity for removal of pure toluene in the biofilter packed with palm shells (T2): (□) the inlet load, and (◆) the elimination capacity.

The patterns of change followed by the EC values are quite similar for all four biofilters although it is clear that the performance of biofilters M2, T1, and T2 is rather more consistent than that of M1. Patterns of behavior in biofilters filled with peanut shells are remarkably similar to those in biofilters filled with palm shells, which means that on the basis of VOC degradation capacity neither has a clearcut advantage over the other. Elimination capacities,

expressed on a $g/m^3/h$ basis, are of a comparable magnitude for methanol and toluene, though somewhat greater for the former. Given that methanol is hydrophilic and toluene is hydrophobic, and that methanol has a simpler structure making it easier to biodegrade than toluene. The closeness of the EC values for the two VOCs is, to some extent, unexpected. This finding is useful for practitioners since it means that industries that need to treat gases containing a variety of VOCs may not have to use custom-designed biofilters for each VOC of concern. Even though the EBRT decreases from 252 seconds to 50 seconds as the gas flow rate is increased from 0.06 m^3/h to 0.3 m^3/h there seems to be no apparent effect on limiting EC values. This suggests that microbial degradation processes rather than mass transfer processes between the gas and liquid phases are the rate controlling step in the overall VOC removal process.

3.1.2.2 Biofilters Treating a Mixture of Methanol and Toluene

For biofilters X1 and X2, there was a period of around 30 days after the end of the start-up period during which the concentration of methanol in the gases entering these biofilters was increased stepwise several times. No toluene was added to the incoming gas at this stage. It was evident from methanol concentrations in the outlet gas streams that the biofilter microbial communities had acclimatized well and had developed a good capacity to degrade methanol. For convenience, stage A on diagrams relating to biofilters X1 and X2 is regarded as encompassing the entire period during which methanol was the only VOC fed to the biofilters. Stage B commenced on day 54. From this point onwards both biofilters were fed with gas containing a mixture of methanol and toluene in varying concentrations and proportions. The gas flow rate was maintained at 0.1 m^3/h, as it had been throughout stage A, and this was left unchanged until day 133. This was done to minimize the extent of physical changes while the microbial community became acclimatized to the methanol-toluene mixture. In stage B the methanol concentration was kept at a moderate level for the first 20 days and then was reduced to roughly half of its initial value when methanol concentrations in the outlet gases started to increase. For the next 40 days, the methanol concentration was maintained close to this level before being increased to comparatively high levels again towards the end of stage B.

During stage B the initial toluene concentration was set at a comparatively low value of around 0.5 g/m^3, well below the concentration level that been treated effectively by the acclimatized toluene-consuming microbial communities in T1 and T2 during their stage B periods.

After 30 days at this concentration level still only around 60% of the toluene was being removed from the incoming gases so the concentration was reduced to around 0.1-0.2 g/m^3. Removal efficiencies then improved considerably so after a further 15 days toluene concentrations were brought back to the initial level and then allowed to increase slightly for the remainder of the stage B period. Stage C commenced at the end of stage B. At this point the gas flow rate was increased to 0.2 m^3/h and kept at this level for 29 days. Gas phase methanol concentrations were reduced to low levels at the start of stage C and then increased stepwise. Toluene concentrations, however, were initially kept at roughly the same levels as they had been at the end of stage B but halfway through stage C these were reduced by around 40%. During stage C and the latter part of stage B both biofilters behaved strangely. This coincided with small but significant increases in pressure drop in stage B followed by massive pressure drop increases in stage C. Therefore, the biofilter columns were washed down to remove excess biomass and to reduce the pressure drop to an acceptably low level as it was done in the case of the other four biofilters.

Biofilters X1 and X2 were then treated in the same way as the other four biofilters, being subjected to changes in gas flow rate and VOC concentration similar to those experienced by the other biofilters in stages E to I. For convenience the same nomenclature was retained for X1 and X2, hence there is no stage D for these two biofilters. Details of inlet VOC concentrations, air flow rates and inlet loadings (IL = air flow rate × VOC concentration / biofilter volume), together with calculated elimination capacities (EC) and VOC removal efficiencies (RE) are presented for the above two biofilters in Figures 3-9 to 3-16. Observations related to methanol removal are presented and discussed first and then the observations relating to toluene removal are described. In both X1 and X2 removal efficiencies at the very start of the experimental run followed a similar pattern to that observed in the other biofilters, and for the same reasons.

3.1.2.2.1 Methanol Removal in X1

In the case of X1 (Figure 3-9 and 3-10), the biofilter filled with peanut shells, elimination capacity (EC) values for methanol were low initially but increased in line with increases in inlet loading over the course of stage A. This behavior is similar to that shown by M1 at an equivalent stage. The introduction of toluene into the inlet gas stream had no noticeable effect on the methanol removal capabilities of the biofilter and, as shown in Figure 3-10, for the first half of stage B the methanol removal efficiencies remained very good. About

midway through stage B, however, the EC and RE values for methanol fell abruptly, for no discernible reason. They then fluctuated widely for the rest of stage B and during stage C. Though pressure drops were very small at the time of the initial fall in EC and RE values, shortly afterwards the pressure drop through biofilter X1 started to increase and during stage C it reached very high levels. Therefore, as was done in other biofilters, X1 was washed down to remove excess biomass and restarted.

Through stage E to midway through stage I, this biofilter performed very much more consistently as far as methanol removal was concerned, with elimination capacities increasing with increasing inlet load and comparatively high removal efficiencies being maintained. The peak EC value attained in each stage increased steadily through stages E to H and the maximum EC value achieved in the experimental run was reached in stage H. Towards the middle of stage I, the performance of the biofilter as far as methanol removal was concerned fell away sharply. As discussed in section 3.61, the pressure drop had by this point built up to a high level again and this drop off in biofilter performance is attributed to a build-up of biomass in the biofilter columns. This build-up had started in stage G but appeared to have only limited impact during stages G and H. It seems likely that the build-up did not occur uniformly through the column, starting near the base and slowly working its way upwards. If this is correct then it would be expected that efficient removal of methanol might still be occurring in the upper parts of the column when the lower section of the column was quite heavily clogged with biomass. Figure 3-27e) shows that during stages H and I the ratios of the EC values for the two upper sections of biofilter X1 increased as a proportion of the EC values for the lowest section, which provides support for this idea.

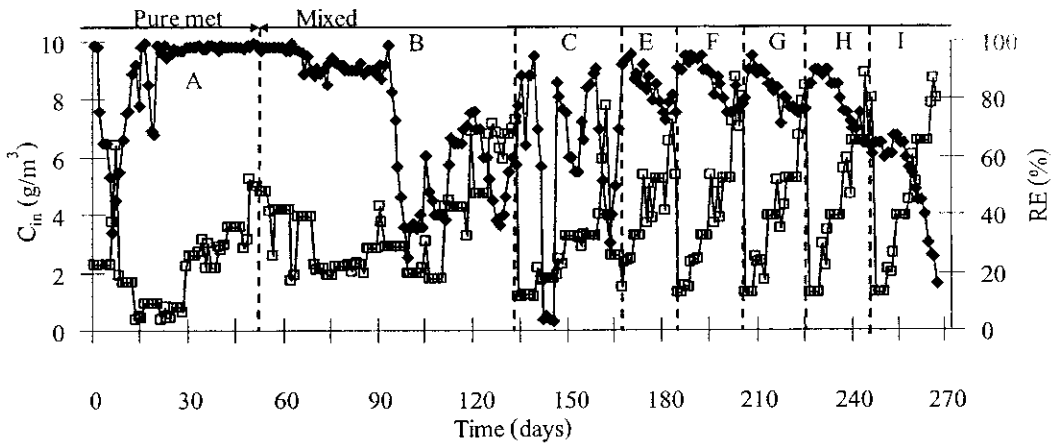


Figure 3-9 The overall performance in terms of removal efficiency for the removal of methanol in a mixture of methanol and toluene in the biofilter packed with peanut shells (X1): (◆) the removal efficiency, and (□) the inlet concentration.

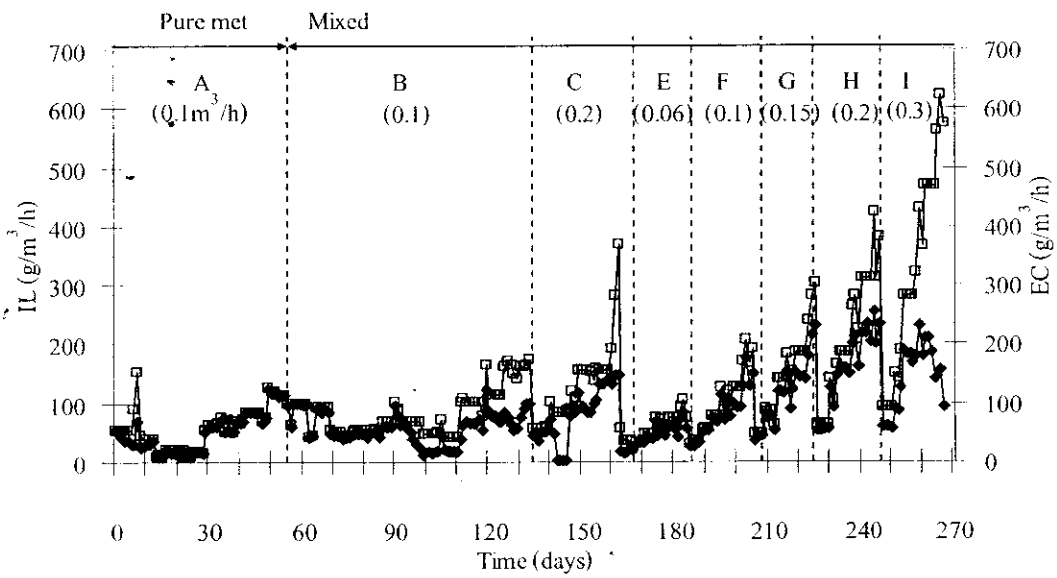


Figure 3-10 The overall performance in terms of elimination capacity for the removal of methanol in a mixture of methanol and toluene in the biofilter packed with peanut shells (X1): (□) the inlet load, and (◆) the elimination capacity.

3.1.2.2.2 Toluene Removal in X1

Initial elimination capacity values for toluene were very low compared with those in biofilter T1 (Figures 3-11 and 3-12). This was expected as some time would obviously be needed for the community of microorganisms in the biofilm to develop the capability to degrade toluene effectively. However, it is evident from Figures 3-15 and 3-16 that no significant improvement in toluene removal effectiveness occurred. Between days 70 and 90 there was an encouraging upward trend in EC values but this was not sustained. Low RE values were observed except at the lowest inlet load values so it was felt to be inappropriate to increase gas phase toluene concentrations to anywhere near those used for T1. In stage C, when the pressure drop increased markedly (as discussed above) EC and RE values fluctuated wildly. After the biofilter column had been washed down to remove excess biomass the EC and RE values were much more stable but still the maximum EC values achieved remained very much lower than those attained in single-component systems. It is quite evident that the microorganism community was unable to develop an effective toluene-degrading community. Also of interest is that EC values for toluene removal were already starting to decline towards the end of stage G, when pressure drops had again started to rise, and this decline continued through stages H and I. This suggests that the toluene-degrading organisms present might well have been concentrated in the lowest section of the biofilter. As will be discussed in more detail later, it would appear that it is very difficult for an effective toluene-degrading community to become established in a biofilm dominated by methanol-degrading organisms.

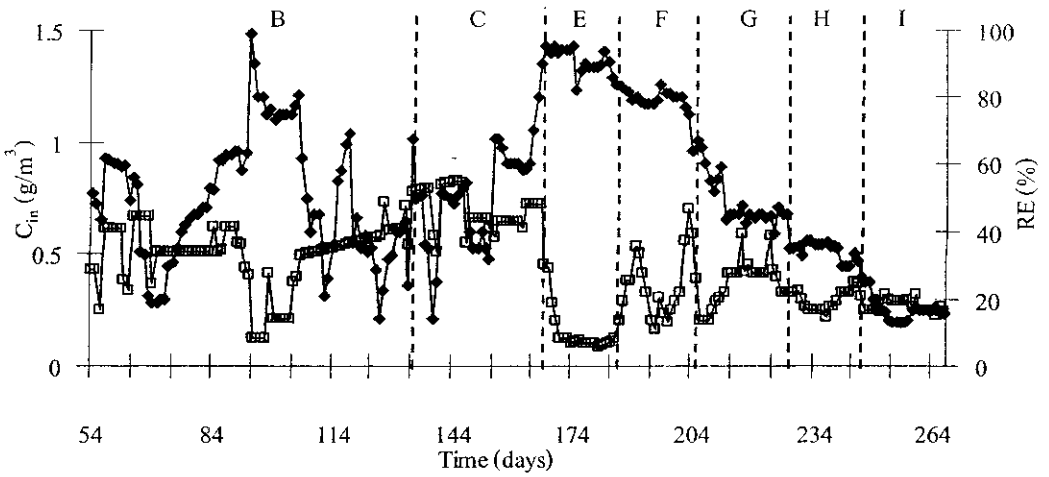


Figure 3-11 The overall performance in terms of removal efficiency for the removal of toluene in a mixture of methanol and toluene in the biofilter packed with peanut shells (X1): (◆) the removal efficiency, and (□) the inlet concentration.

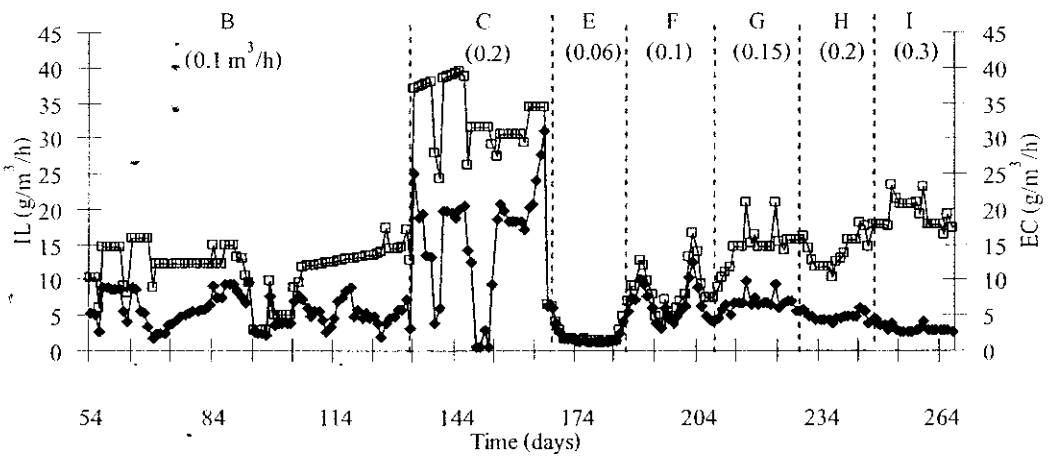


Figure 3-12 The overall performance in terms of elimination capacity for the removal of toluene in a mixture of methanol and toluene in the biofilter packed with peanut shells (X1): (□) the inlet load, and (◆) the elimination capacity.

3.1.2.2.3 Methanol Removal in X2

In the case of X2 (Figures 3-13 and 3-14), the biofilter filled with palm shells, elimination capacity (EC) values for methanol were low initially but increased and fluctuated in line with increases in inlet loading over the course of stage A and at the beginning of

stage B. An acclimatization period of 22 days was allowed after toluene additions to the system began. During and after this period, the behavior of X2 as far as methanol removal was concerned was consistent with that shown by X1 at an equivalent stage. The introduction of toluene into the inlet gas stream had no noticeable effect on the methanol removal capabilities of the biofilter and, as shown in both figures, from stage B to the first half of stage C, the methanol removal efficiencies remained very good. In the second half of stage C, the EC fell sharply and fluctuated. At the same time, pressure drops gradually increased (see section 3.61) up to very high levels. Therefore, as was done in other biofilters, X2 was washed down to remove excess biomass and restarted. Through stage E to midway through stage I this biofilter performed very much more consistently as far as methanol removal was concerned, with elimination capacities increasing with increasing inlet load and comparatively high removal efficiencies being maintained. Towards the middle of stages G, H, and I, the performance of the biofilter as far as methanol removal was concerned fell away sharply when the inlet concentration was raised to 6-9 g/m^3 and the pressure drop reached 9 mmH_2O.

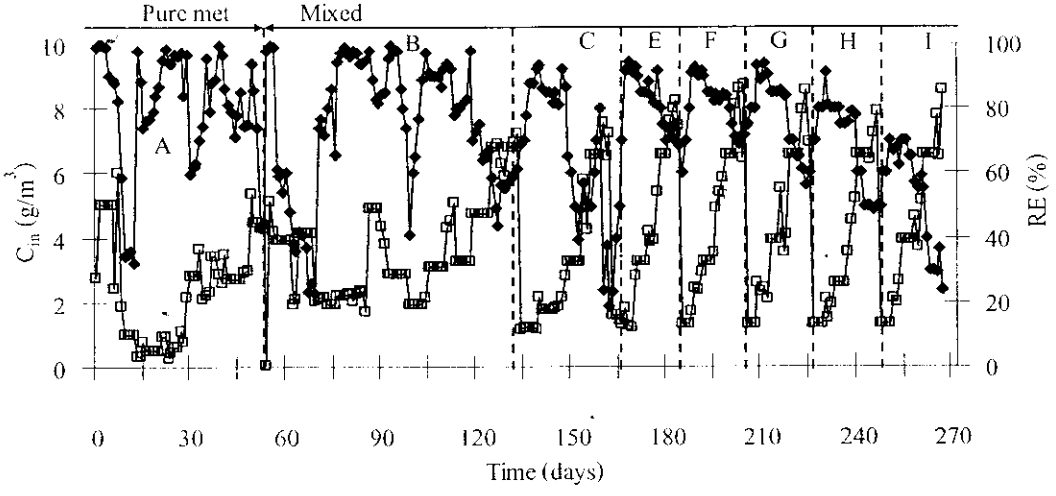


Figure 3-13 The overall performance in terms of removal efficiency for the removal of methanol in a mixture of methanol and toluene in the biofilter packed with palm shells (X2): (◆) the removal efficiency, and (□) the inlet concentration.

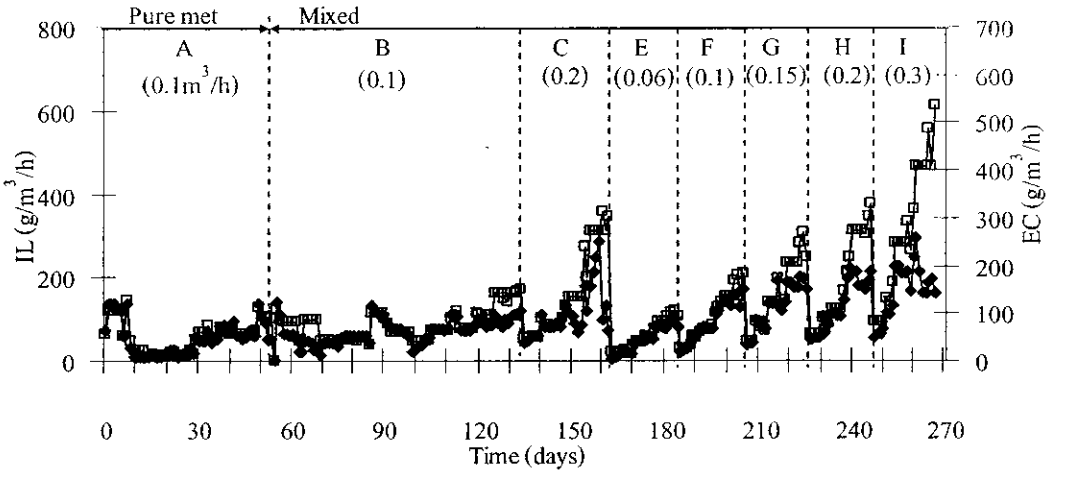


Figure 3-14 The overall performance in terms of elimination capacity for the removal of methanol in a mixture of methanol and toluene in the biofilter packed with palm shells (X2): (□) the inlet load, and (◆) the elimination capacity.

3.1.2.2.4 Toluene Removal in X2

Initial elimination capacity values for toluene in Figures 3-15 and 3-16 were very low compared with those in biofilter T2. This was expected as some time would obviously be needed for the community of microorganisms in the biofilm to develop the capability to degrade toluene effectively. Halfway through stage C, the RE was reduced to less than 60% at the same time that the pressure drop rose to 62 mm H_2O. After the biofilter column had been washed down to remove excess biomass the EC and RE values were much more stable but still the maximum EC values achieved remained very much lower than those attained in single-component systems. Quite evidently the microorganism community was unable to develop an effective toluene-degrading community. These results confirmed what was observed in X1, namely that although toluene had been present in the inlet gases for a long time, in a biofilm with a well-established community of methanol-degrading organisms it could not compete with the methanol as a carbon resource for microorganisms.

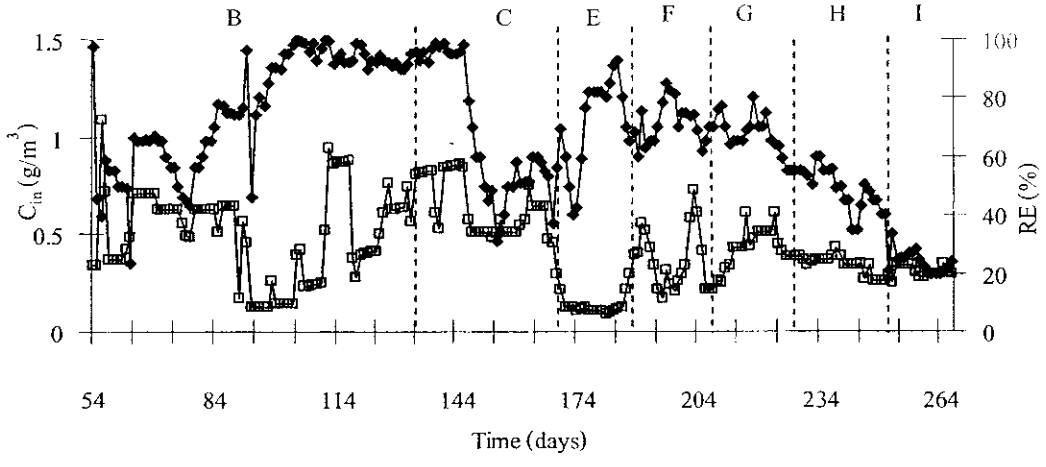


Figure 3-15 The overall performance in terms of removal efficiency for the removal of toluene in a mixture of methanol and toluene in the biofilter packed with palm shells (X2): (◆) the removal efficiency, and (□) the inlet concentration.

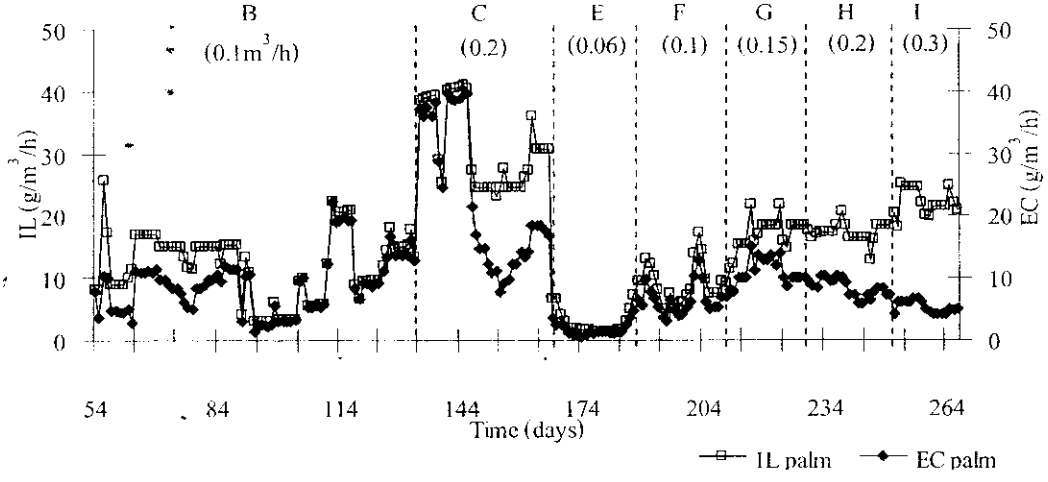


Figure 3-16 The overall performance in terms of elimination capacity for the removal of toluene in a mixture of methanol and toluene in the biofilter packed with palm shells (X2): (□) the inlet load, and (◆) the elimination capacity.

3.1.3 Random Shock Loading Period

One of the major practical problems associated with waste gas treatment is that the industrial processes generating the waste gas often operate intermittently. This leads to sudden fluctuations in both the gas flow rate and also the VOC concentration (Rene et al., 2005). The

effect of exposing the laboratory scale biofilters to such random changes was therefore investigated. At the end of the main experimental runs, which lasted 267 days for M1 and M2, and 214 days for T1 and T2, each of these four biofilters was subjected to a series of stepwise changes in inlet loading; these changes were made every three days over a period of 30 days and involved changes to both the gas flow rate and the VOC concentration. Details of air flow rates, inlet loading and calculated elimination capacity values are shown for the above biofilters in Figures 3-17 to 3-20. Also shown on the Figure for each biofilter is the highest EC (EC_{max}) value recorded during the main experimental run. In all cases the EC values measured during the shock loading period were much lower than corresponding EC_{max} values and appeared to have a slight overall downward trend. There was a slight tendency for EC values to rise when inlet loadings rose and to fall when inlet loadings were reduced, but the magnitude of these changes was relatively small. There were no obvious differences between the EC value plots for M1 and M2 or between the EC value plots for T1 and T2. This suggests that the nature of the packing media was not responsible for the comparatively poor performance of the biofilters over the shock loading period. No dependence of EC value on air flow rate was discernible, which suggests that rates of VOC removal and degradation were being controlled by processes within the biofilm. A possible explanation for the above observations is that a high level of biomass accumulation had occurred in the biofilters, which would limit the area of active biofilm and reduce overall VOC bioconversion levels considerably. Certainly pressure drops were high to very high in each of the four biofilters at the end of the main experimental runs (see section 3.61) and no wash down of the biofilter columns was undertaken prior to the random shock loading experiments. It is also possible that the low EC values are partly due to the impact of the sudden load changes on the microorganisms. However, no such behavior was evident when stepwise changes in inlet loading were made during stages E to G when pressure drops were low. These results make clear how important it is to prevent excess biomass accumulation in the biofilters.

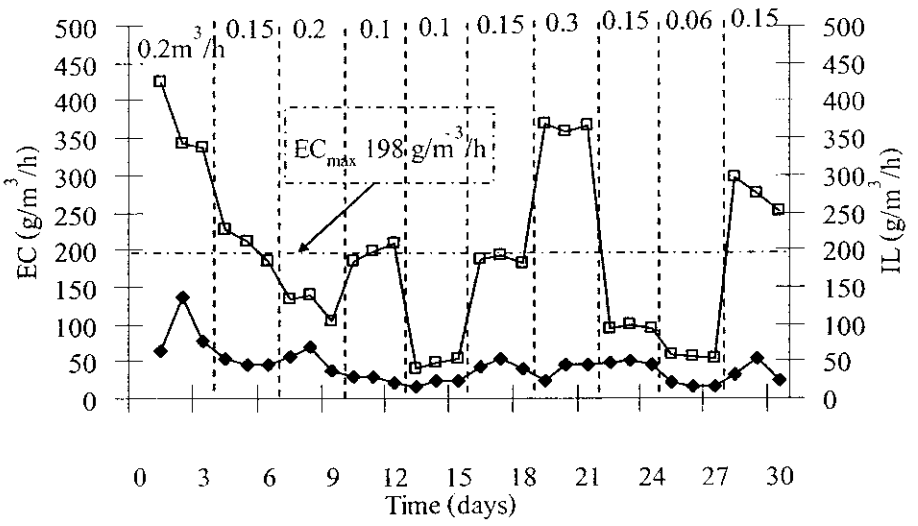


Figure 3-17 The overall performance for the removal of methanol in the biofilter packed with peanut shells (M1) during the shock loading period: (□) the inlet load, and (◆) the elimination capacity.

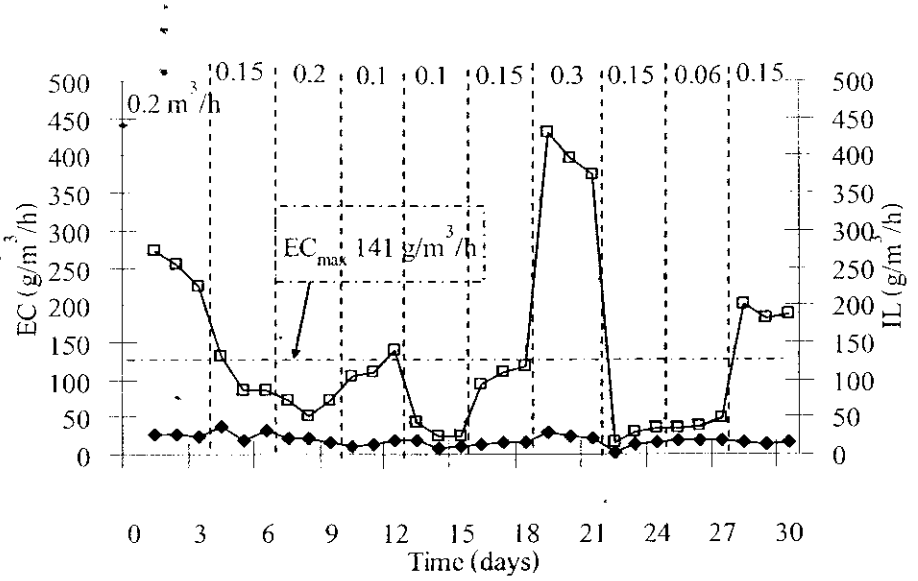


Figure 3-18 The overall performance for the removal of toluene in the biofilter packed with peanut shells (T1) during the shock loading period: (□) the inlet load, (◆) and the elimination capacity.

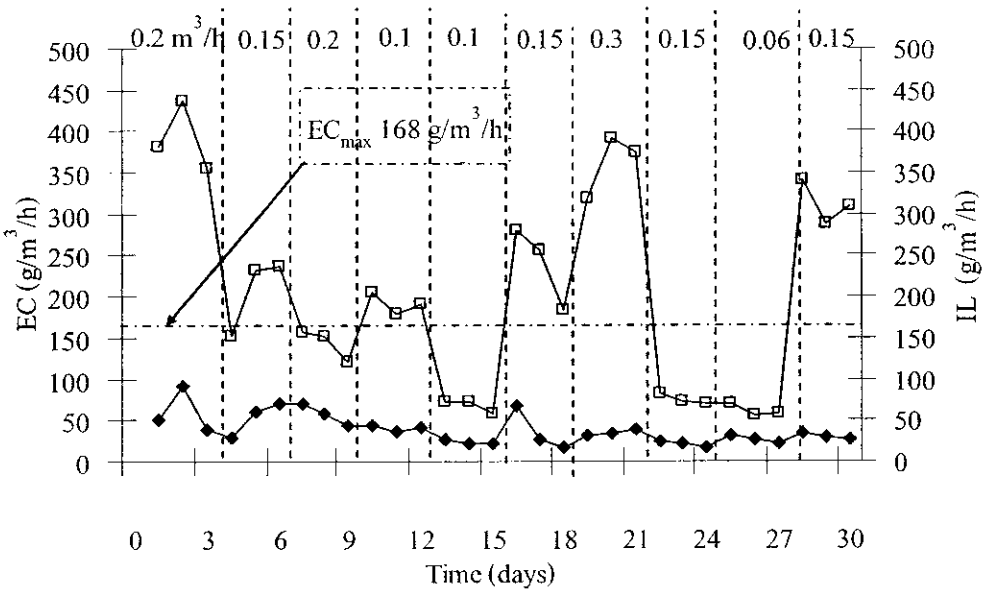


Figure 3-19 The overall performance for the removal of methanol in the biofilter packed with palm shells (M2) during the shock loading period: (□) the inlet load, and (♦) the elimination capacity.

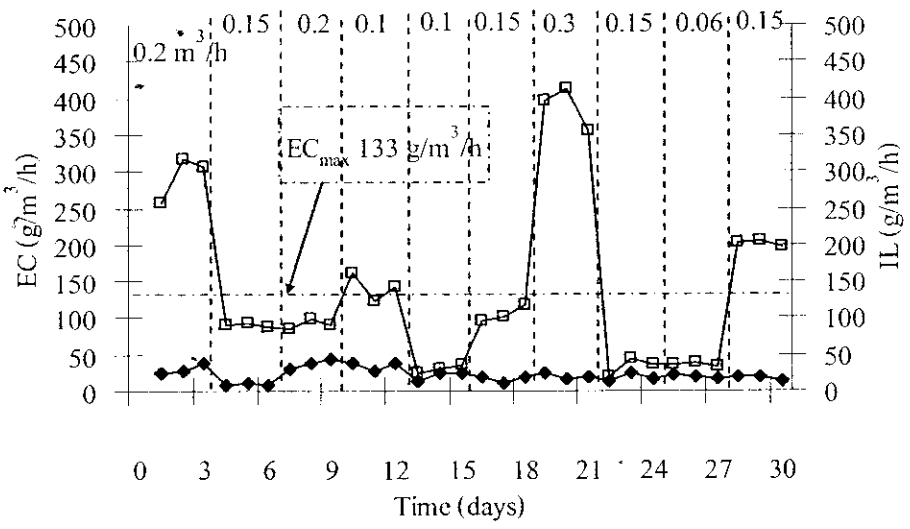


Figure 3-20 The overall performance for the removal of toluene in the biofilter packed with palm shells (T2) during the shock loading period: (□) the inlet load, and (♦) the elimination capacity.

3.2 Influence of the Choice of Packing Media on Biofilter Performance

Conclusions can be drawn about the comparative efficiencies of the chosen packing media by using Figures 3-21 and 3-22. By comparing methanol removal performance of biofilters with peanut shells or palm shells and toluene removal performance of biofilters with peanut shells or palm shells, it can be seen that the efficiencies obtained in the peanut shell and palm shell systems are quite similar. Hence the choice of one packing media over another should depend on local availability and cost efficiency of the materials.

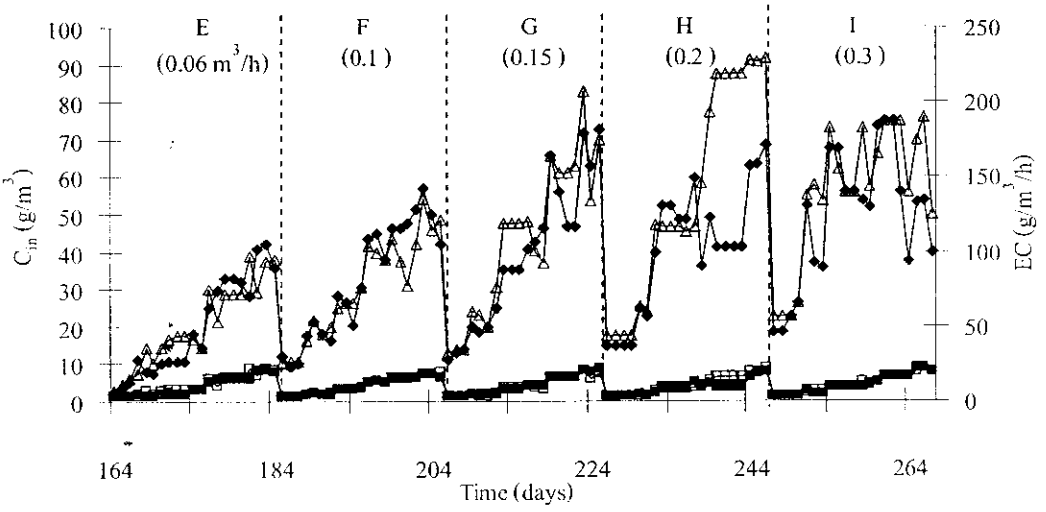


Figure 3-21 The overall performance in terms of elimination capacity for removal of pure methanol in the biofilter packed with peanut shells (M1): (□) the inlet concentration, and (Δ) the elimination capacity in the biofilter packed with palm shells (M2): (■) the inlet concentration, and (◆) the elimination capacity.

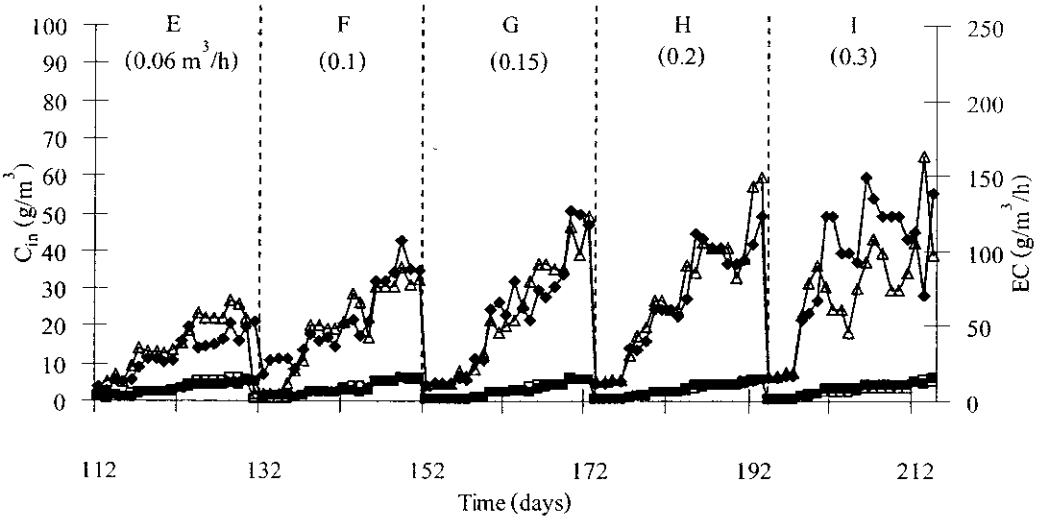


Figure 3-22 The overall performance in terms of elimination capacity for removal of pure toluene in the biofilter packed with peanut shells (T1): (□) the inlet concentration, and (Δ) the elimination capacity in the biofilter packed with palm shells (T2): (■) the inlet concentration, and (◆) the elimination capacity.

3.3 Comparison of VOC Removals in Pure Component and Mixed Systems

It is of considerable practical interest to know how removal rates achievable for a particular VOC in a single component biofilter system are affected when another VOC is introduced into the gas to be treated. The removal rates achieved in the experimental biofilters receiving a mix of toluene and methanol are compared below with removal rates obtained in biofilters receiving gas flows containing a single VOC component.

3.3.1 Methanol

EC values achieved for methanol in M1 and X1, both of which used peanut shells as packing media, are shown for the stage E to stage I segment of the experimental program in Figure 3-23. This Figure shows that the air flow rate and inlet methanol concentration changes followed an identical pattern in both biofilters. Figure 3-23 also shows that the EC values for methanol in both the single component system (M1) and the mixed system (X1) are very similar.

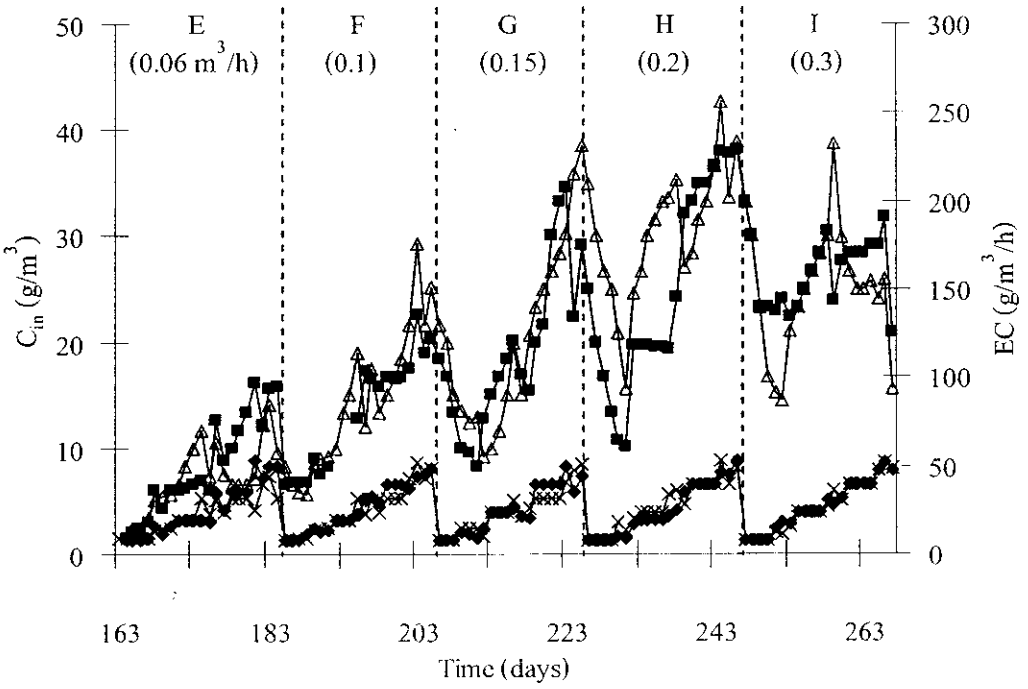


Figure 3-23 Comparison of overall performance of the biofilter packed with peanut shells for the removal of methanol from the pure system (M1): (◆) Inlet concentration, and (■) the elimination capacity, and from the mixed system (X1): (×) inlet concentration, and (△) the elimination capacity.

Figure 3-24 is similar to Figure 3-23 except that it shows the EC values obtained for methanol in biofilters M2 and X2, for which palm shells were used as packing media. It can be seen again that the air flow rate and inlet methanol concentration changes followed an identical pattern in both biofilters. In addition, the EC values for methanol in both the single component system (M2) and the mixed system (X2) are also very similar. The closeness of the EC values for single component and mixed systems in both the above cases show that the addition of toluene to the incoming gas has not affected the capacity of the biofilters to remove and degrade methanol. This is true for both of the packing media used.

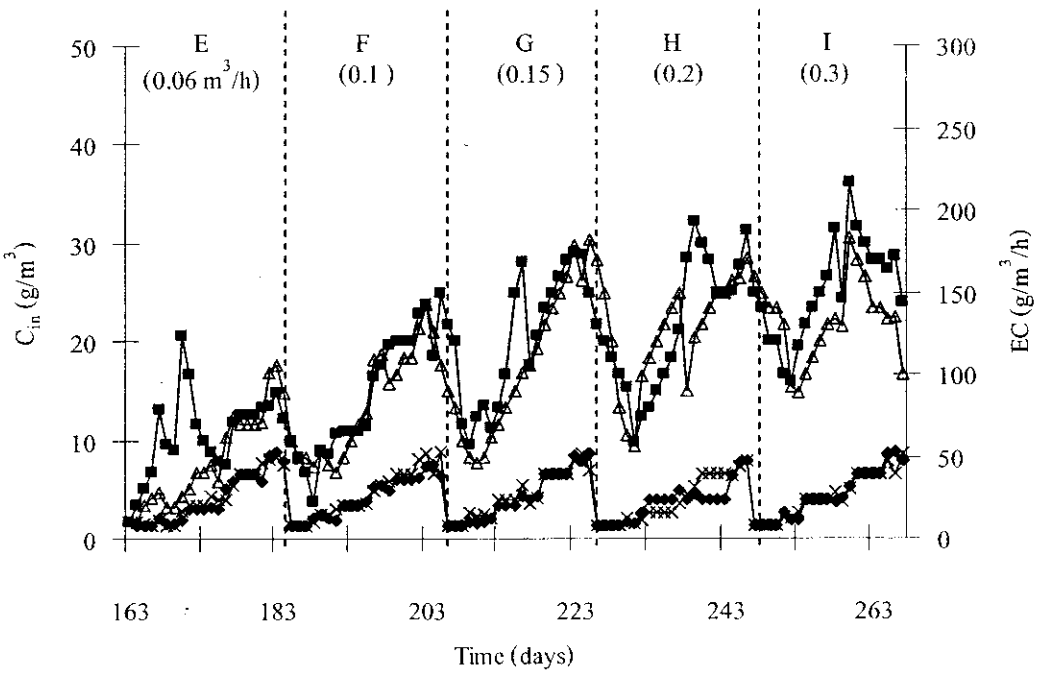


Figure 3-24 Comparison of overall performance of the biofilter packed with palm shells for the removal of methanol from the pure system (M2): (◆) Inlet concentration, and (■) the elimination capacity, and from the mixed systems (X2): (×) inlet concentration, and (△) the elimination capacity.

3.3.2 Toluene

Plots corresponding to Figures 3-23 and 3-24 but showing toluene elimination capacities in single component and mixed systems are presented in Figures 3-25 (T1 and X1) and 3-26 (T2 and X2). In both these cases no direct comparisons of EC values are possible since the mixed systems were only able to handle toluene inlet loadings well below those treated effectively in the single component systems. The EC values obtained for toluene in the mixed system are well below those obtained in a previous investigation in which a different start-up procedure was used, as will be discussed later (Nitipavachon, 2005). It can be inferred from this that the toluene-degrading microorganisms found it very hard to establish an effective presence in a biofilm dominated by an active community of methanol degrading organisms. This suggests that where mixtures of VOCs are expected in waste gas streams the microbial community should be exposed to all the expected VOCs from the beginning. There is evidently much still to be learnt about interactions between

microorganisms responsible for degrading different VOCs and this could be a fruitful area for further research.

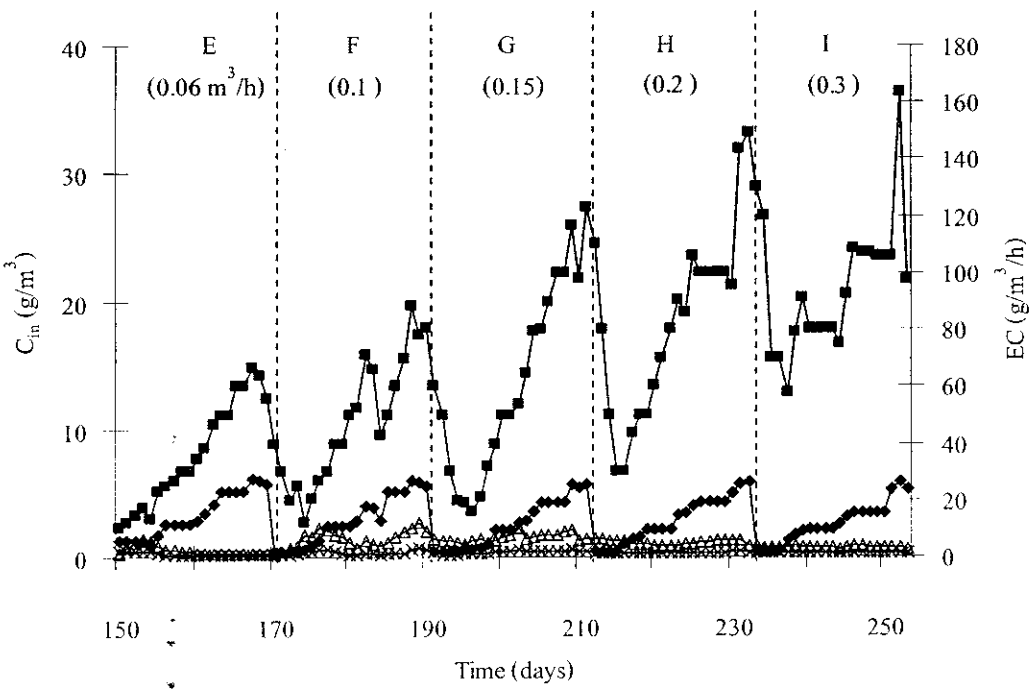


Figure 3-25 Comparison of overall performance of the biofilter packed with peanut shells for the removal of toluene from the pure system (T1): (◆) Inlet concentration, and (■) the elimination capacity, and from the mixed systems (X1): (×) inlet concentration, and (△) the elimination capacity.

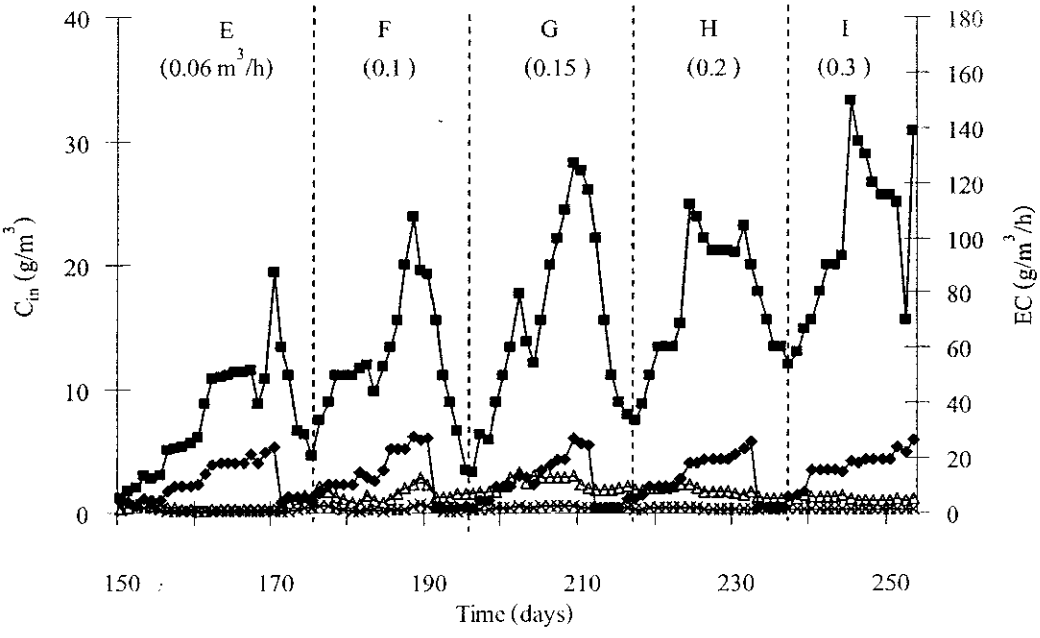


Figure 3-26 Comparison of overall performance of the biofilter packed with palm shells for the removal of toluene from the pure system (T2): (◆) Inlet concentration, and (■) the elimination capacity, and the mixed systems (X2): (×) inlet concentration, and (△) the elimination capacity.

3.4 Removal Capabilities of Individual Bed Sections

As described in chapter 2, each biofilter column comprised five sections, an inlet section, and three central sections each containing a 20 cm depth of packing, and an outlet section. During the experimental runs, gas phase VOC concentrations were regularly measured not only at the inlet and outlet but also at the top of the first and second bed sections. This enables EC values for each of the three sections of each biofilter bed to be determined. EC values would be expected to be greatest in the first or lowest section since gas phase VOC concentrations would be highest here, diminishing as the gas moves upwards through the bed (Prado et al., 2005). This should result in higher rates of VOC transfer into the biofilm, higher VOC concentrations in the biofilm and a more active microbial community (Torkian et al., 2003). Figure 3-27 shows methanol and toluene EC values for each of the three sections of each biofilter. From Figure 3-27 it is evident that, as would be expected, EC values are generally greatest in the lowest or first section and decrease as one moves further upwards through the biofilter.

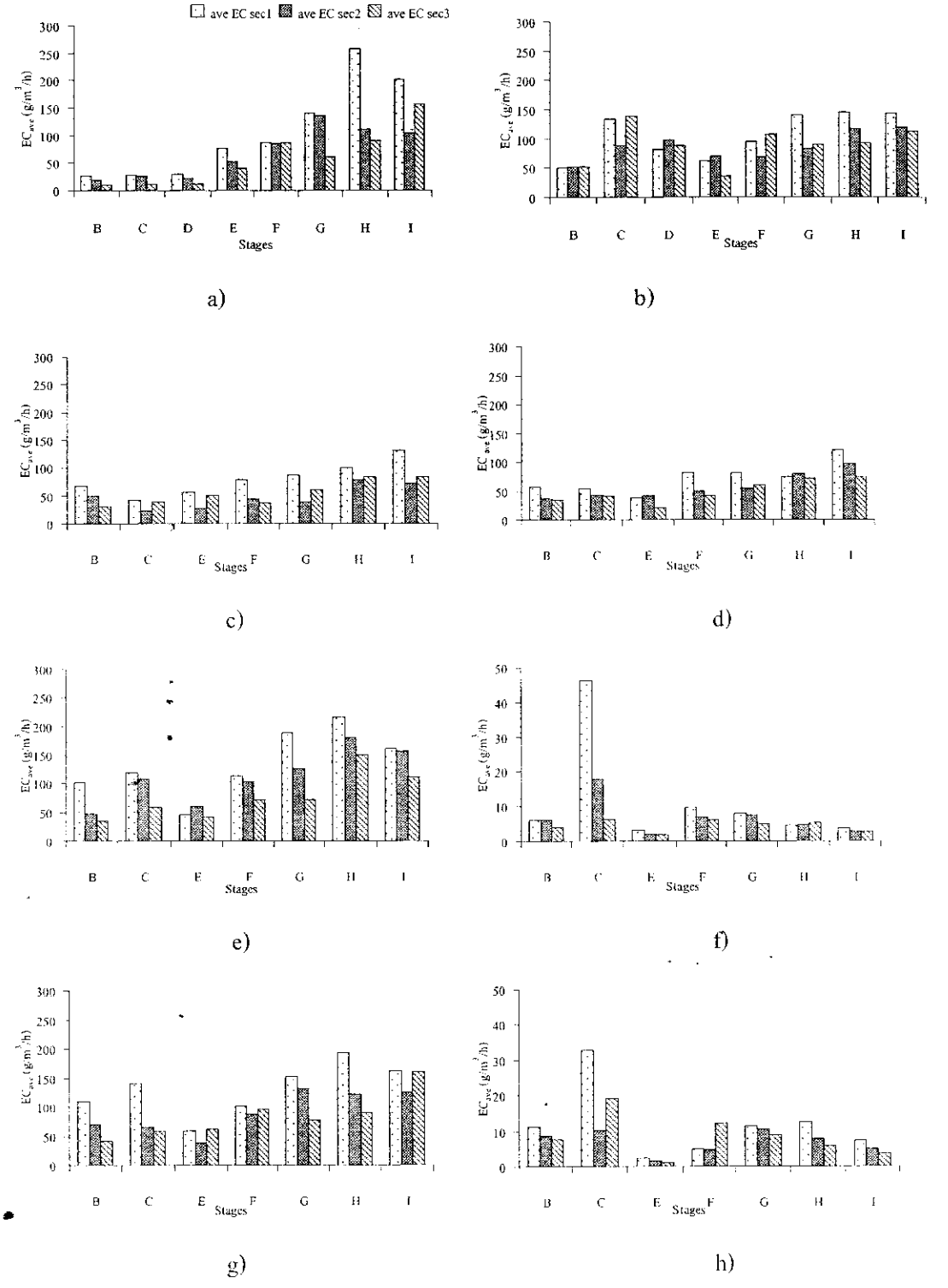


Figure 3-27 Comparison of overall performances of the biofilters packed with a) peanut shells for the removal of methanol in the pure system (M1), b) palm shells for the removal of methanol in the pure system (M2), c) peanut shells for the removal of toluene in the pure system (T1), d)

palm shells for the removal of toluene in the pure system (T2), e) peanut shells for the removal of methanol in the mixed system (X1), f) peanut shells for the removal of toluene in the mixed system (X1), g) palm shells for the removal of methanol in the mixed system (X2), and h) palm shells for the removal of toluene in the mixed system (X2) based on the inlet concentration of each section.

3.5 Elimination Capacity and Inlet Load

The effectiveness of a biofilter in removing a VOC is best expressed in terms of its elimination capacity (Devinny et al., 1999). For low inlet loads, the elimination capacity is equal to the inlet load (RE = 100%) while at higher inlet loads, the elimination capacity is less than the inlet load (RE < 100%).

Figures 3-28 through 3-30 show EC values relating to the removal of pure methanol in biofilter M1, which was packed with peanut shell, for the three concentration ranges: 1-3 g/m^3, 3-6 g/m^3, and 6-9 g/m^3 respectively. On these plots, points corresponding to each of the five flow rates 0.06 m^3/h, 0.1 m^3/h, 0.15 m^3/h, 0.2 m^3/h, and 0.3 m^3/h are given different symbols Only the information obtained during stages E through I was used in preparing these plots as it was only during these stages that the biofilters operated consistently well.

For all three concentration ranges, the EC versus IL plots show a very similar pattern. Initially, as might be expected, EC values and IL values are the same, indicating that all the incoming VOC is being taken up by the biofilter. However, at a fairly low inlet load the EC plot starts to diverge from the RE = 100% line; the point where this happens is often called the critical elimination capacity (EC_{crit}). This is most accurately determined from Figure 3-28, which for biofilter M1 gives a value for EC_{crit} of 25 $g/m^3/h$. At high inlet loads, EC values reach a maximum value and stabilize at this level. This is known as the maximum elimination capacity (EC_{max}); from Figure 3-30, for biofilter M1 this has a value of 198 $g/m^3/h$.

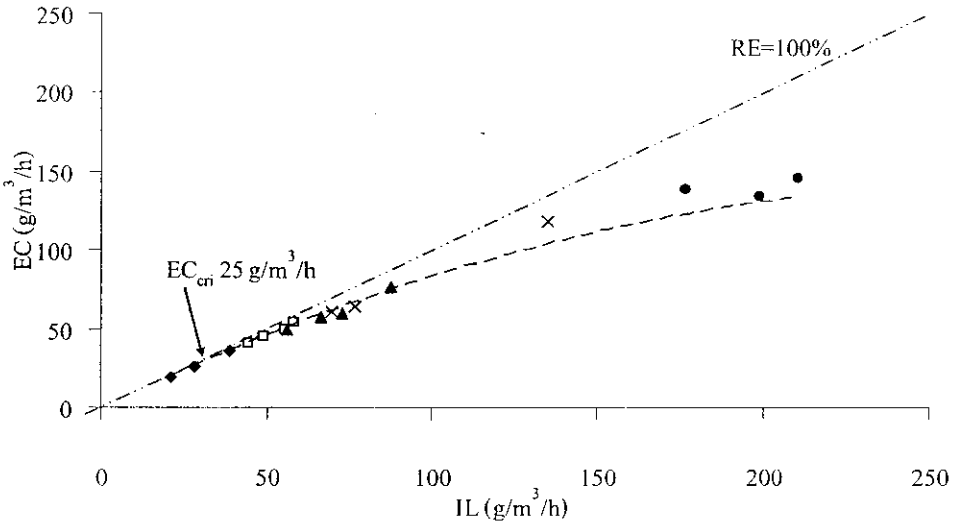


Figure 3-28 Inlet load and methanol elimination capacity for methanol in the single component biofilter packed with peanut shells (M1) for the concentration range of 1-3 g/ m^3 and flow rates of (♦) 0.06, (□) 0.1, (▲) 0.15, (×) 0.2, and (●) 0.3 m^3/h.

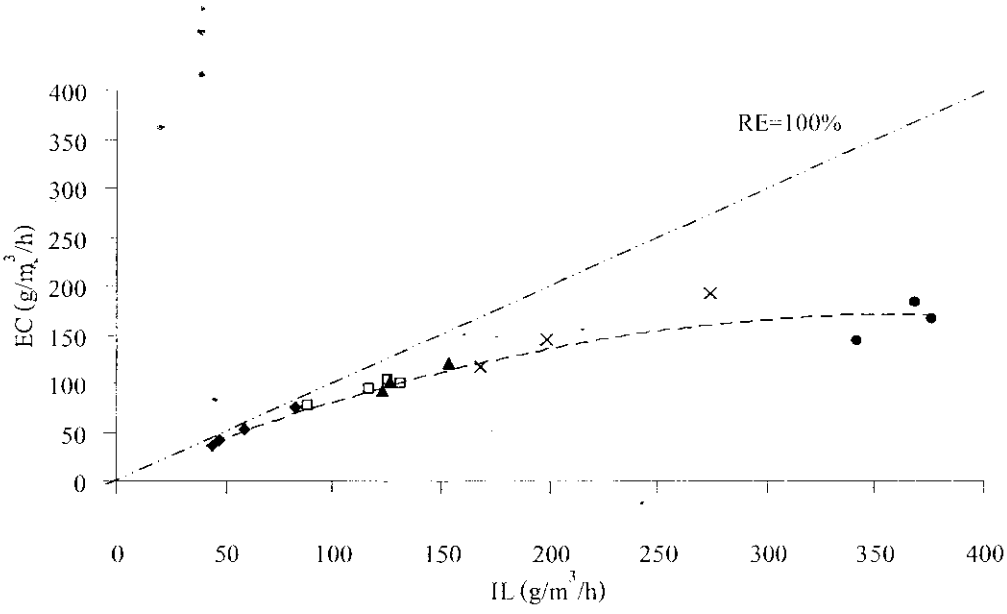


Figure 3-29 Inlet load and methanol elimination capacity for methanol in the single component biofilter packed with peanut shells (M1) for the concentration range of 3-6 g/ m^3 and flow rates of (♦) 0.06, (□) 0.1, (▲) 0.15, (×) 0.2, and (●) 0.3 m^3/h.

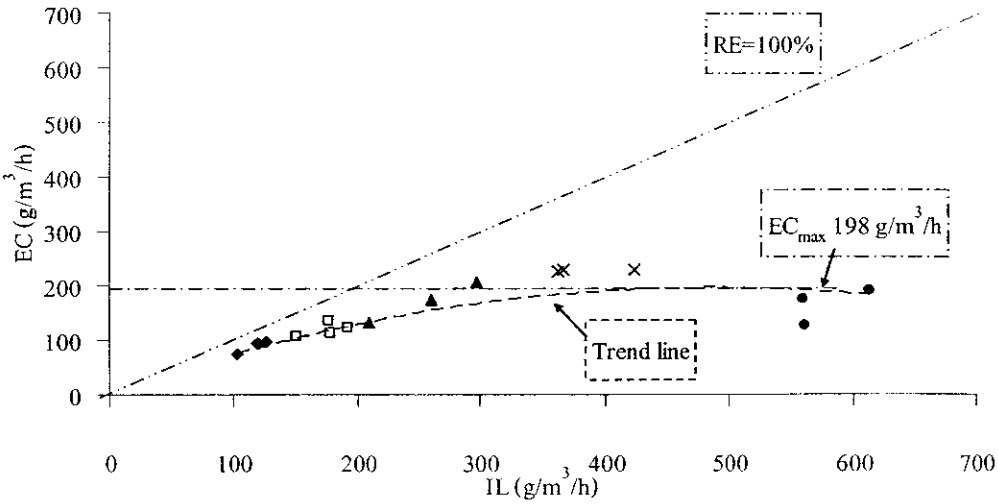


Figure 3-30 Inlet load and methanol elimination capacity for methanol in the single component biofilter packed with peanut shells (M1) for the concentration range of 6-9 g/ m^3 and flow rates of (♦) 0.06, (□) 0.1, (▲) 0.15, (×) 0.2, and (●) 0.3 m^3/h.

Figures 3-31 and 3-32 confirm that there is no obvious dependence of EC on VOC concentration or air flow rate, indicating that the rate controlling step in the overall removal process is the microbial degradation process. The results observed for biofilters M2, T1 and T2 (these can be found in Appendix B) show trends similar to those in Figures 3-33 and 3-34. These plots all confirm the lack of dependence of EC on air flow rate and VOC concentration.

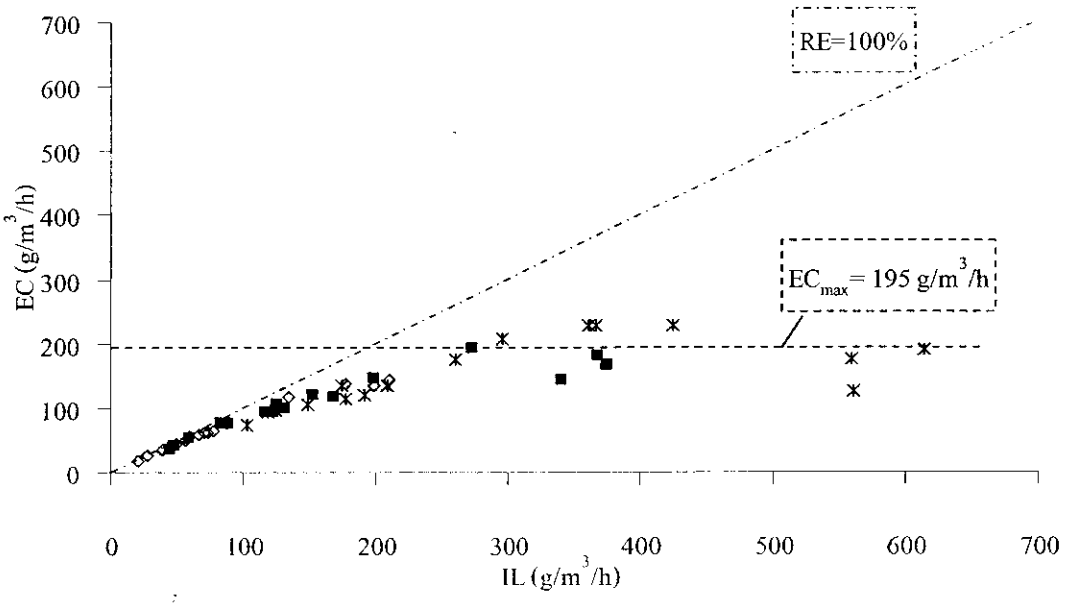


Figure 3-31 Elimination capacity as a function of inlet load for biofilter M1 for the three concentration ranges: (◊) 1-3, (■) 3-6, and (✳) 6-9 g/m^3.

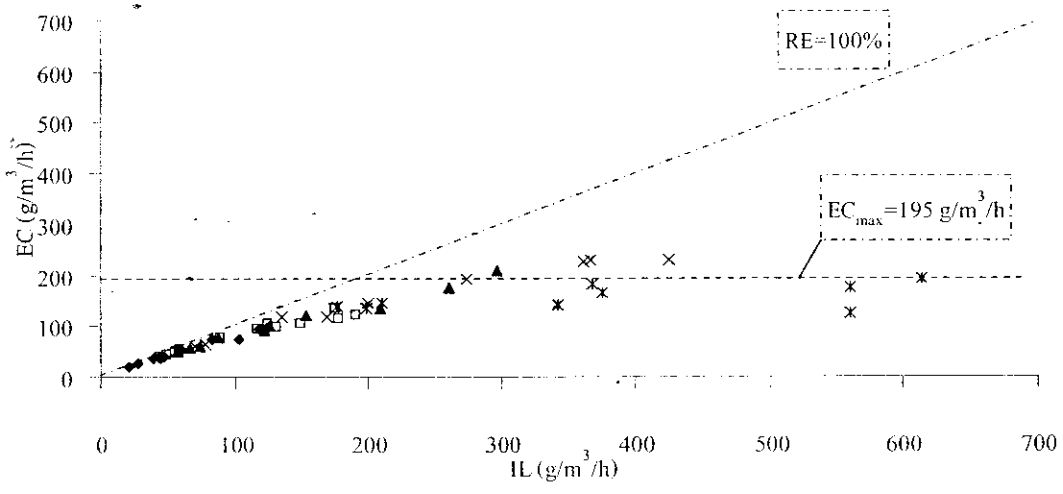


Figure 3-32 Elimination capacity as a function of inlet load for biofilter M1 for the five air flow rates: (♦) 0.06, (□) 0.1, (▲) 0.15, (×) 0.2, and (✳) 0.3 m^3/h.

Average elimination capacities were determined for all biofilters for each combination of inlet VOC concentration and air flow rate. These values are presented in Table 3.1 This table makes it clear that the performances of the biofilters packed with palm shells are very similar to those of the corresponding biofilters packed with peanut shells.

Table 3-1 The average elimination capacity (EC_{ave}) of pure system and mixed system biofilters for different concentration ranges during stages E through I

Air flow rate (m^3/h)	Range of C_{in} (g/m^3)	EC_{ave} in pure system ($g/m^3/h$)				EC_{ave} in mixed system ($g/m^3/h$)			
		Methanol		Toluene		Methanol		Toluene	
		peanut	palm	peanut	palm	peanut	palm	peanut	palm
0.06	1-3 [0.1-2]	29	23	18	16	29	24	4.7	2.7
	3-6 [2-4]	51	58	40	34	88	54	1.3	1.0
	6-9 [4-6]	90	98	57	62	72	81	1.3	1.3
0.10	1-3 [0.1-2]	47	46	20	28	49	52	8.6	7.5
	3-6 [2-4]	94	98	58	51	92	98	4.4	4.6
	6-9 [4-6]	119	125	83	94	147	135	10	11
0.15	1-3 [0.1-2]	61	52	22	21	72	77	5.5	7.5
	3-6 [2-4]	105	72	66	65	123	133	7.4	13
	6-9 [4-6]	172	173.	112	123	209	166	7.4	11
0.20	1-3 [0.1-2]	81	73	41	36	122	75	5.1	8.9
	3-6 [2-4]	152	121	94	96	192	164	4.3	9.9
	6-9 [4-6]	228	163	129	99	230	168	5.2	7.2
0.30	1-3 [0.1-2]	139	104	76	60	101	105	3.2	5.6
	3-6 [2-4]	164	149	92	126	197	184	3.4	5.2
	6-9 [4-6]	163	123	122	107	131	160	2.9	5.0

Value in [ ] is range of toluene inlet concentration.

The dependence of methanol elimination capacity on inlet load is shown in Figure 3-33 for both the single component methanol biofilters (M1 and M2) and the mixed system biofilters (X1

and X2). It is evident that the EC value plots for all four biofilters are very similar indicating that methanol removal is unaffected by whether the biofilters are packed with peanut shells or palm shells, or by the absence or presence of toluene in the incoming gas.

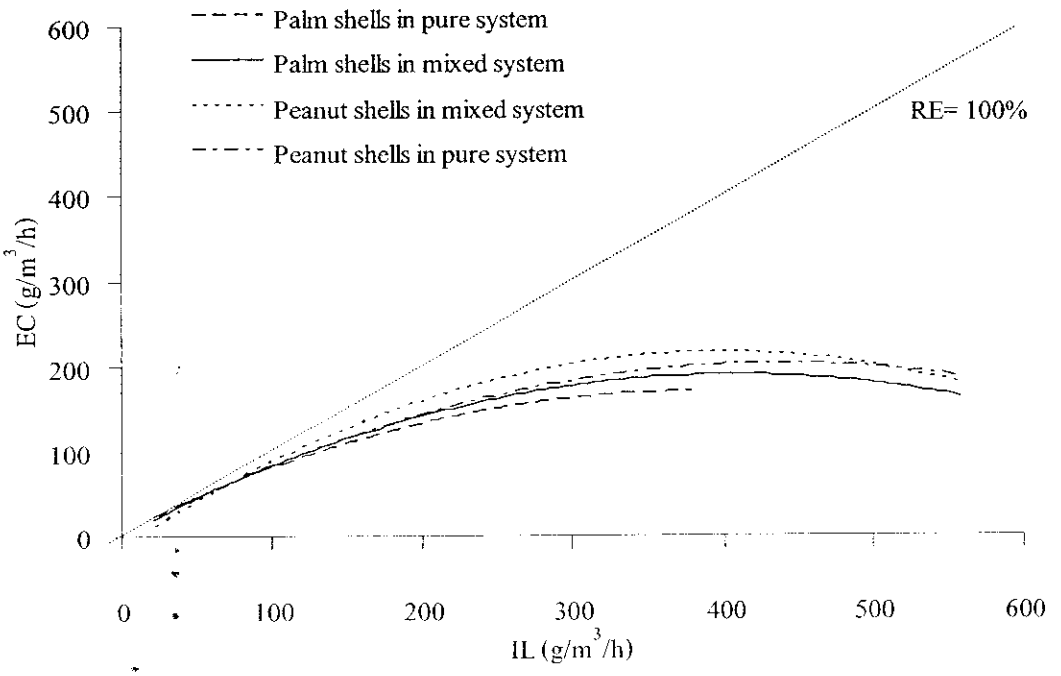


Figure 3-33 Methanol elimination capacity as a function of inlet load in both the single component system and mixed system biofilters (M1, M2, X1 and X2).

In Figure 3-34, elimination capacities for toluene in both the single component and mixed systems, packed with either peanut shells or palm shells, are compared. The maximum elimination capacities were 141 g toluene/m^3/h and 6.6 g toluene/m^3/h for the single component and mixed system biofilters packed with peanut shells, and 133 g toluene/m^3/h, and 8.8 g toluene/m^3/h for the corresponding biofilters packed with palm shells. This Figure shows that EC values were much the same no matter whether peanut shells or palm shells were used as the packing material. It also illustrates very clearly the marked disparity in EC values between the single component systems and the mixed systems. The section of Figure 3-34 relating to the mixed systems is enlarged in Figure 3-35. There is a suggestion from these results that the biofilter packed with peanut shells is

performing slightly better than that packed with palm shells but the scatter in the data is too large to be certain about this.

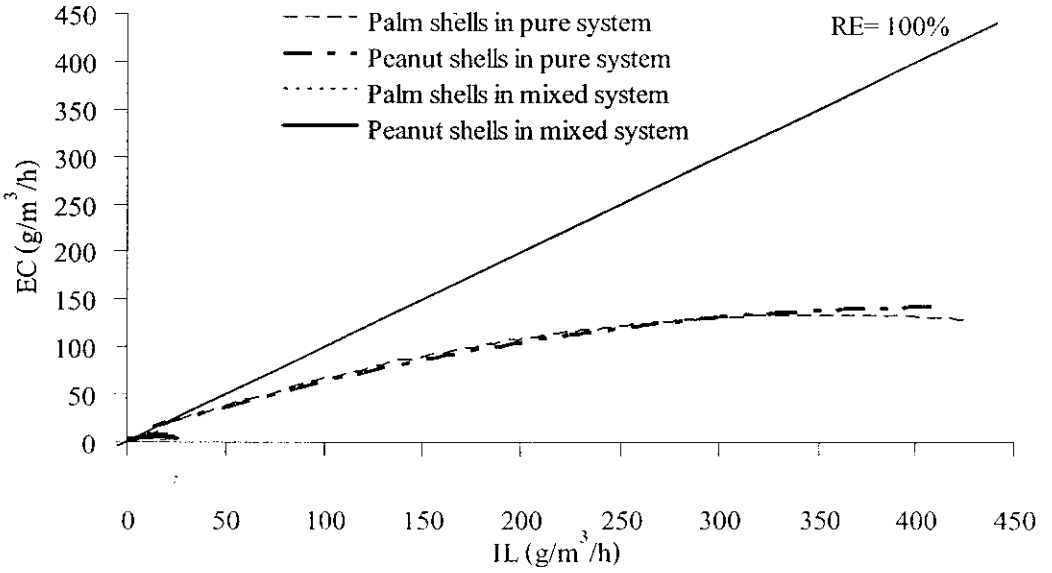


Figure 3-34 Toluene elimination capacity as a function of inlet load in both the single component system and mixed system biofilters (T1, T2, X1 and X2).

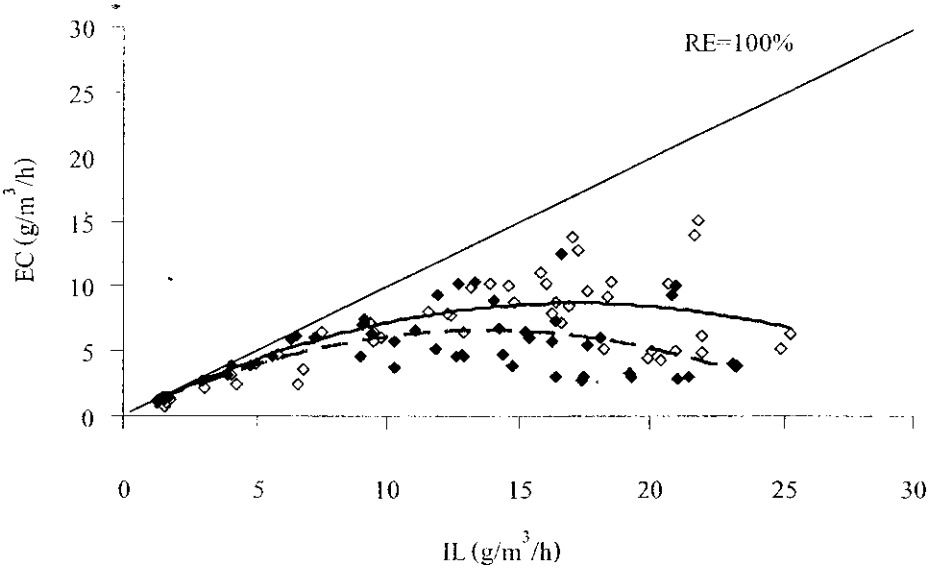


Figure 3-35 Toluene elimination capacity as a function of inlet load in the mixed system biofilters packed with (◇) peanut shells (X1) or (◆) palm shells (X2). (-) is the trend line for the peanut shells and (---) is the trend line for the palm shells.

The EC values obtained for mixed systems in this study are markedly different from results obtained in work undertaken prior to starting the present project. In the previous work, a palm shell packed biofilter was used to study toluene and methanol removal from a gas containing both these VOCs. This biofilter received a gas containing both toluene and methanol from the first day of operation onwards. It was shown in this preliminary study that, as in the present study, the presence of methanol in the incoming gas significantly decreased removal rates of toluene (compared with those obtained in a biofilter receiving solely toluene) while the removal rates for methanol were not affected by the presence of toluene (Chetpattananondh et al., 2005). However, in the earlier study maximum elimination capacities for toluene in the mixed system only dropped by half compared with those in the pure toluene system; decreasing from 181 $g/m^3/h$ to 90 $g/m^3/h$. The results obtained in the previous study are compared with those from the palm shell packed biofilter in the present study in Figure 3-36.

This Figure shows that the EC plot obtained for toluene removal in a single component biofilter in the present study lies significantly below that obtained in the corresponding biofilter in the previous study. Nevertheless the EC values for equivalent inlet loads on the two plots are of comparable magnitude. However, there is a massive difference between the EC values obtained in the mixed system biofilters from the two studies. In the present study the maximum elimination capacity fell from 129 $g/m^3/h$ to 8.8 $g/m^3/h$, i.e. a fifteen-fold decrease. All indications are that the difference in EC_{max} values between the two studies is attributable to the different start-up procedures used. As indicated above, in the previous study the microbial community was exposed to a mixture of methanol and toluene from day one, which should have given both methanol-degrading organisms and those degrading toluene an equal chance of establishing strong and viable colonies. In the present study, however, it would appear that toluene-degrading organisms found it very hard to establish themselves in an environment dominated by a well-established community of methanol-degrading organisms. These results highlight the importance of choosing an appropriate start-up procedure when developing a biofilter system that will treat more than one VOC component. It also shows that more research is needed into the way biofilms develop under different conditions.

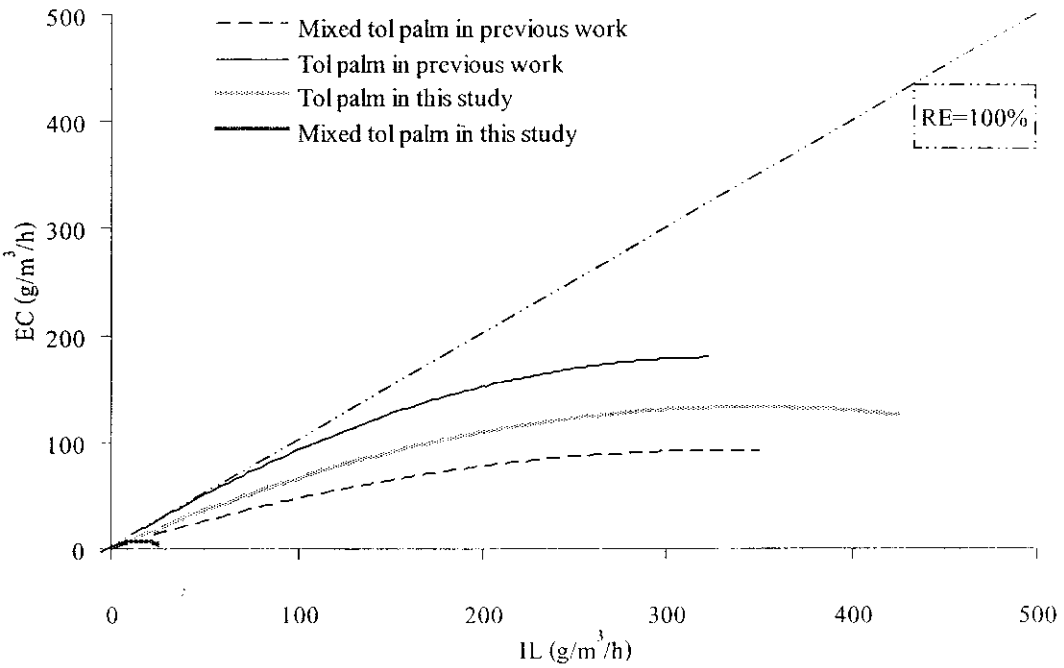


Figure 3-36 Toluene elimination capacity as a function of inlet load for single component and mixed system palm shell biofilters used in previous work and in this study.

Values of critical and maximum elimination capacities obtained in this study are shown in Table 3-2. The critical load or critical elimination capacity was estimated to be 25 $g/m^3/h$ for the removal of methanol in a biofilter packed with peanut shells, and 20 $g/m^3/h$ for the corresponding palm shell system. Given the difficulty of determining exactly where the EC plot and the RE = 100% line start to diverge these values are not significantly different. Estimated critical elimination capacities for the removal of toluene were distinctly lower, being less than 10 g/m^3h for both packing materials.

Table 3-2 The values of the critical and maximum elimination capacities.

Study	Biofilter media	EC_{crit} ($g/m^3/h$)	EC_{max} ($g/m^3/h$)
This study	Pure methanol system		
	- Peanut shells	25	198
	- Palm shells	20	168
	Pure toluene system		
	- Peanut shells	<10	141
	- Palm shells	<10	133
	Methanol in mixed system		
	- Peanut shells	100	215
	- Palm shells	50	185
	Toluene in mixed system		
	- Peanut shells	1	6.6
	- Palm shells	2	8.8

The maximum elimination capacities obtained in this study were comparable to the results obtained by other researchers, as shown in Table 3-3. The VOCs examined in Table 3-3 were from a synthetic and real gas stream. These results indicate that, from a removal performance standpoint, peanut shells and palm shells are as suitable for use as packing media for a high-performance biofilter as more conventional materials. The practical value of this, for industries in Thailand, is that since these peanut and palm shells are both readily available and cheap, one of the major disincentives to installing biofilters to treat waste gases containing VOCs has been removed.

Table 3-3 Comparison of the maximum elimination capacity by other researchers.

Researchers	Substance	Packing media	EC_{max} ($g/m^3/h$)
Prado et al. (2005)	Methanol	Lava rock	173
Zilli et al. (2001)	Toluene	Peat/glass beads	242
Delhoménie et al. (2002a)	Toluene	Compost based	55
Liu et al. (2002)	Toluene	Lava/compost/soil	50
Chetpattananondh et al. (2005)	Toluene	Palm shells	190
Rene et al. (2005)	Toluene	Compost/ceramic beads	128
Wright et. al. (2005)	Toluene	Diatomaceous earth	232
Vergara-Fernández et. al. (2007)	Toluene	Compost/sea shells	82

3.6 The Other Parameters

The physical and chemical/biochemical processes that occur within a biofilter can be affected not only by the inlet gas flow rate and VOC concentration but also by changes in inlet gas properties such as temperature and relative humidity. Changes in parameters such as pH and void fraction within the biofilter can also influence biofilter behavior. In this section relationships between biofilter performance (elimination capacity and removal efficiency) and changes in the above and related parameters (such as pressure drop) are examined.

3.6.1 Pressure Drop

Whilst the pressure drop in the biofilters remained comparatively low in the initial stages of the experimental runs, marked and rapid increases in pressure drop occurred at the mid-stage of a number of runs while more gradual increases occurred towards the end of most runs, as shown in Figures 3-37 through 3-39. Such increases can be caused by increases in gas flow rate, by accumulation of biomass on the packing media, or by a combination of both these factors. The pressure drop increases occurring in the middle stages of the runs were due to biomass accumulation and, as explained earlier, made it necessary to wash down the biofilter columns to remove excess biomass. In the case of biofilter T2, the palm shell filled biofilter fed with a gas

containing toluene, the biofilter was not washed down to remove biomass and the pressure drop increased to 230 mmH_2O. Despite this, the trend of elimination capacity values in T2 was similar to those of the other systems.

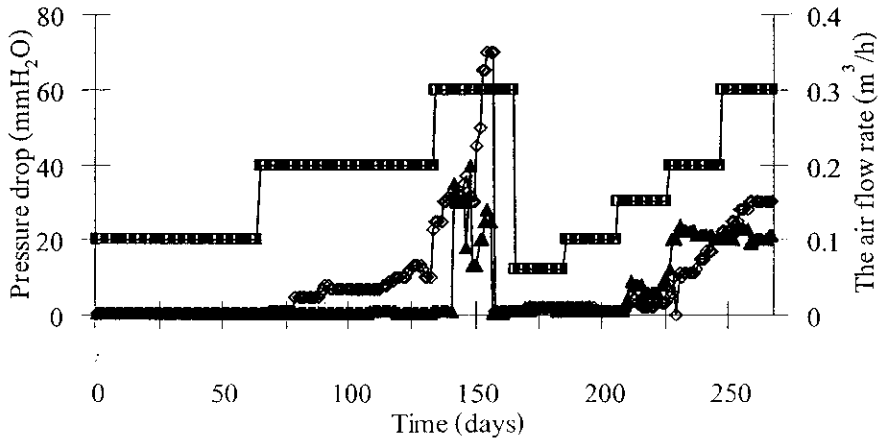


Figure 3-37 The relationship between air flow rate (□) and pressure drop in the pure methanol systems packed with (▲) peanut shells (M1) and (◇) palm shells (M2).

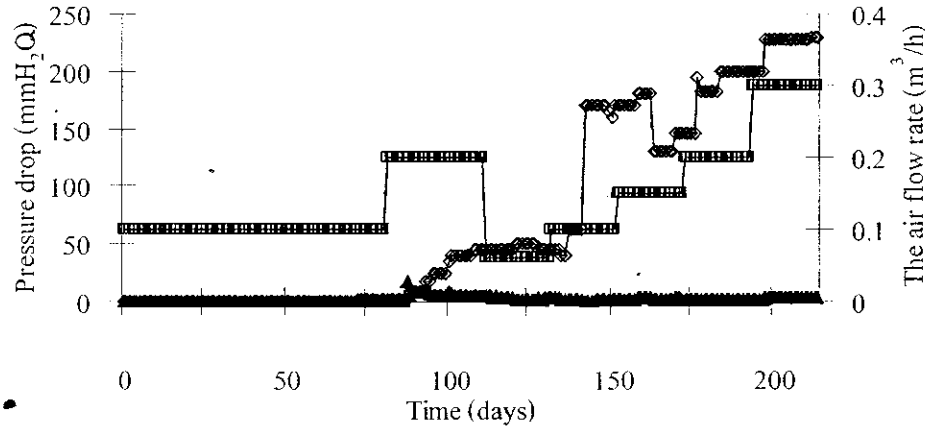


Figure 3-38 The relationship between air flow rate (□) and pressure drop in the pure toluene systems packed with (▲) peanut shells (T1) and (◇) palm shells (T2).

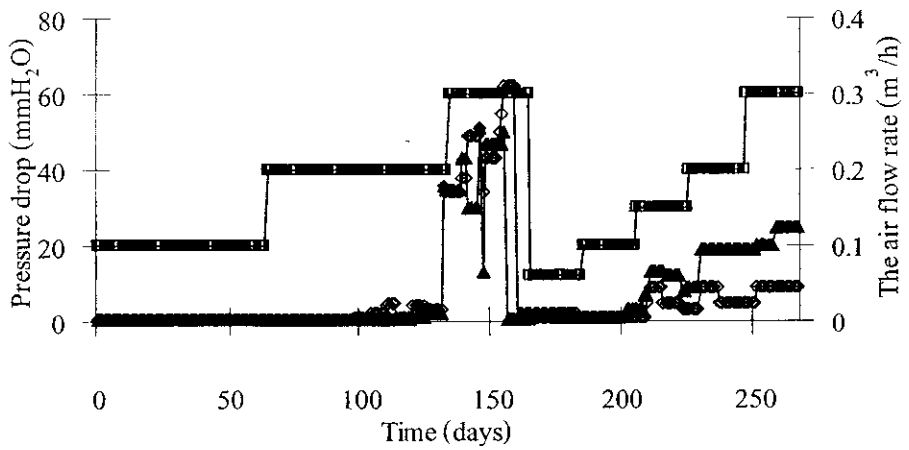


Figure 3-39 The relationship between air flow rate (□) and pressure drop in the mixed systems packed with (▲) peanut shells (X1) and (◇) palm shells (X2).

Pressure drop increases are of concern to biofilter operators as they can increase considerably the cost of passing the gas through the biofilter bed. However, the extent to which they influence biofilter behavior may be much less marked. If it is the microbial breakdown of VOC in the biofilm that is the rate-controlling step in the overall VOC degradation process then changes in pressure drop, whether caused by biomass accumulation or by an increase in a gas flow rate, are unlikely to show any correlation with biofilter performance. However, if it is the diffusion of VOC to the biofilm surface that is rate-controlling (which may be the case when the biofilter is underloaded, or in the packing materials towards the outlet end of the biofilter where gas phase VOC concentrations are low), then some association may be found between pressure drop changes and overall degradation rates. This is because an increase in pressure drop is likely to be accompanied by an increase in turbulence in the gas passing through the packing materials and this should increase diffusion rates. However, if the pressure drop increase is due to a reduction in the void fraction within the biofilter, gas residence times may decrease, partly offsetting or more than offsetting the beneficial effects of any increase in diffusion coefficients.

In order to see what insights could be gained into the processes occurring in the biofilter at various stages in the experimental runs, plots showing how elimination capacity, gas flow rate,

inlet load and pressure drop varied over time were prepared for each of the biofilters. These are discussed separately below.

Figure 3-40 shows the relationships between elimination capacity, inlet load, gas flow rate and pressure drop for the biofilter (M1) containing peanut shells that was used to treat a gas flow containing methanol as the sole VOC. Pressure drop increased quite rapidly once Stage C (0.2 m^3/h) had finished and stage D (0.3 m^3/h) began, getting up to 40 mmH_2O before falling back to 0.5 mmH_2O after removal of the excess biomass. At this point the air flow rate was reduced from 0.3 to 0.06 g/m^3 to help the biomass remaining on the packing to re-acclimatize. Based on the good EC values obtained in stages E to I this re-acclimatization occurred rapidly. In Stages E and F the pressure drop was relatively stable at around 1 mmH_2O and was unaffected by the increase in air flow rate between the two stages. In stage G a quite considerable increase in pressure drop occurred but in Stages H and I it stabilized at around 20 mmH_2O, remaining unaffected by the increase from 0.2 to 0.3 m^3/h that took place between these two stages. From these observations it does not appear that changes in pressure drop were linked to changes in flow rates. Instead it seems that the observed pressure drop increases were due to a build-up of biomass and that it was this build-up that adversely affected the performance of the biofilter system.

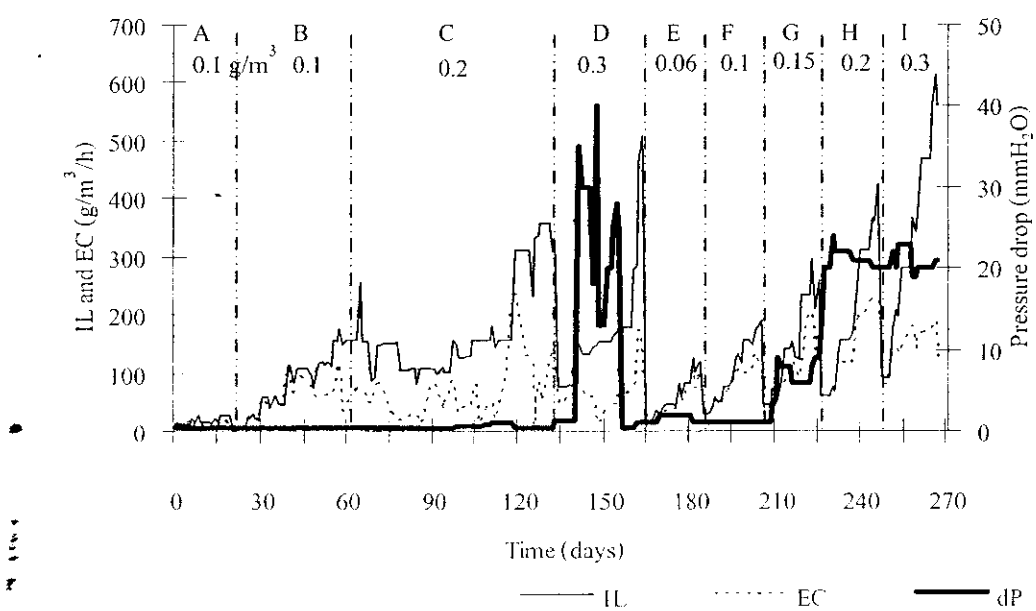


Figure 3-40 Inlet load, elimination capacity and pressure drop for methanol removal in the pure system packed with peanut shells (M1).

Figure 3-41, which relates to M2, the biofilter packed with palm shells and receiving methanol as a VOC, shows similar trends. At first sight the increases in pressure drop appear as if they could be linked to changes in the air flow rate. However, the pattern of change in the pressure drop plot suggests that the pressure drop increase has another cause. Pressure drops are not constant at particular air flow rates and nor are the pressure drops at different flow rates in the non-linear ratio that would be expected if flow rate were the dominant factor influencing pressure drops.

In this biofilter, the pressure drop started increasing in stage C and then rose rapidly in stage D (0.3 m^3/h), reaching 70 mmH_2O. This was accompanied by a decrease in removal efficiencies. Vergara-Fernández et al. (2007) suggested that pressure drop should not exceed 60 mmH_2O, therefore this and the other biofilters (with the exception of T2) were washed by passing water from the top section to the bottom section on day 155. The excess biomass below the beds was mopped up with cotton wool and removed. After the excess biofilm had been washed off, the performance of the system was still poorer than before washing was carried out. This was not unexpected as most of the active microorganisms would have been close to the surface of the biofilm and would have been washed away. To assist the microorganism community to re-acclimatize, the air flow rate was reduced to 0.06 m^3/h (stage E). As in M1, re-acclimatization appears to have been rapid and good EC values were soon being obtained. The pressure drop remained low until the end of stage G when it again began to increase. It then rose more or less linearly with time as the air flow rate increased from 0.15 to 0.3 m^3/h (stages G through I). Up until midway through Stage I methanol was still being effectively removed, even though the pressure drop had by then risen to 30 mmH_2O. In the latter half of stage I, however, EC values started to fall away quite rapidly, suggesting that there was once again an excess biomass problem.

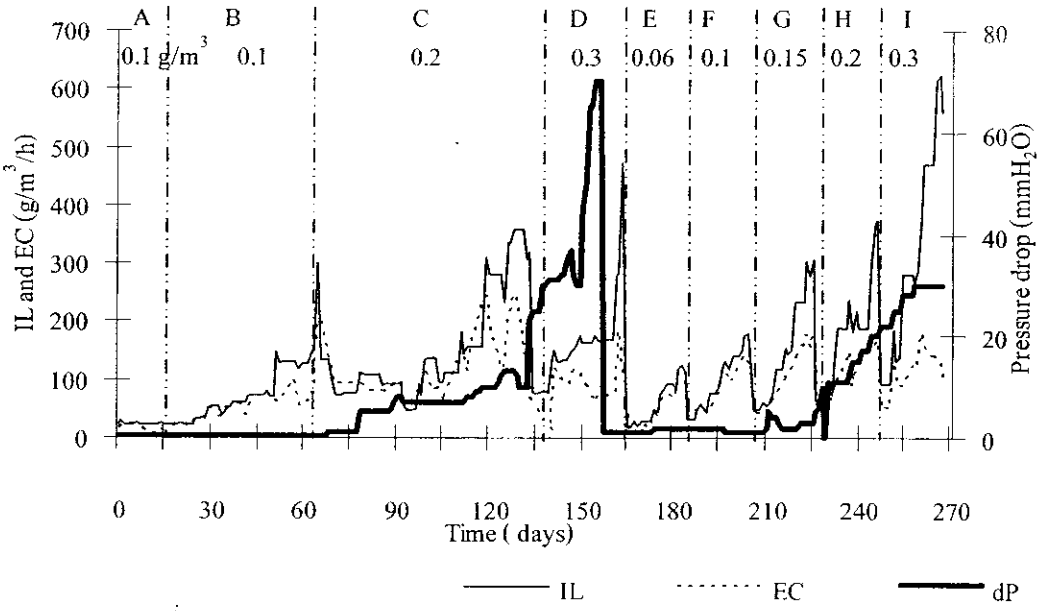


Figure 3-41 Inlet load, elimination capacity and pressure drop for methanol removal in the pure system packed with palm shells (M2).

Figures 3-42 and 3-43 are plots relating to toluene removal corresponding to the methanol removal plots shown above, namely Figures 3-40 and 3-41. The pressure drop patterns in these two plots are not only very different from those in the previous two Figures but they also differ markedly from each other.

Figure 3-42 shows that the pressure drop in biofilter T1 stayed very low through stages A and B before rising abruptly in stage C. This behaviour was not that different from what was observed in biofilters M1 and M2. However, in T1 the washing of the biofilter column failed to achieve as great a reduction in the pressure drop as happened in the previous biofilters. Dropping the gas flow rate from 0.2 to 0.06 m^3/h brought about a significant further drop, suggesting that in this biofilter at least there may have been some relationship between pressure drop and gas flow rate, but this is highly speculative. The pressure drop bottomed out in stage F and then increased slowly again in succeeding stages but was still only at the comparatively low level of 4 mmH_2O when the main experimental run ended.

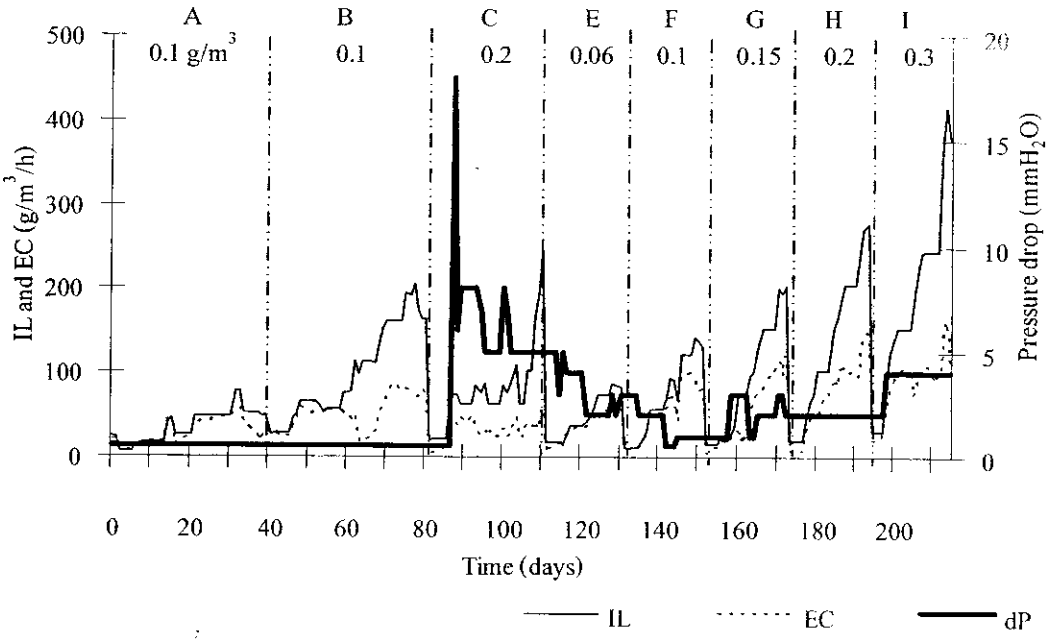


Figure 3-42 Inlet load, elimination capacity and pressure drop for toluene removal in the pure system packed with peanut shells (T1).

As is shown in Figure 3-43, the pressure drop changes in biofilter T2 are markedly different from those in T1. This was mainly because, in the absence of a pressure drop spike in stage C, it was decided not to wash down the biofilter beds as was done with other biofilters. This meant that when the pressure drop did start to increase significantly, as happened some time into stage C, no steps were taken that would cause it to decrease again and so it continued to climb, eventually reaching a very high maximum of 230 mmH_2O during stage I (0.3 m^3/h). Rather surprisingly, and in contrast to what was observed elsewhere, despite the high pressure drop levels, EC values were good right up until midway through stage I. As in M1 and M2 the pattern of pressure drop change suggests that it is related to biomass accumulation rather than gas flow rate. In stages B and F, for example the gas flow rates are the same (0.1 m^3/h) but the pressure drops are vastly different.

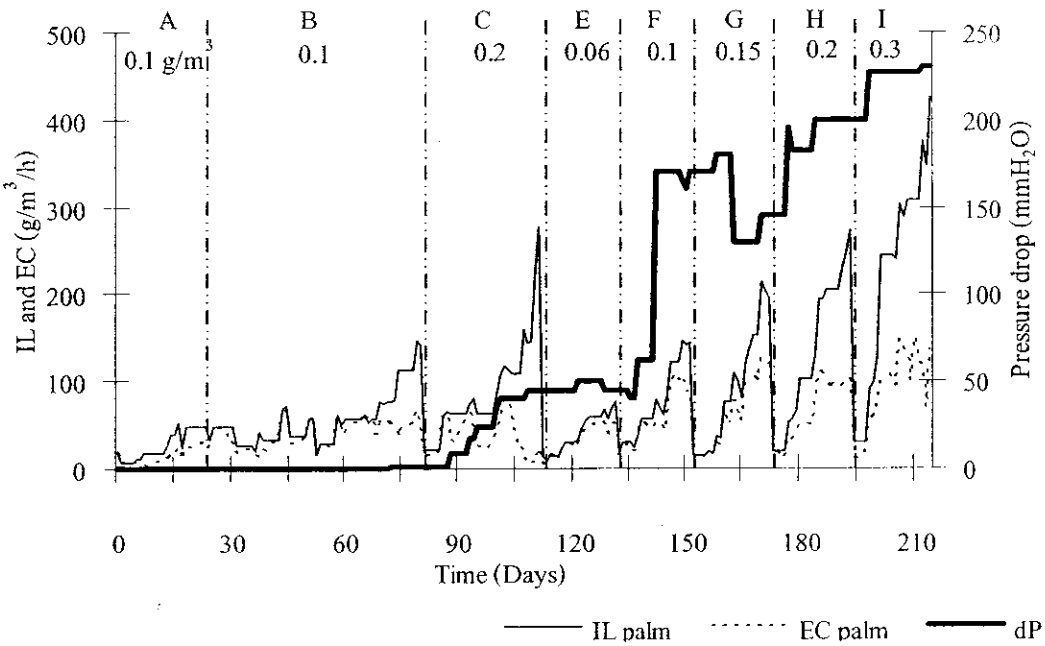


Figure 3-43 Inlet load, elimination capacity and pressure drop for toluene removal in the pure system packed with palm shells (T2).

Figures 3-44 through 3-47 show plots comparable to Figures 3-40 to 3-43 but this time for the mixed system biofilters X1 and X2. In Figures 3-44 and 3-46 the EC values refer to methanol while in Figures 3-43 and 3-45 the EC values are for toluene. Figures 3-44 and 3-46 show that the relationships between pressure drop and EC values for methanol are very similar in the mixed systems to those for the single component systems.

Because of the very poor EC values achieved for toluene in the mixed systems no attempt was made to draw conclusions from Figures 3-45 and 3-47.

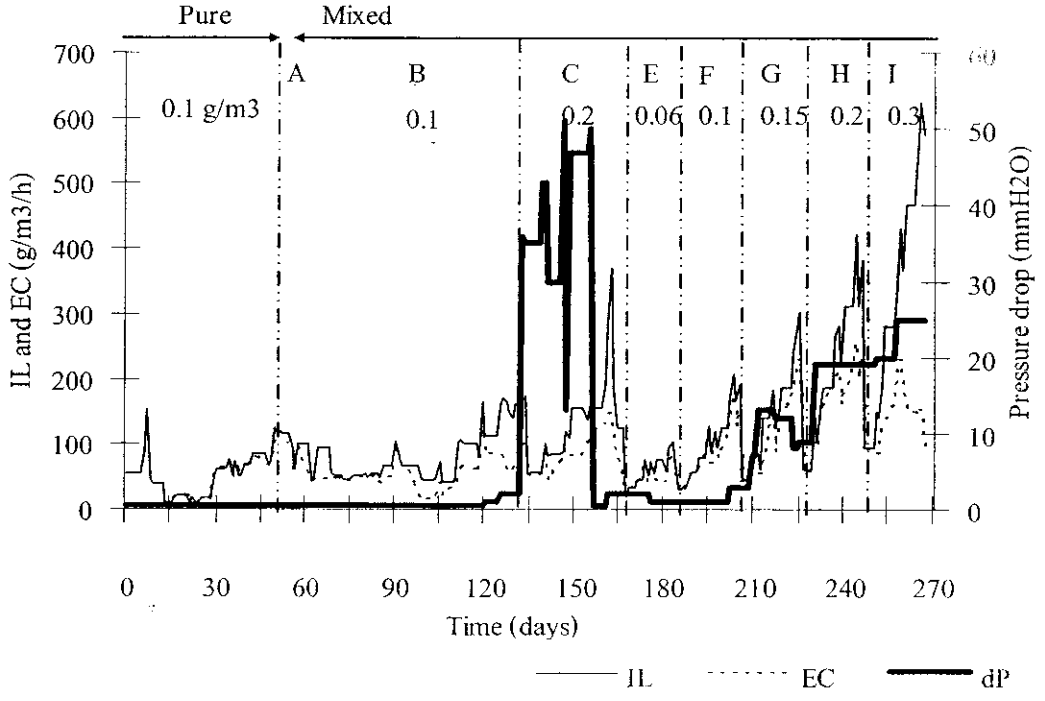


Figure 3-44 Inlet load, elimination capacity and pressure drop for methanol removal in the mixed system packed with peanut shells (X1).

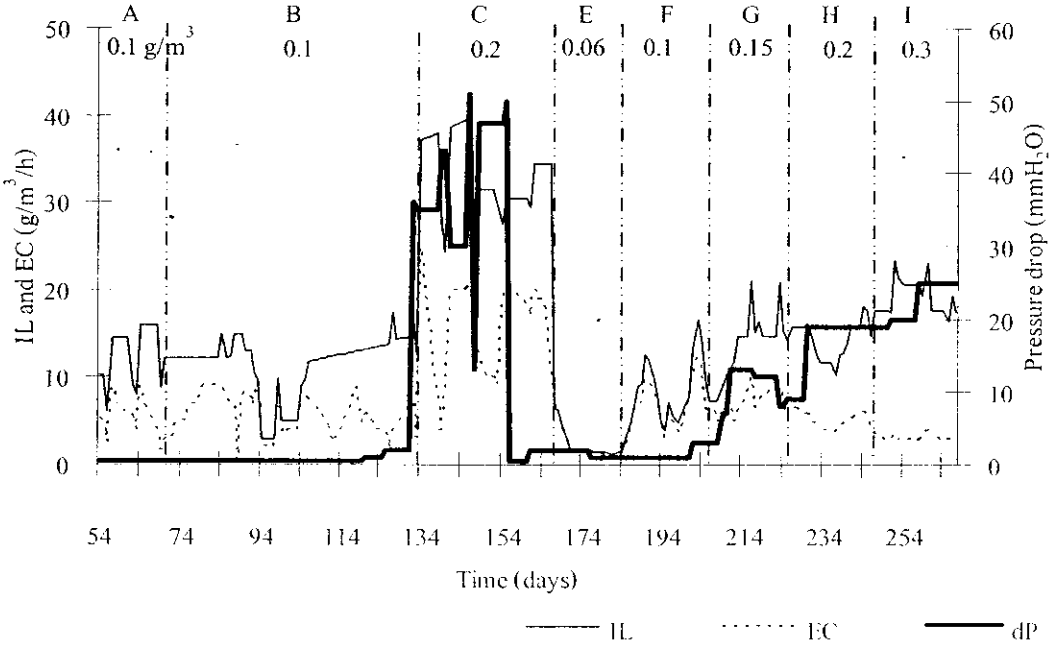


Figure 3-45 Inlet load, elimination capacity and pressure drop for toluene removal in the mixed system packed with peanut shells (X1).

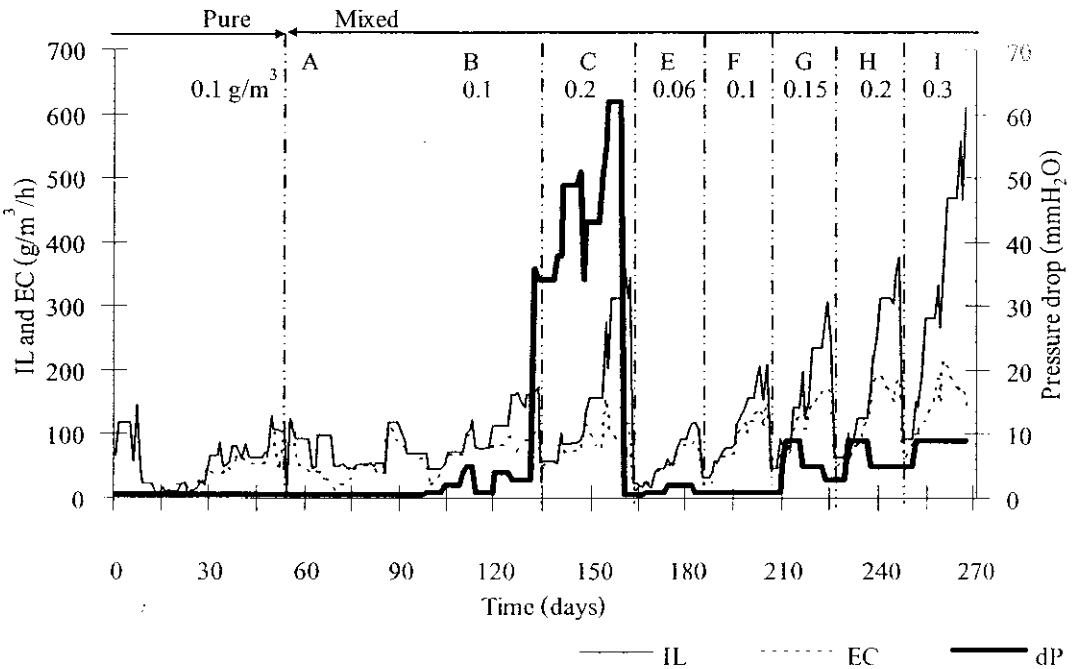


Figure 3-46 Inlet load, elimination capacity and pressure drop for methanol removal in the mixed system packed with palm shells (X2).

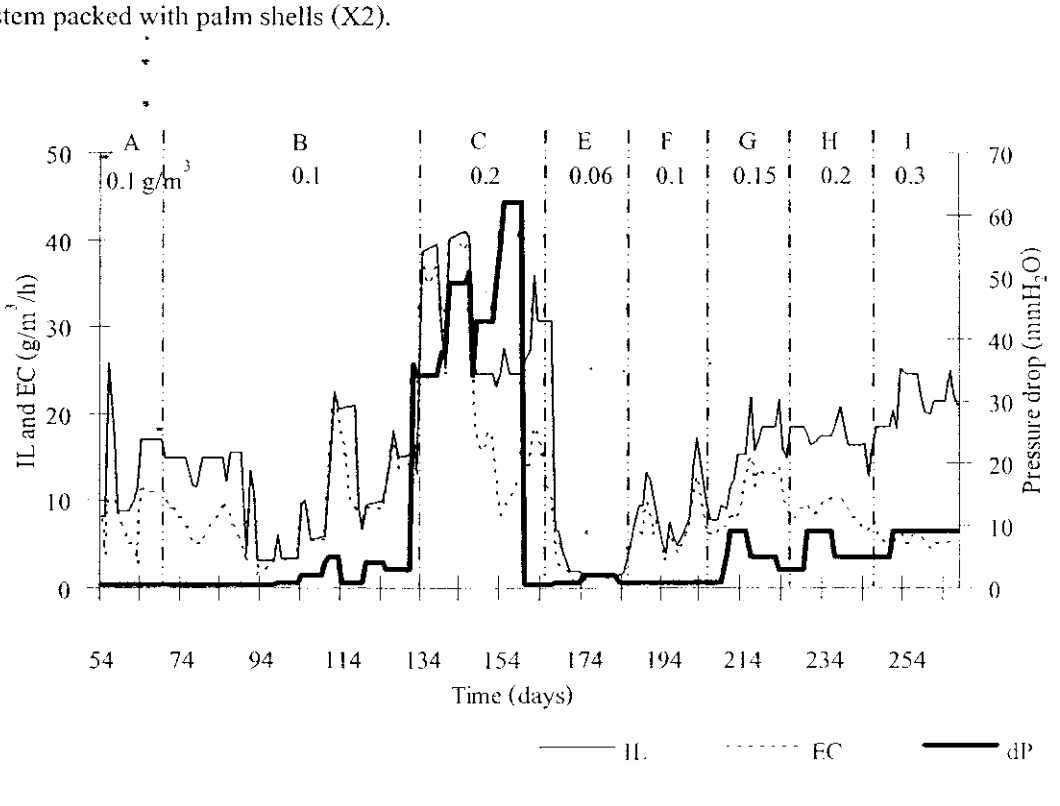


Figure 3-47 Inlet load, elimination capacity and pressure drop for toluene removal in the mixed system packed with palm shells (X2).

3.6.2 The Other Parameters (temperature, relative humidity and pH)

Both inlet gas temperature and relative humidity have the potential to affect what happens within the biofilter. As discussed earlier, changes in temperature occur within the biofilter because of the energy liberated during microbial oxidation of the VOCs; however, these tend to be small because the bulk of the energy released is used to provide latent heat of evaporation rather than sensible heat. This means that the temperatures within the biofilter, which have a significant effect on reaction rates, are largely determined by the inlet gas temperature. The relative humidity of the incoming gas also has an effect on biofilter conditions since it affects rates of evaporation of water from the biofilm. If the relative humidity of the inlet gas is too low, drying out of the packing close to the gas inlet is likely to occur, effectively reducing the active biofilter volume. To minimize problems associated with temperature and relative humidity, inlet gas from the compressors used to supply the biofilters was passed through a series of humidifiers (see Chapter 2). Ambient air temperatures ranged from 24 to 31°C and the inlet gas temperatures were within the range of 25-29°C. Ambient relative humidities ranged from 51% to 90%; after passage through the humidifiers, they were always higher than 90%. The pH within the column was controlled and kept in the range of 6-7 in all biofilters throughout the experimental runs.

Figure 3-48 a) to f) shows plots, for each of the biofilters, of ambient temperature and temperatures at the biofilter inlet and at the end of each of the three biofilter sections; of ambient and inlet gas relative humidity and of relative humidity at the end of each biofilter section; and of pH. It is evident that the only parameter showing significant variation was the ambient relative humidity; within the biofilter very little variation was observed and it was concluded, therefore, that the influence of these parameters on biofilter performance was minimal. It is noteworthy that neither temperature nor relative humidity changed significantly along the biofilter.

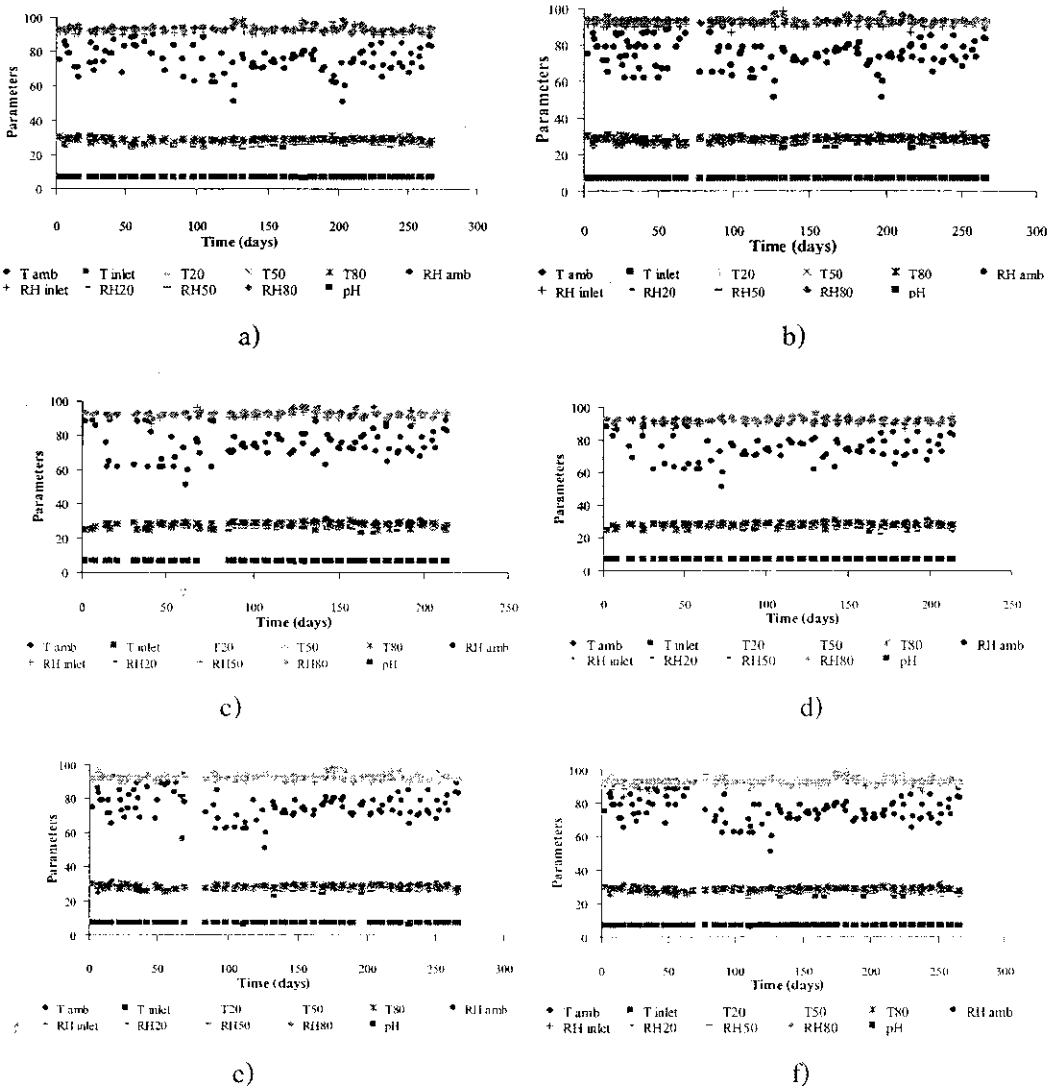


Figure 3-48 The measured values of temperature (T), relative humidity (RH), and pH of the biofilter for the removal of a) methanol in the pure system packed with peanut shells, b) methanol in the pure system packed with palm shells, c) toluene in the pure system packed with peanut shells, d) toluene in the pure system packed with palm shells, e) methanol and toluene in the mixed system packed with peanut shells, and f) methanol and toluene in the mixed system packed with palm shells. ('amb' denotes ambient conditions; 'inlet' denotes conditions at the inlet port; while '20', '50' and '80' denote conditions at bed heights of 20, 50 and 80 cm, respectively.)

3.7 Characteristics of Packing Materials

3.7.1 Bulk Density and Void Fraction

As stated earlier, both peanut shells and palm shells used as packing materials were similar in size (range from 0.5 to 1.0 cm). However, the structure of both shells is very different, which is why the raw peanut shells have a bulk density (71 kg/m^3) which is much lower than that of raw palm shells (490 kg/m^3). This suggests that structurally stronger and more robust filter bed supports would be needed if using the latter material (i.e. palm shell).

The void fractions in the columns packed with two different materials also differed, 0.8 for peanut shells and 0.65 for palm shells. According to Shareefdeen and Singh (2005), media with a high void fraction are preferred; this is because they enable more microorganisms to attach to packing material surfaces under conditions of low shear (Malhautier et al., 2005). Once experiments began and biofilms grew on the packing materials the void fractions in the columns decreased, as did the differences between the two types of materials. As shown in Table 3-4, void fractions measured at the end of the main experimental runs were not dissimilar for biofilters treating the same VOC or VOC mixture. The extent of the change in void fraction in these experiments is of comparable magnitude to that observed by Delhoménie et al. (2003), who observed a decrease from 53% to 33% over a 35 day period in a biofilter packed with compost and used to remove toluene. The change in void fraction appears to be mostly attributable to biomass growth rather than to loss of structural integrity in the packing materials.

After 113 days, the packing heights in middle sections of biofilter columns had decreased by only 0.1 cm (original height 20 cm) except in the case of M1, which contained peanut shells and was receiving a gas containing only methanol. In this biofilter the packing material dropped 0.5 cm. These observations contrast strongly with those of other researchers. Jin et al. (2008) point out that some organic media, such as compost, tend to decay easily, which leads to bed compaction. This was the experience by Singh et al. (2006) whose experiment ran over a 50 day period and recorded a total drop of 8 cm in a 3 section biofilter column, with a total height of 70 cm, packed with yellow-gram stalks. To overcome this compaction problem and extend the life of organic packing media that decay rapidly, large size inert materials such as glass beads, polystyrene spheres and lava rocks are often added to the organic media (Jin-Ying et al., 2005). However, most inert media are more expensive than natural organic media (Kennes et al., 2002).

In addition, in order to obtain a uniform mix of materials they need to be carefully mixed with the organic media, adding considerably to the complexity and cost of the media preparation step. It would appear that use of inert media is unnecessary with peanut shells and palm shells, which is encouraging since part of the aim of this project was to find cheap and easy to use biofilter media that would assist Thai industry to find economical and effective ways to remove VOCs from waste gases.

Table 3-4 The physical characteristics of peanut shells and palm shells.

Characteristics	Peanut shells		Palm shells	
	Before packing	After packing	Before packing	After packing
Pellet size (cm)	0.5-1	0.5-1	0.5-1	0.5-1
pH	6.1		4.94	
Packing density (kg/m^3)	71		490	
Void fraction (%)	80		65	
Methanol system		48.0		44.8
Toluene system		58.0		58.7
Mixed system		42.2		49.4

3.7.2 Chemical Composition and Properties

Samples of packing materials were dried at 105°C for 5 hours to determine their moisture contents. These analyses were carried out by an external laboratory (Central Analytical Laboratory, Faculty of Natural Resources, Prince of Songkla University). The moisture content of the two packing materials was comparatively low: 6.6% for peanut shells and 8.9% for palm shells. It is noteworthy that this is about half that of typical equilibrium moisture contents for materials like wood in a climate similar to that in southern Thailand. In Table 3-5 the moisture contents of the dry packing materials are compared with the moisture contents of the biofilter beds as measured at the end of the experimental runs. Tables 3-6 and 3-7 show the elemental composition and ash content of peanut shells and palm shells, on a wet basis and a dry basis respectively.

Table 3-5 The moisture content of peanut shells and palm shells (wet basis).

Moisture content (%)	Peanut shells		Palm shells	
	Before packing	After packing	Before packing	After packing
Raw material	7		9	
Methanol system		74		30
Toluene system		85		50
Mixed system		83		35

Table 3-6 The elemental composition and ash content of the peanut shells and palm shells (wet basis).

Characteristics	Peanut shells		Palm shells	
	Before packing	After packing	Before packing	After packing
Organic carbon (%)	52		51	
Methanol system		14		40
Toluene system		7		28
Mixed system		9		37
Total nitrogen (%)	0.8		0.4	
Methanol system		0.5		0.3
Toluene system		0.5		0.3
Mixed system		0.4		0.4
Total phosphorus (mg/kg)	636		203	
Methanol system		-		162
Toluene system		379		138
Mixed system		379		-
Ash content (%)	3.2		2.8	
Methanol system		1.3		1.2
Toluene system		-		1.2

Table 3-7 The elemental composition and ash content of the peanut shells and palm shells (dry basis).

Characteristics	Peanut shells		Palm shells	
	Before packing	After packing	Before packing	After packing
Organic carbon (%)	56		56	
Methanol system		13		36
Toluene system		7		25
Mixed system		8		34
Total nitrogen (%)	0.9		0.4	
Methanol system		0.5		0.3
Toluene system		0.5		0.3
Mixed system		0.4		0.4
Total phosphorus (mg/kg)	680		223	
Methanol system		-		148
Toluene system		353		125
Mixed system		352		-
Ash content (%)	3.4		3.1	
Methanol system		1.2		1.1
Toluene system		-		1.1

The organic carbon levels are typical of those in many plant materials. The nutrient content of the peanut shells is substantially better than that of the palm shells. This therefore gives peanut shells a potential advantage over palm shells as both nitrogen and phosphorus are essential nutrients for microorganisms (Liu et al., 2002). The ash contents of the two packing materials are quite similar and a good deal lower than ash contents of some other locally available agricultural wastes such as rice husk (16-22%). The pH of raw peanut shells, measured as described in chapter 2, was 6.1, a good deal higher than that of raw palm shells (4.9).

3.7.3 BET Surface Areas

BET surface areas of the packing materials were measured prior to the beginning and at the end of the experiments; the results are shown in Table 3.8. Tests were also done to check whether exposure of the peanut shells and palm shells to the VOCs might affect BET surface areas.

Table 3.8 The BET surface area of peanut shells and palm shells.

Characteristics	Peanut shells		Palm shells	
	Before packing	After packing	Before packing	After packing
BET surface area (m^2/g)	1.23-1.31		0.17-0.34	
Methanol system		0.81-1.04		0.29-0.42
Toluene system		1.29-1.64		0.31-0.64
Mixed system		0.79-1.23		0.33-0.44

The raw palm shells have much lower BET surface areas than the raw peanut shells. After 3 days immersion in methanol or toluene the following BET surface area measurements were obtained:

Peanut shells: for methanol 0.89 m^2/g for toluene 1.17 m^2/g

Palm shells: for methanol 1.46 m^2/g for toluene 0.41 m^2/g

In the case of palm shells an increase in BET surface areas occurred no matter which VOC was being removed. A small increase also occurred when peanut shells were used in experiments to remove toluene. However, in biofilters packed with peanut shells and used for removal of methanol, whether present on its own or in a mixture with toluene, measured BET surface areas decreased significantly. Decreases in BET surface areas over time have been observed for other packing materials, for example when hydrogen sulfide was being removed in a biofilter packed with activated carbon (Ng et al., 2004). In the latter case the decrease was attributed to biofilm developing on some of the pore surfaces in the carbon. However, in the present project the decrease could also be linked to chemical reaction of methanol with the surface

of the peanut shells; the BET surface area of raw peanut shells immersed in methanol for three days was 0.89 m^2/g, which is around 30% lower than the value obtained for the untreated raw peanut shells, and this contrasts strongly with the 10% increase in BET surface area observed after palm shells had been immersed in methanol for three days. However, packing media immersed for three days in pure solvents experience conditions very different from those they are exposed to in operating biofilters. Therefore the relevance of the BET changes given above to what occurs in actual biofilter packing media remains uncertain. In the case where the packing materials were immersed for three days in toluene rather than methanol, decreases in BET surface areas of around 8% and 69% were observed for peanut shells and palm shells respectively; this trend is opposite to that observed in the operating biofilters (percent of decreasing of the BET surface area was based on raw palm shells at 1.32 m^2/g).

3.7.4 BJH Pore Size Distribution

BJH pore size distribution measurements were made on sample surface areas of the packing materials prior to the beginning and at the end of the experiments. The volumes of both mesopores (2-50 nm in size) and macropores (>50 nm in size) were measured. Figures 3-49 and 3-50 show the measured pore volumes of seven different pore size ranges for single component system packings and mixed component system packings respectively. These measurements provide further evidence of the different impacts that methanol and toluene have on the peanut shell and palm shell packings.

Figure 3-49 shows the relationships between pore size and pore volume for both packing media when treating gas streams containing methanol or toluene separately. For palm shells there is an increase in both the mesopore volume and the macropore volume over the course of the experiments using methanol and those using toluene. The increases in mesopore volume are similar for both VOCs but a substantially greater increase in macropore volume occurred when using toluene. For the peanut shells, however, VOC-related differences are much greater. When experiments were conducted using methanol, small decreases in pore volume occurred across the entire range of pore sizes.

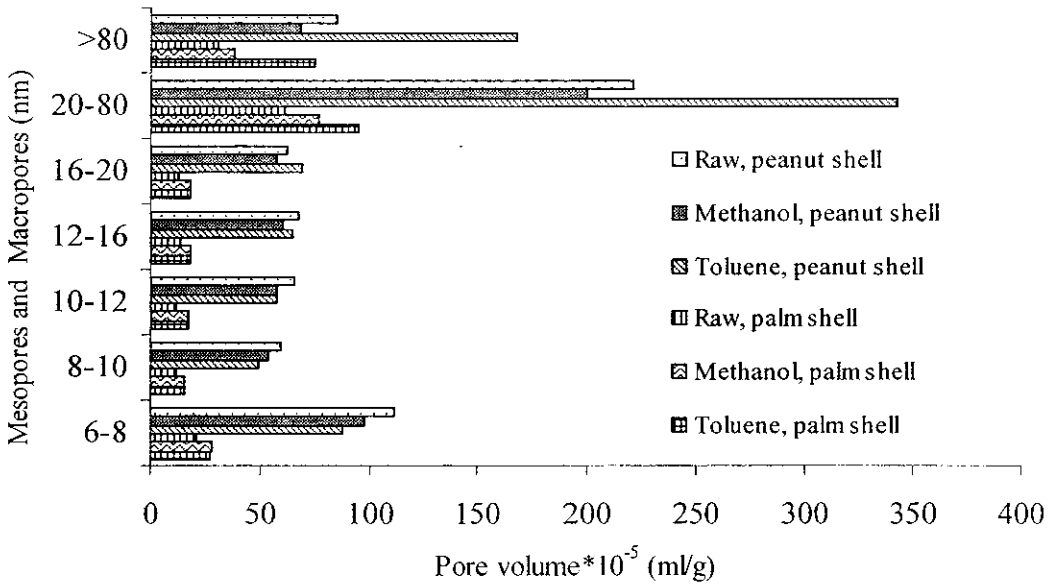


Figure 3-49 The BJH pore size distributions in single VOC systems.

Figure 3-50 shows that at the end of the experimental period both peanut shell and palm shell packings exposed to a mixture of methanol and toluene showed an increase in pore volume over all of the measured pore size ranges. This suggests that even though toluene concentrations in the gases that were fed to these mixed system biofilters were comparatively small, the toluene concentrations present in the biofilm were sufficiently large to have a significant effect on the packing surfaces.

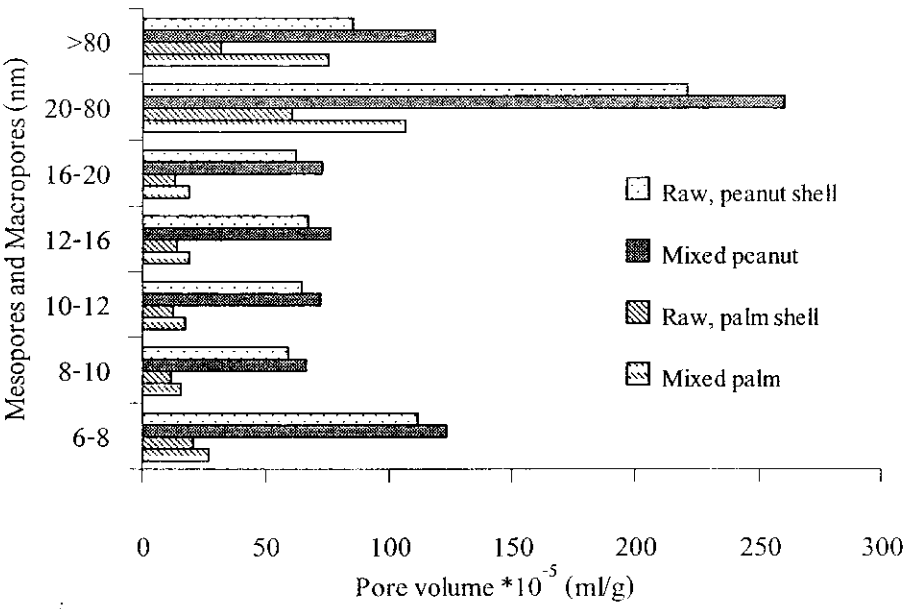


Figure 3-50 The BJH pore size distributions in mixed VOCs systems.

3.7.5 Discussion

Combining the observations of changes in bed height, BET surface areas and pore volume distributions suggests that both packings are to some extent susceptible to attack by the VOCs themselves, and possibly also by intermediates formed in the course of biodegradation (such as benzoic acid in the case of toluene). In the case of palm shells, and of peanut shells exposed to toluene, the structural integrity of the packings does not seem to be compromised to any significant extent. With peanut shells exposed to methanol, though, the reduction in macropore volume coupled with the 0.5 cm decrease in bed height points to a more serious level of structural breakdown. Clearly, when using agricultural products as packing materials attention needs to be paid to the types of VOC involved before packing materials are selected.

3.8 Biofilm Characteristics

3.8.1 Biofilm Thickness

The thickness of biofilm that built up on the packing materials at the end of the experimental runs was measured using a vernier device. There was considerable variation in thickness from one point on the surface to the next point: hence a number of measurements were taken on each sample. The results are shown in Table 3-9.

Table 3-9 Biofilm thickness measured by vernier device.

System	Packing media	Section	Biofilm thickness (mm)	Average biofilm thickness (mm)
Pure methanol	Palm shells	middle	0.14 0.15 0.11 0.15	0.14
		top	0.13 0.15 0.12 0.14	0.14
	Peanut shells	middle	0.24 0.20 0.24 0.20	0.22
		top	0.26 0.25 0.22 0.19	0.23
Pure toluene	Palm shells	middle	0.15 0.16 0.14 0.11	0.14
		top	0.16 0.15 0.12 0.16	0.15
	Peanut shells	middle	0.15 0.26 0.21 0.19	0.20
		top	0.25 0.24 0.18 0.22	0.22
Mixed VOCs	Palm shells	middle	0.04 0.16 0.11 0.08	0.10
		top	0.14 0.15 0.17 0.13	0.15
	Peanut shells	middle	0.14 0.25 0.23 0.16	0.20
		top	0.25 0.19 0.23 0.16	0.21

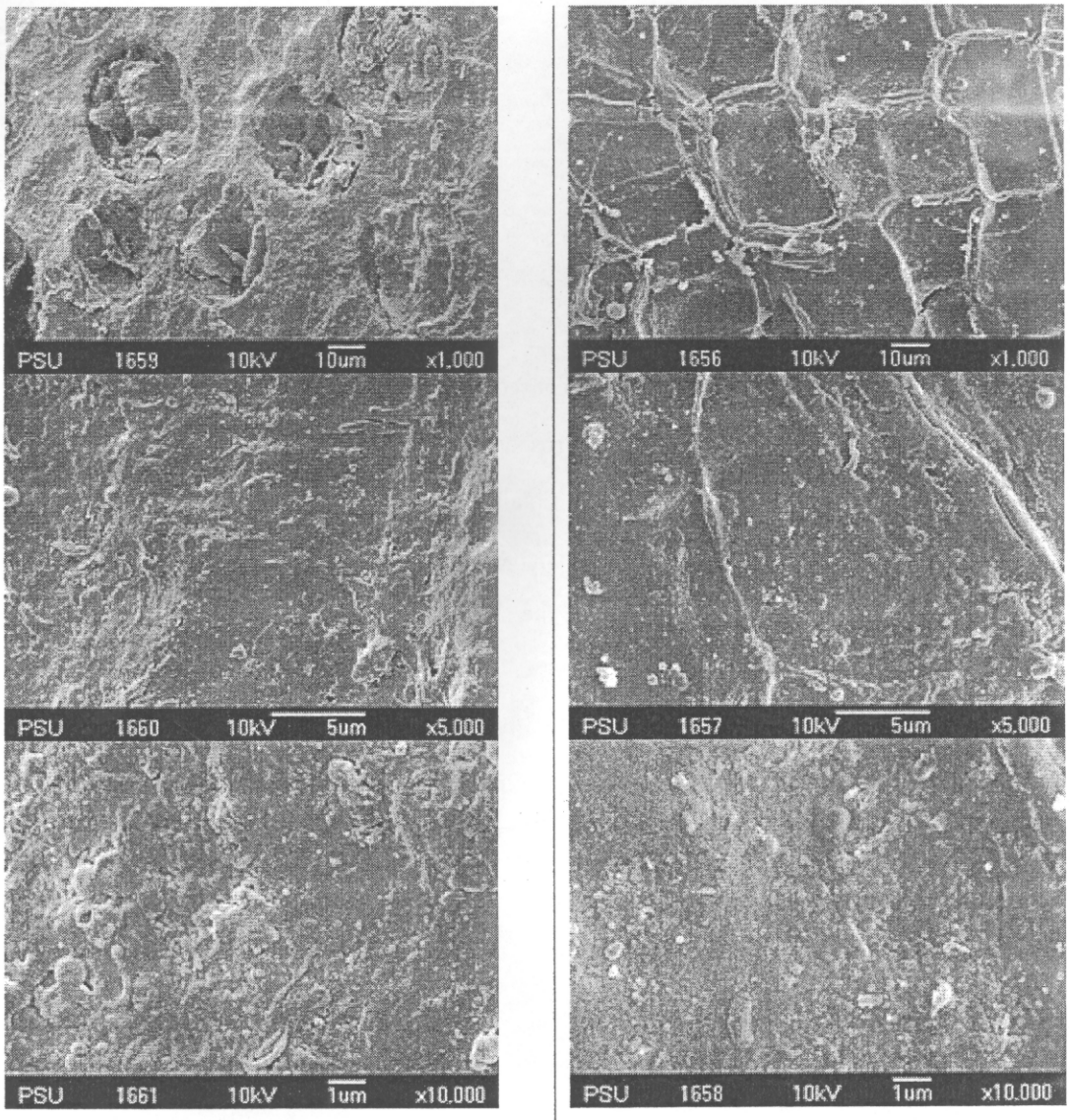
Mean biofilm thicknesses differed significantly between the two packing materials, being in the range 0.1 to 0.15 mm (100-150 μm) for the palm shells and 0.2 to 0.23 mm (200-230 μm) for peanut shells. These are comparable to measurements made by Pineda et al. (2000) who reported thicknesses of biofilm ranging from 150 to 200 μm, and well within the range of biofilm thicknesses (30-2500 μm) reported by Singh et al. (2006) in a biofilter treating gases containing toluene. As pointed out by Deshusses (1997), the biofilm thickness is not necessarily related to biofilter performance. In his experiments, the biofilm thickness increased from 80 μm on day 35 to 280 μm on day 300 but no improvement in pollutant elimination occurred. During this time, the total protein amount in the biofilter remained approximately constant, suggesting that the mass of active microorganisms also remained constant. Hence, it demonstrates that most of the biofilm was made of inactive cells (Deshusses, 1997).

3.8.2 Microbial Fauna

Changes in the microbial fauna in the biofilter columns were followed at both the microscopic and the macroscopic levels. To learn about the various microbial species present on the packing media a series of SEM examinations of packing material surfaces were carried out. At the same time notes were kept on the appearance of the biofilters, which were photographed regularly.

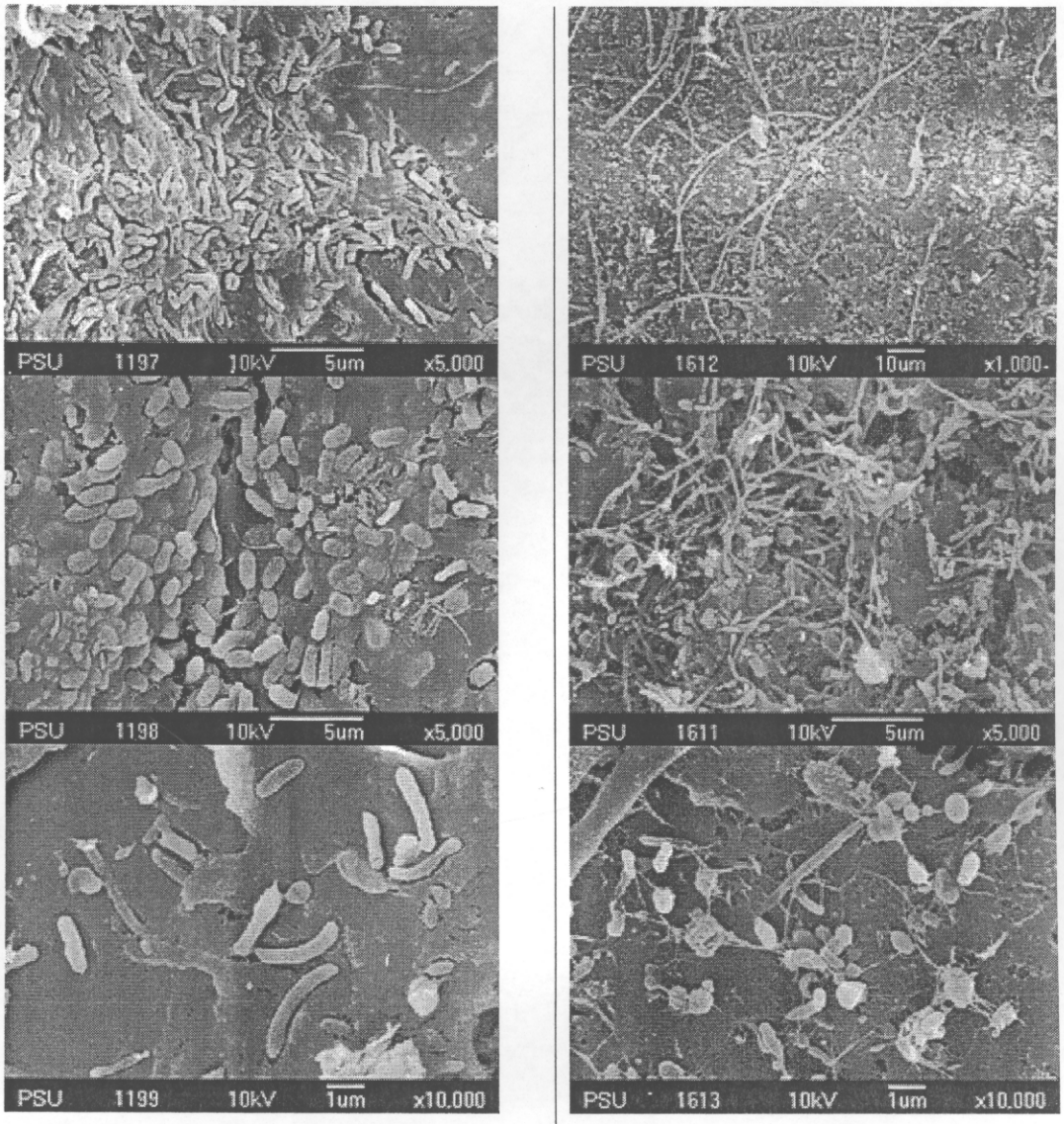
3.8.2.1 Scanning Electron Microscope Studies

Scanning electron microscope (SEM) studies of both the raw and the used packing materials were undertaken to obtain a better understanding of how the microbial community in the biofilm developed and changed over the course of the experimental period. Figure 3-51 shows SEM micrographs of the surfaces of raw peanut shell and raw palm shell at magnifications of 1000x, 5000x and 10000x. The surfaces of both materials contain depressions 20-40 μm across and appear sufficiently irregular to facilitate attachment of microorganisms during biofilm formation. Samples of packing media were taken from each of the biofilter columns on days 93 and 147 and examined using the SEM. SEM micrographs of these samples are presented in Figures 3-52 to 3-57.).



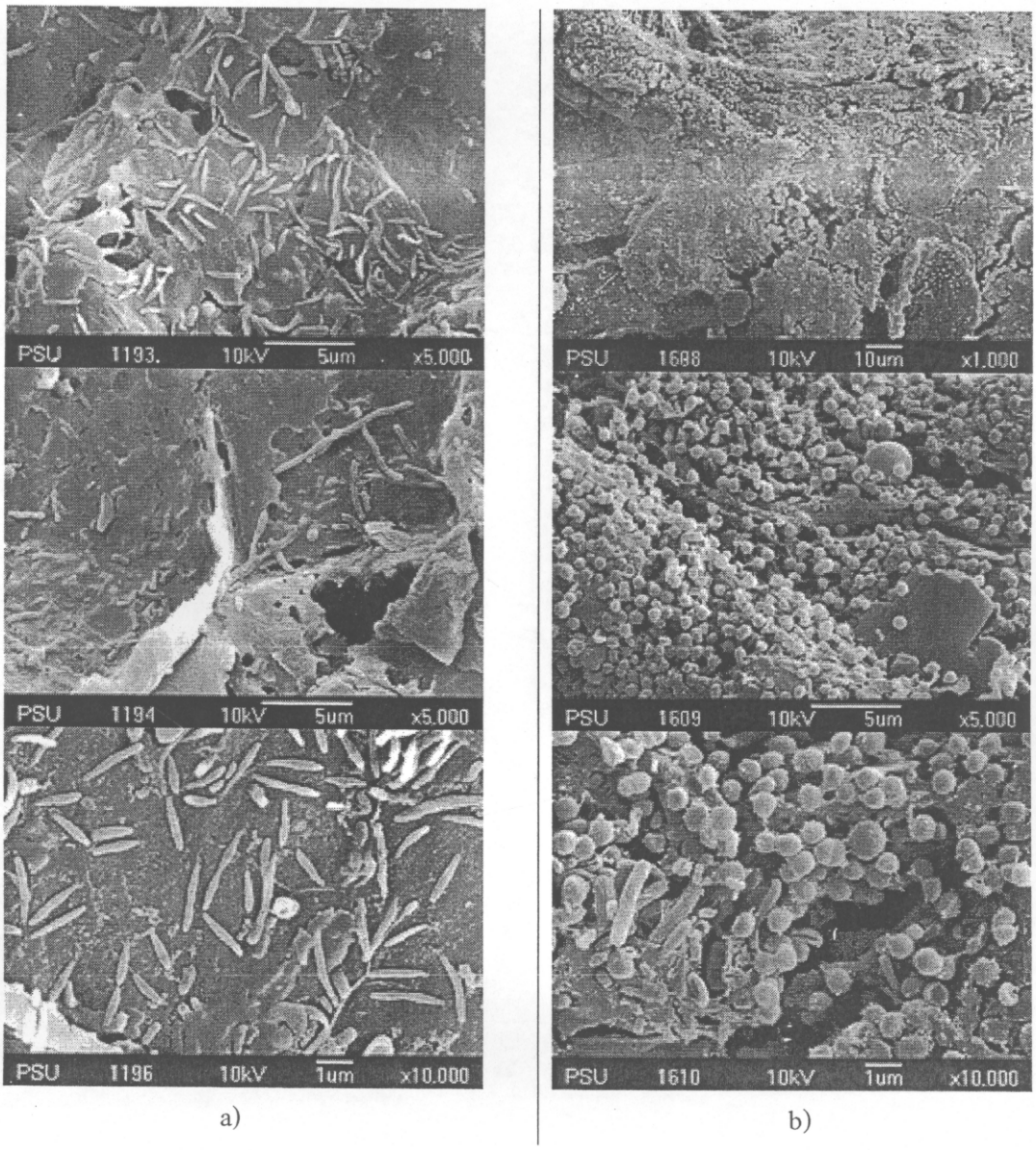
a) b)

Figure 3-51 The structure of palm shell a) and peanut shell b) at x1000, x5000, and x10000 magnification.



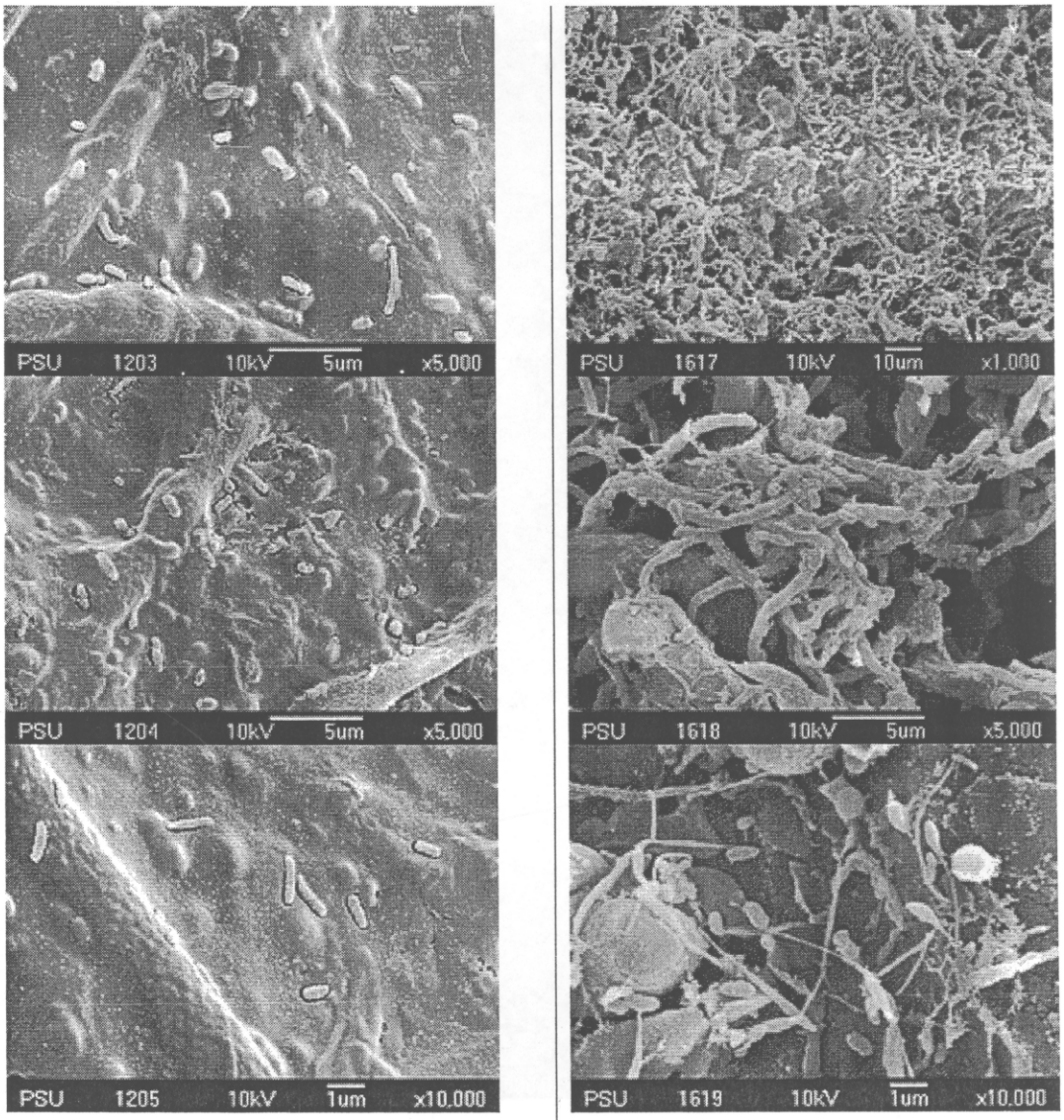
a) b)

Figure 3-52 The types of microorganisms present on the surfaces of the peanut shell packings in biofilter M1 (pure methanol system) on day 93 a) and day 147 b) at x1000, x5000, and x10000 magnification.



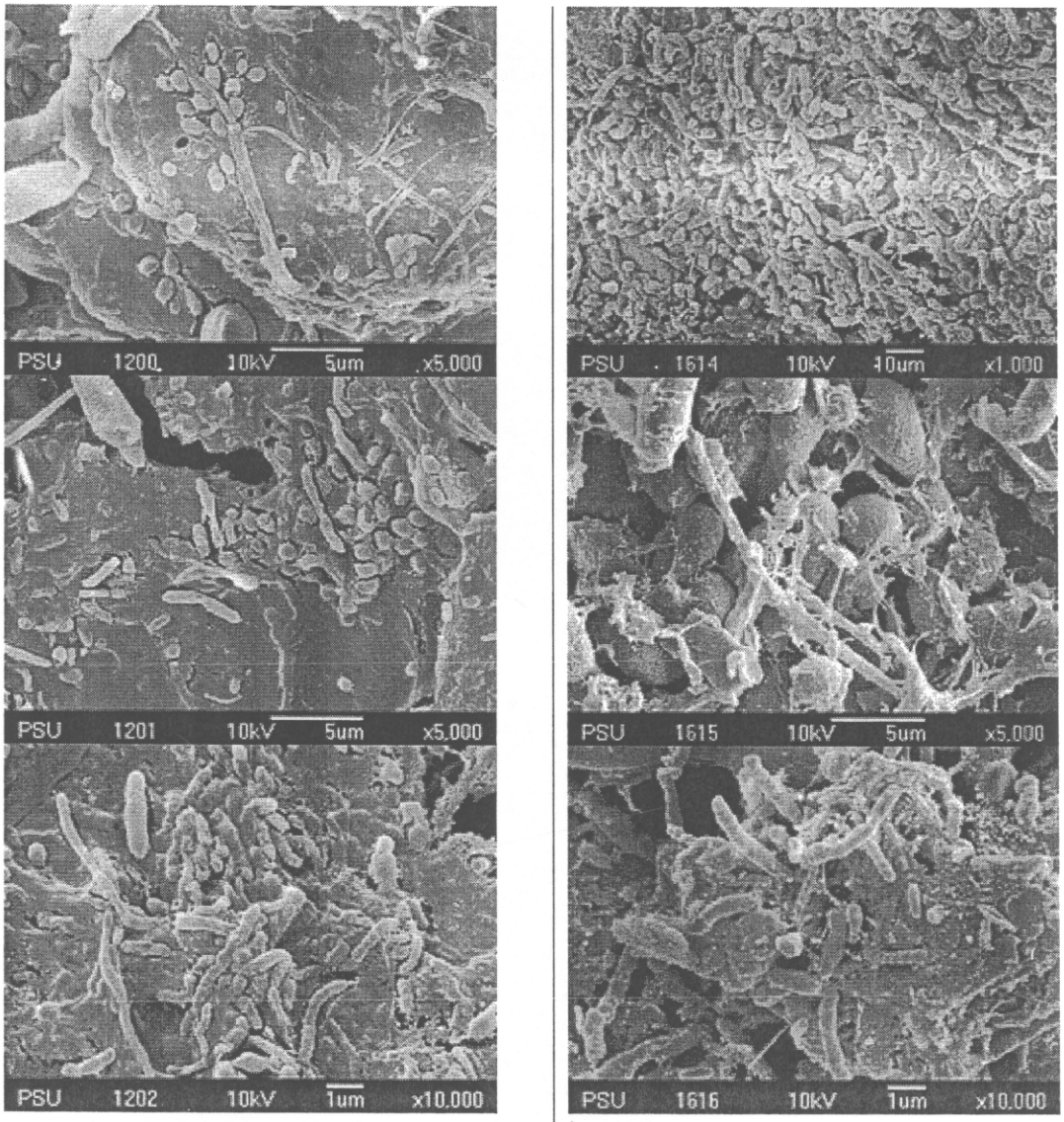
a) b)

Figure 3-53 The types of microorganisms present on the surfaces of the palm shell packings in biofilter M2 (pure methanol system) on day 93 a) and day 147 b) at x1000, x5000, and x10000 magnification.



a) b)

Figure 3-54 The types of microorganisms present on the surfaces of the peanut shell packings in biofilter T1 (pure toluene system) on day 39 a) and day 54 b) at x1000, x5000, and x10000 magnification.



a) b)

Figure 3-55 The types of microorganisms present on the surfaces of the palm shell packings in biofilter T2 (pure toluene system) on day 39 a) and day 54 b) at x1000, x5000, and x10000 magnification.

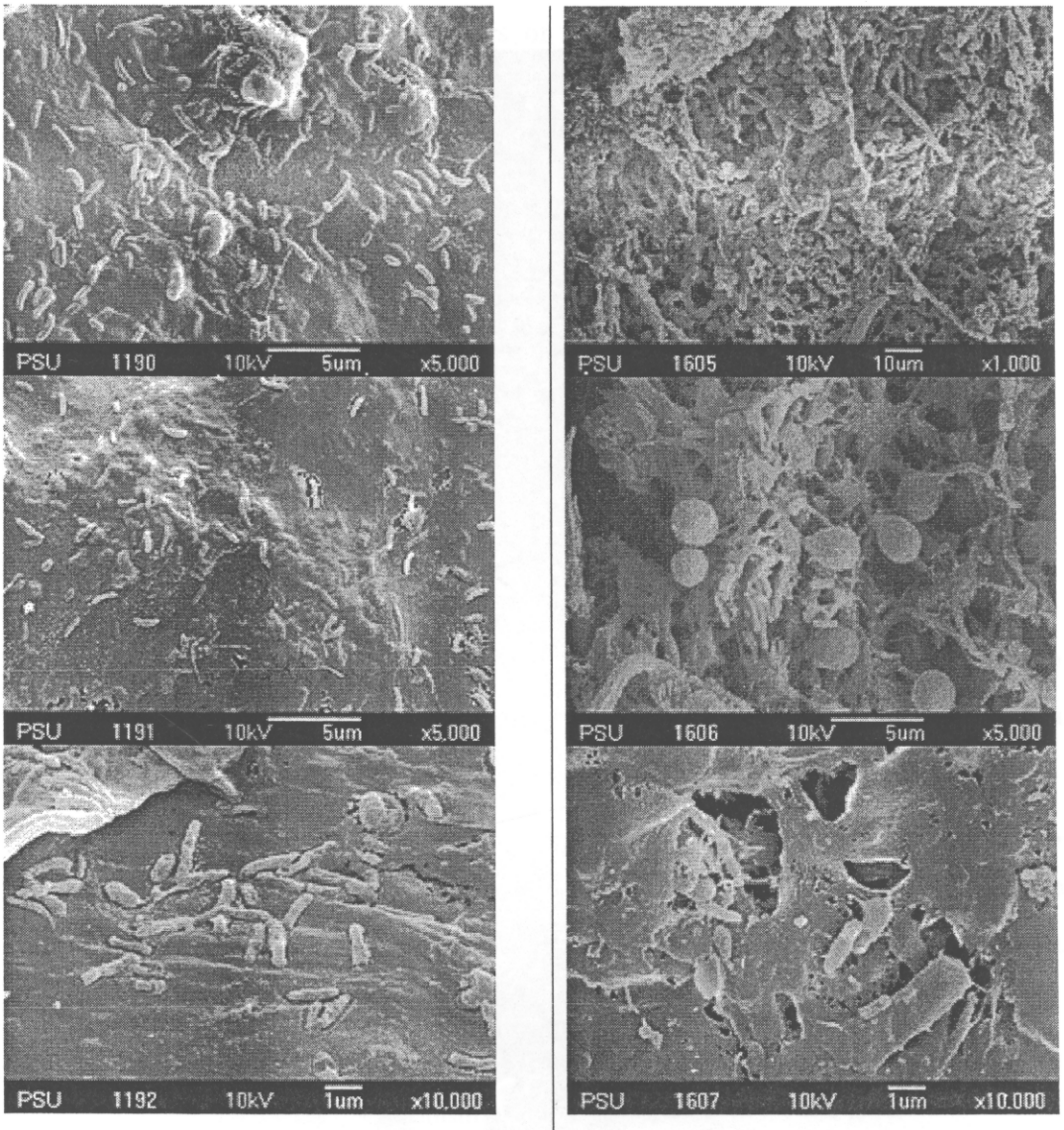
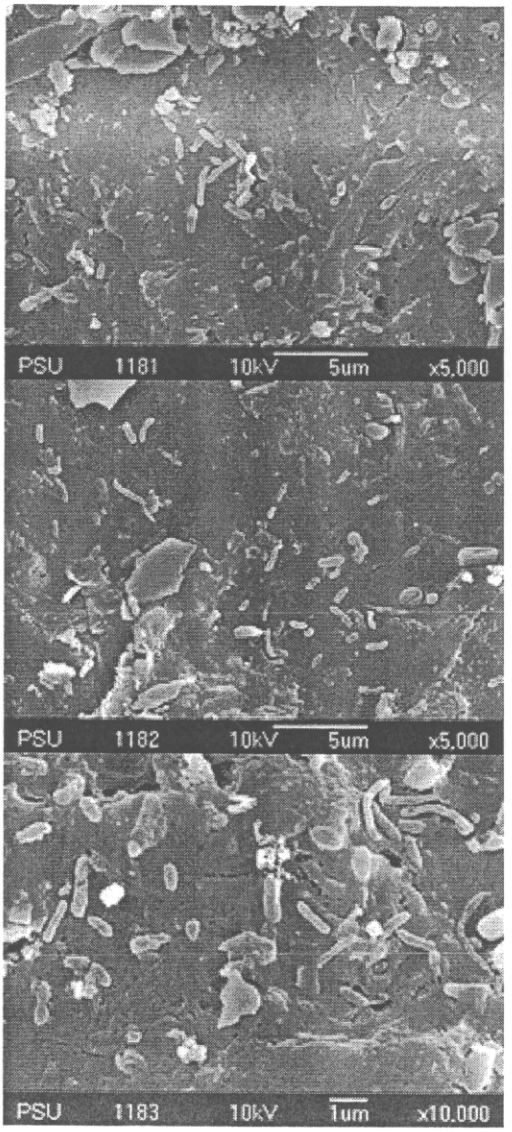
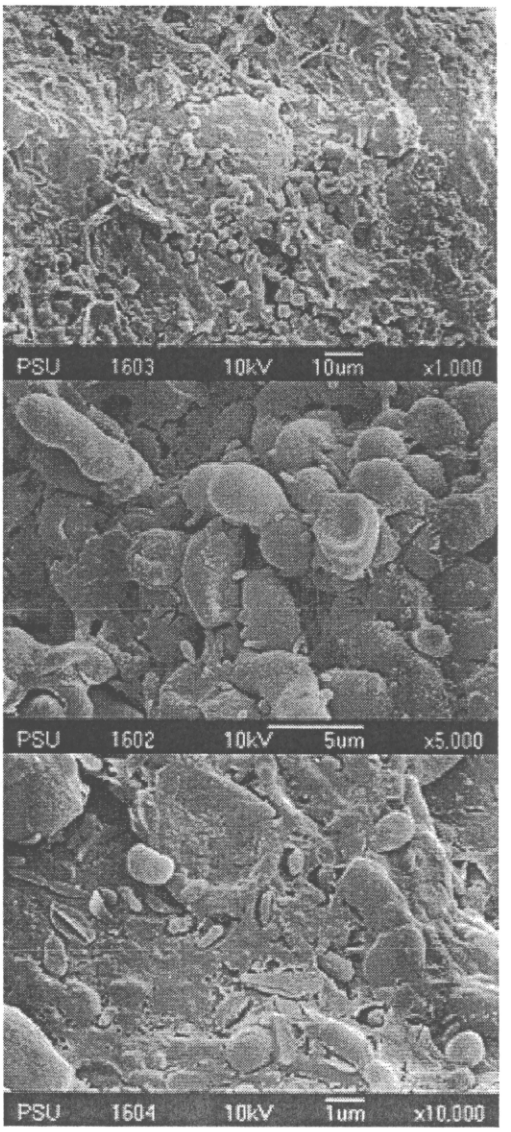


Figure 3-56 The types of microorganisms present on the surfaces of the peanut shell packings in biofilter X1 (mixed system) on day 93 a) and day 147 b) at x1000, x5000, and x10000 magnification.



a)



b)

Figure 3-57 The types of microorganisms present on the surfaces of the palm shell packings in biofilter X2 (mixed system) on day 93 a) and day 147 b) at x1000, x5000, and x10000 magnification.

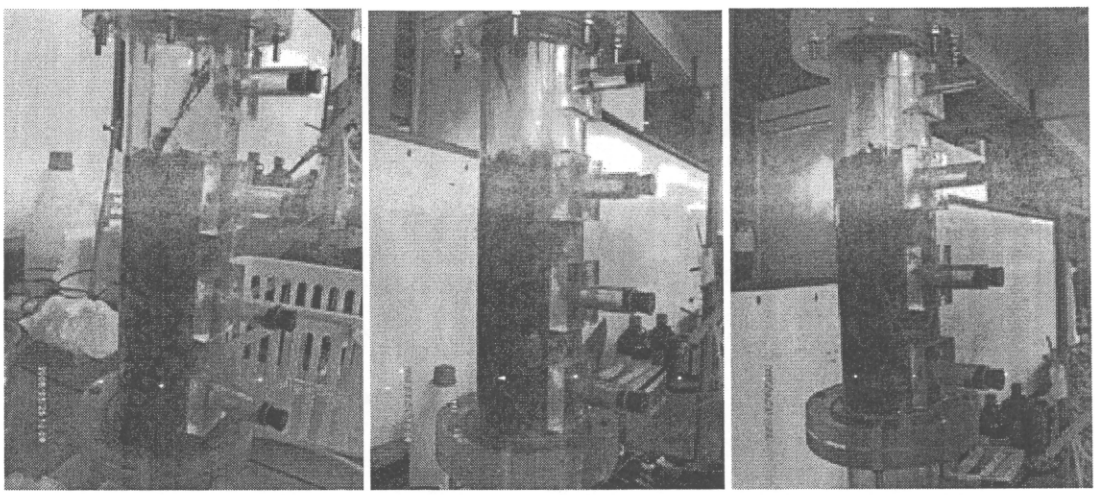
SEM pictures of packing media samples taken on days 93 and 147 confirm that the surfaces were readily colonized by microorganisms. On day 93, the surfaces of packing materials from all biofilters were dominated by rod shaped microorganisms, as shown in Figures 3-52 to 3-57 in images a. At this stage no differences related to the nature of the VOC involved were apparent.

By day 147 the numbers of microorganisms present on the surfaces had increased considerably and the nature of the microbial fauna was very different. As illustrated in Figure 3-52, 3-54, and 3-56 in images b at 5000x magnification, peanut shell surfaces appeared to be dominated by mycelial mats, with a scattering of cocci. Fungal mycelia are known to cause damage to peanut crops in the field (Nalim et al., 1995; Okabe and Matsumoto, 2000). Mycoflora or fungi develop easily on the peanut shells in moist atmospheres (Hanlin, 1968; Fonseca, et al. 1994); therefore, given the moist aerobic conditions under which peanut shells exist in the biofilters it is not surprising that fungal mats have become established on their surfaces. These mats were present on all peanut shell surfaces, irrespective of the VOC(s) to which they had been exposed, so that they do not seem to be implicated in the changes to BET surface areas and pore distributions experienced by peanut shells exposed to methanol. The methanol does seem to have had an effect on the fungal growths, however, as the mycelial strands found on packings exposed to methanol (images b in Figures 3-52, 3-54, and 3-56) are very much finer than those present on the surfaces exposed only to toluene (image (b) in Figure 3-54).

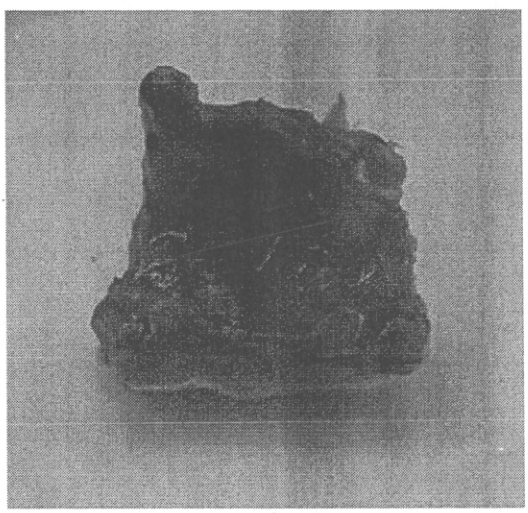
As Figures 3-53, 3-55, and 3-57 shows in image b at 5000x magnification, by day 147 the microbial fauna on the palm shell surfaces was very different from that on the peanut shells. Here coccus-shaped microorganisms predominate, with only a small amount of mycelial growth apparent. Again, the methanol appears to have an impact on the size of the organisms. As Figure 3-53 in image b at 5000x magnification shows, on the surface exposed solely to methanol there is only one coccus-shaped organism of the same size as those in Figure 3-56 in image b at 5000x magnification; the remaining organisms are only 20% as large, with a diameter of less than 1 μm.

3.8.2.2 Biofilter Appearance

As shown in Figures 3-58 to 3-63 it was easy to see when the packing media had developed a good covering of biofilm. These Figures show the appearance of each of the biofilters at an intermediate stage during the experimental runs. Also shown are samples of the packing material from the top of the biofilters showing the extent of biofilm development.

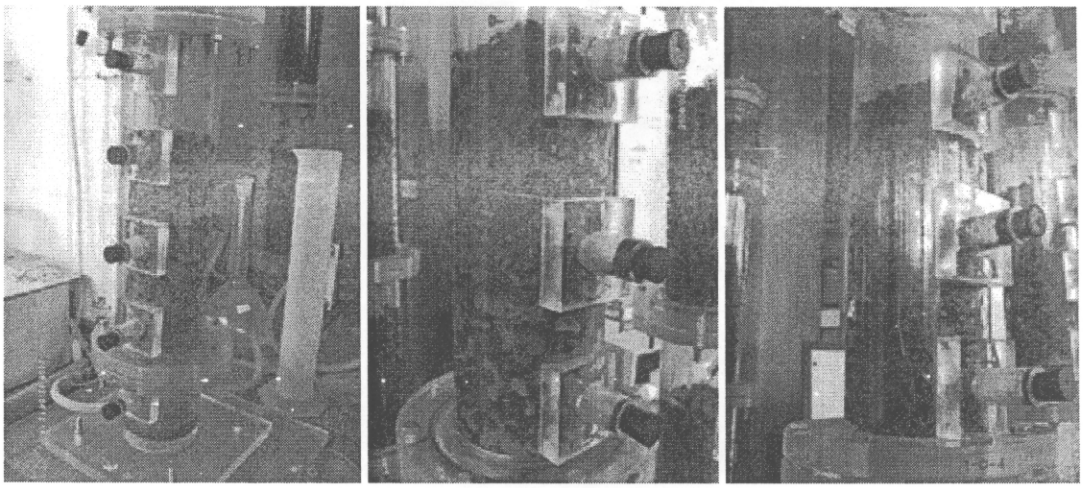


a) b) c)

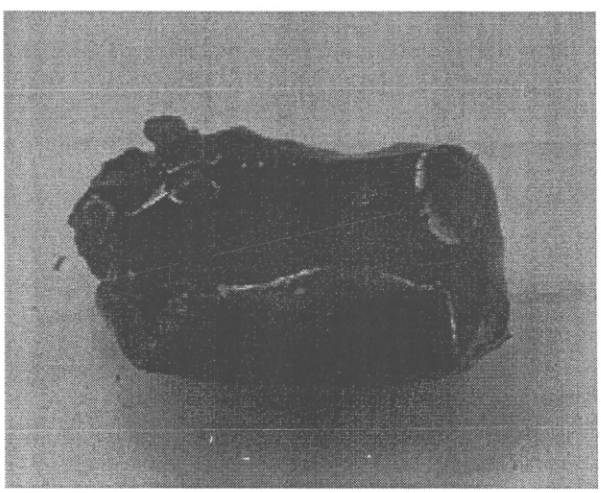


d)

Figure 3-58 The appearance on day 147 of the three sections of biofilter M1 (peanut shell packing; methanol): bottom section a), middle section b), top section c), and a SEM picture of a sample from the top section d).

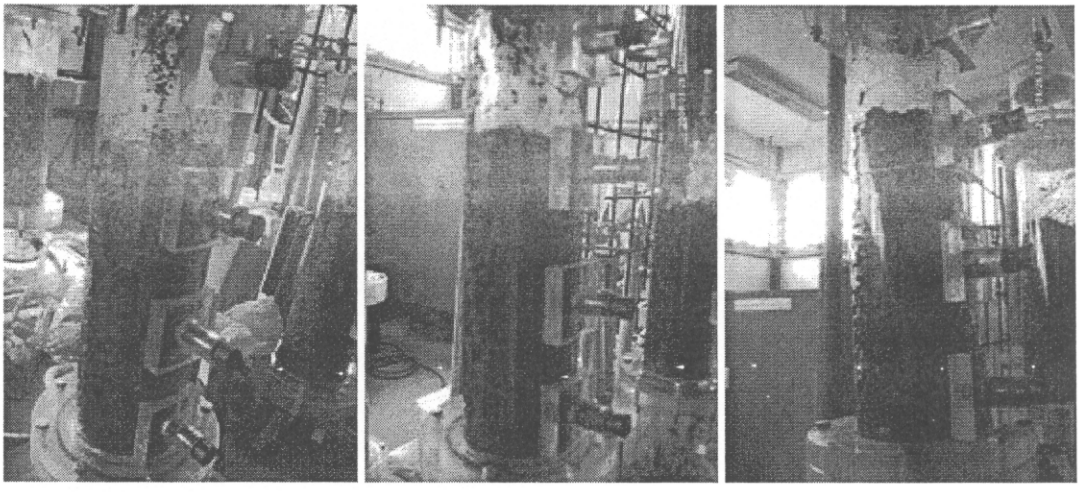


a) b) c)

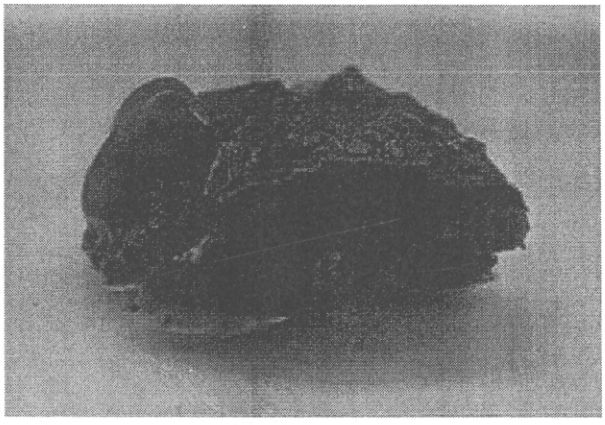


d)

Figure 3-59 The appearance on day 147 of the three sections of biofilter M2 (palm shell packing; methanol): bottom section a), middle section b), top section c), and a SEM picture of a sample from the top section d).

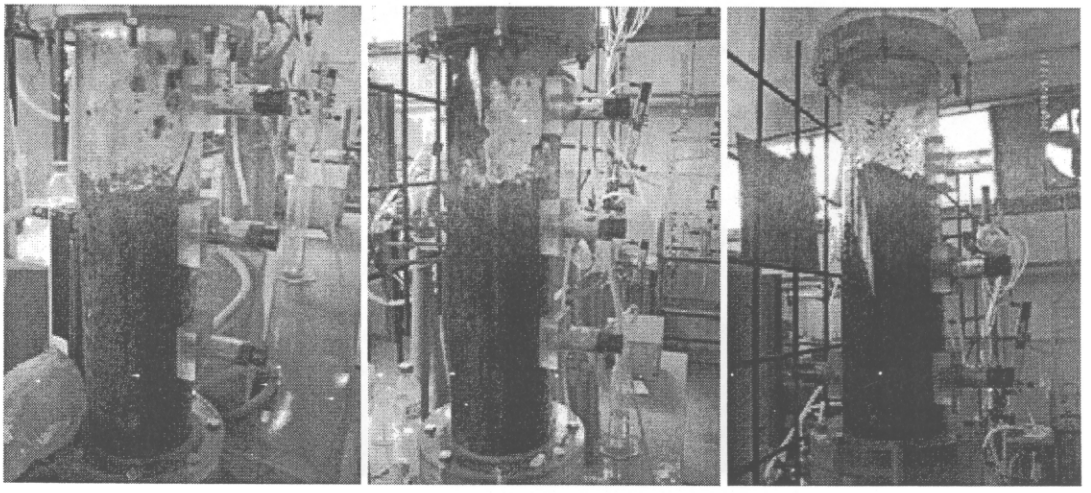


a) b) c)

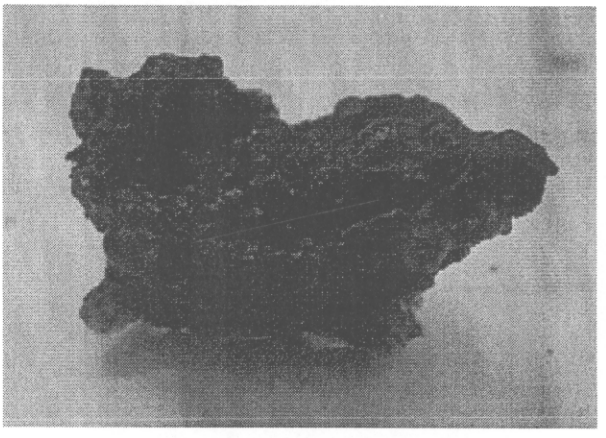


d)

Figure 3-60 The appearance on day 54 of the three sections of biofilter T1 (peanut shell packing; toluene): bottom section a), middle section b), top section c), and a SEM picture of a sample from the top section d).

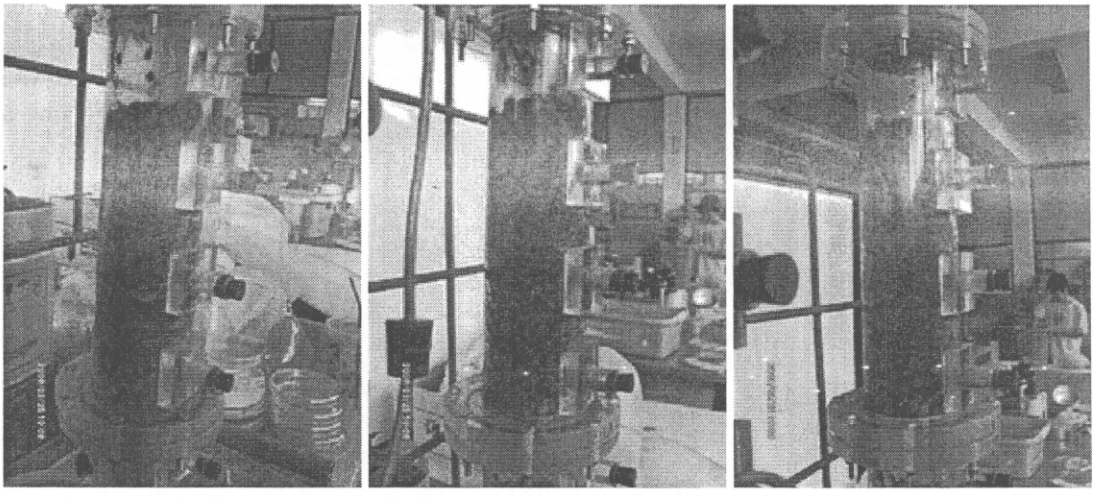


a) b) c)

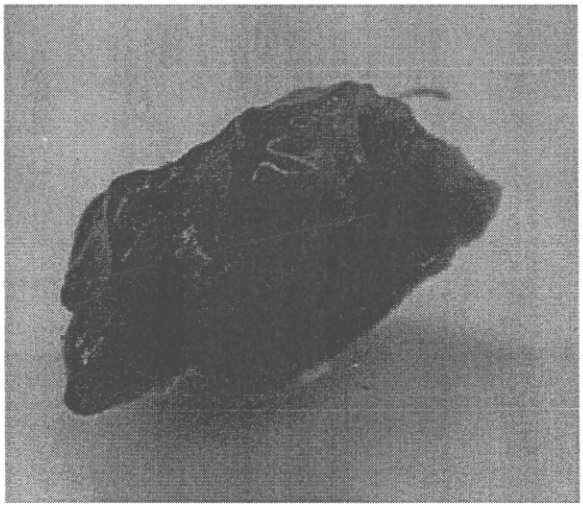


d)

Figure 3-61 The appearance on day 54 of the three sections of biofilter T2 (palm shell packing; toluene): bottom section a), middle section b), top section c), and a SEM picture of a sample from the top section d).



a) b) c)



d)

Figure 3-62 The appearance on day 147 of the three sections of biofilter X1 (peanut shell packing; mixture of methanol and toluene): bottom section (a), middle section (b), top section (c), and a SEM picture of a sample from the top section (d).

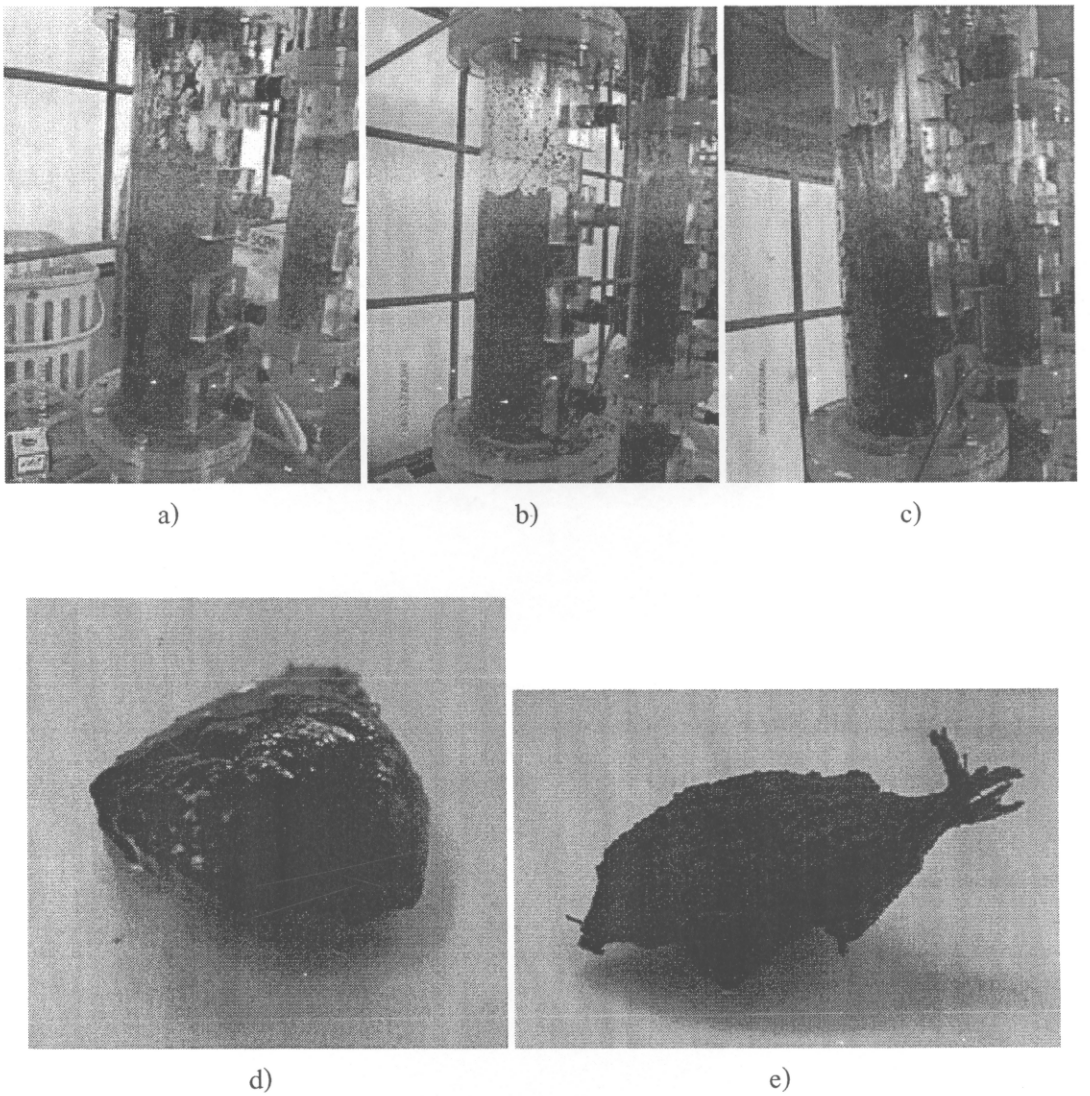


Figure 3-63 The appearance on day 147 of the three sections of biofilter X2 (palm shell packing; toluene and methanol mixture): bottom section (a), middle section (b), top section (c), and SEM pictures of samples from the top section (d) and middle section (e).

Patterns of change in the biofilter columns could also be followed by visual inspection. This is illustrated in Figures 3-64 to 3-67 taken of biofilter X1.

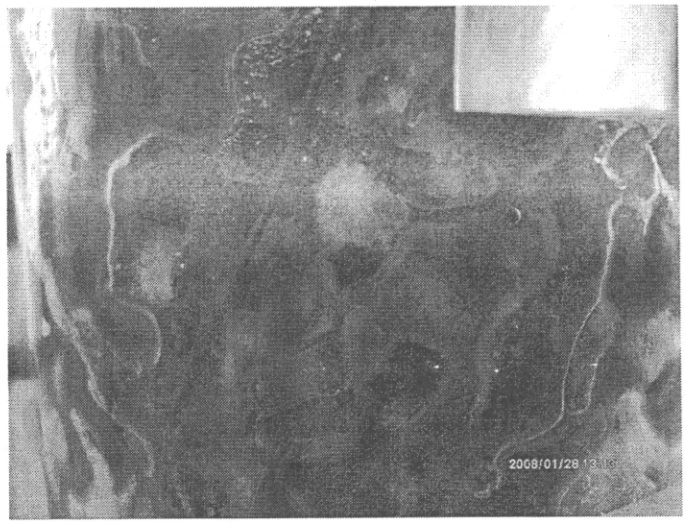


Figure 3-64 White fungi in the mixed system biofilter packed with peanut shells (X1).

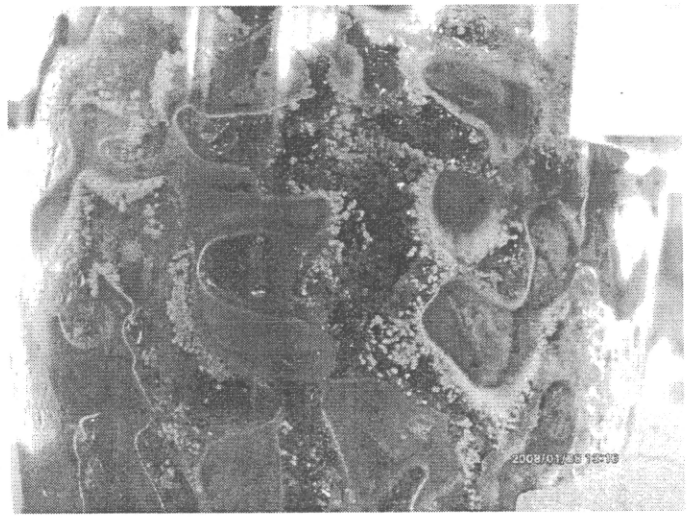


Figure 3-65 Green growths (probably algae) in the mixed system biofilter packed with peanut shells (X1).

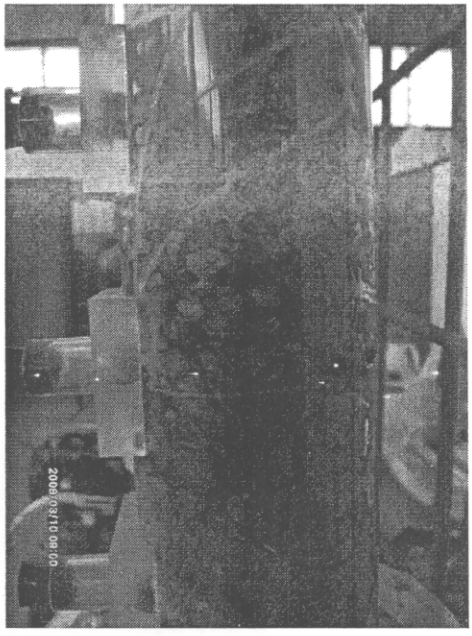


Figure 3-66 Black fungi in the mixed system biofilter packed with peanut shells (X1).

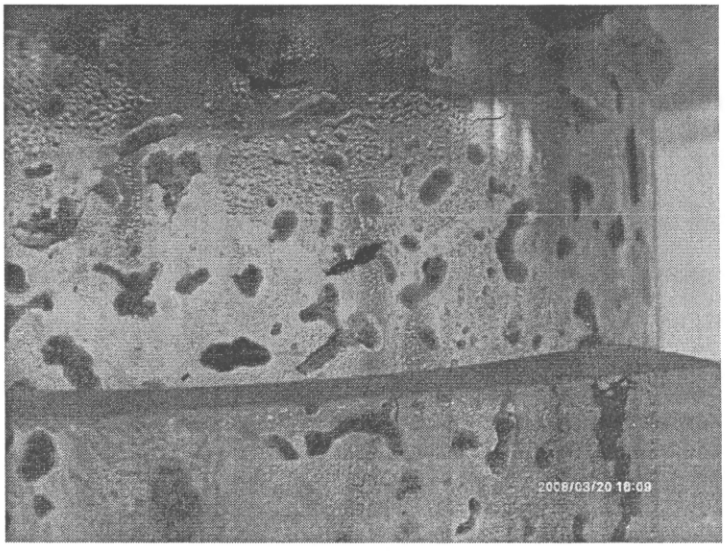


Figure 3-67 Worms in the mixed system biofilter packed with peanut shells (X1).

Figures 3-64 and 3-65 show the appearance of segments of the lower and middle sections of the biofilter column on day 134. The lower section appears to have developed an extensive white fungal mass while the green in the middle section is presumably caused by algae.

A similar green patch was also noted in column M1 on day 180, as shown in Figure 3-68. In both biofilters, X1 and M1, the packing media was peanut shells. By day 170 the green on biofilter X1 had disappeared and been replaced by what appeared to be a black fungal mass (Figure 3-66).

Figure 3-68 The algae in the pure methanol system packed with peanut shells (M1).

Then, 10 days later an infestation of what appeared to be nematode worms could be seen on the inside of the column (Figure 3-67). These photographs emphasize the dynamic nature of biofilters and the dangers of assuming that steady state conditions can be achieved and maintained in these systems. The appearance of fungal colonies in some of the biofilters is similar to what was observed by Maestre et al. (2007) in a biofilter packed with pine leaves and used to remove toluene. They described how fungi were progressively colonizing the biofilters and becoming the predominant degrading organisms. They observed a simultaneous decrease in pH in the biofilters which they attributed to the production of benzoic acid, an intermediate in the degradation pathway of toluene. Fungi are favoured over bacteria at low pH values, which suggests that the pH in some of the biofilters used in the present study may also have experienced a drop in pH. No measurements were taken to confirm this however.

No such obvious algal and fungal colonies were observed in other biofilters; all those observed occurred in the peanut shell packings suggesting that despite the similar elimination capacities achieved in biofilters with different packings but treating the same VOC, the microbial fauna in both were different – which is what the SEM studies confirmed. In one respect it was strange that the fungi were more prevalent in the peanut shell packing than in the palm shell packing. Sun et al. (2002) showed that a moisture content of 70% in the biofilter bed favoured bacterial growth over the growth of yeast, moulds and actinomyces. In the present study measured moisture contents in the biofilters containing peanut shells were 74%, 85% and 83% (for M1, T1, and X1 respectively) whilst for the biofilters containing palm shells the corresponding values were 30%, 50% and 35% (for M2, T2, and X2 respectively). According to the findings of Sun et al. (2002) it should have been the palm shells rather than the peanut shells that were colonized by fungi.

Differences in biofilm colour between columns treating different VOCs also became apparent, as shown in Figures 3-69 to 3-71. Originally the raw peanut shells were a soft brown in colour whilst the raw palm shells were a darker brown. However, in both columns treating methanol the biofilm that developed was red brown in colour whilst in the columns treating toluene the biofilm colour was blackish brown. In the systems treating a mixture of methanol and toluene the colour was again red brown, suggesting that the methanol degrading organisms were dominant, which is consistent with the very low EC values achieved for toluene in the mixed system columns.

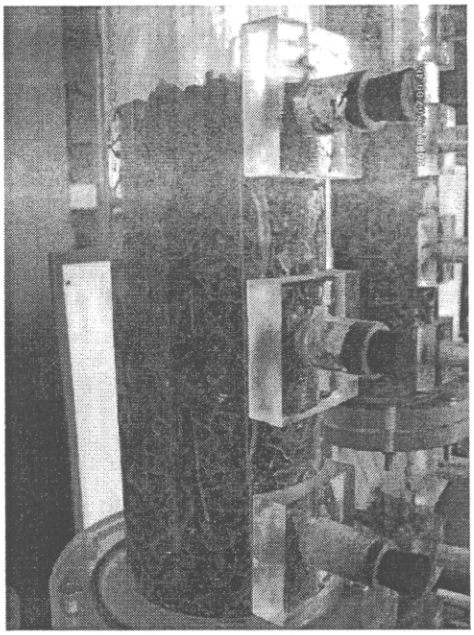


Figure 3-69 The color of biofilm in the pure methanol system packed with peanut shells (right) and palm shells (left).

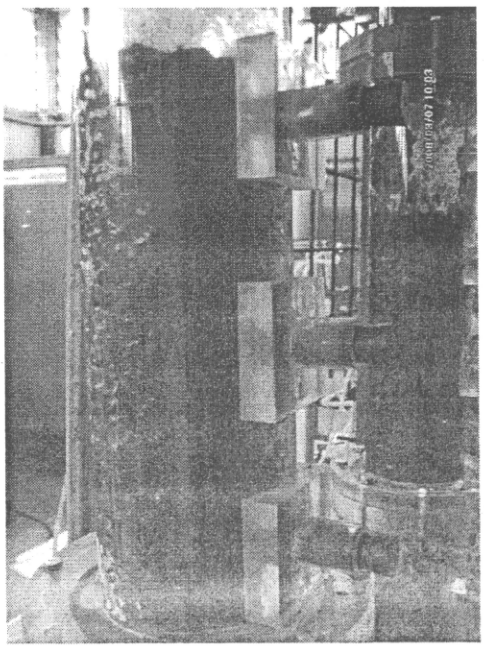


Figure 3-70 The color of biofilm in the pure toluene system packed with peanut shells (left) and palm shells (right).

Figure 3-71 The color of biofilm in the mixed system packed with peanut shells (right) and palm shells (left).

3.9 Macrokinetic Models

A macrokinetic model forbears from calculating individual processes in detail and instead treats the biofilter as "a black box" that is influenced by the operational conditions, like substrate concentrations, flow rates, moisture content and temperatures. The parameters needed for a macrokinetic model are determined experimentally. Therefore, these models are also referred to as empirical models (Streese et al., 2005).

The elimination capacity is always equal to or less than the load (Devinny et al., 1999), therefore a model based on elimination capacity was chosen for modeling biofilter performance as a function of inlet load. Such a model would be decidedly useful to anyone setting out to design a biofilter. The equation of elimination capacity vs. the load curve is shown in Equation 3.1. The underlying basis of this model is that microbially mediated VOC degradation processes follow Michaelis-Menten kinetics, so that in any given biofilter there is a maximum VOC degradation rate that can be achieved. At low inlet loads it would be expected that a first order relationship would exist between elimination capacity and inlet load; however, as the inlet load increases, the relationship ceases to be first order and moves progressively towards a zero-order relationship.

Once some maximum elimination capacity value is reached, further increases in inlet load have no further effect on the elimination capacity. Even though the bed height was kept constant during the present project it has been included as a variable in this model so as to enhance the model's usefulness to those wishing to design biofilters for other purposes.

$$EC = aH_{max}(1 - e^{-bIL}) \quad \textbf{(3.1)}$$

where a and b are constant values, H_{max} is maximum bed height (m).

The empirical model predicts elimination capacity as a function of inlet load and bed height. Implicit in this model is the assumption that degradation rates were not oxygen limited, which seems reasonable given the relatively low VOC concentration levels used. The parameters a and b were individually fitted to describe their relationship with the elimination capacity at different inlet load. The data used in developing the model are given in Appendix C.1 and C.2. A sample calculation showing how the relevant information was calculated is also available in this Appendix.

The Excel Solver tool in Microsoft Office was used in determining the constants in the model. It employs a quasi-Newton method and is an effective way to create a nonlinear model with adjustable parameters (Morrison, 2005). The Solver input values were obtained from experimental data and the adjustable parameters were the constants a and b. The Target Cell registered the average difference between actual data and those predicted by the model. The Solver program adjusted values of the constants a and b so as to minimize this difference. The results are presented in Tables 3-10 and 3-11.

Table 3-10 The calculated values of the constants a and b in the elimination capacity model, for a bed height of 0.66 m, in biofilters packed with palm shells and peanut shells and treating gases containing a single VOC component.

Constant	Methanol		Toluene	
	Peanut	Palm	Peanut	Palm
a	300.0	258.5	222.2	222.9
b	0.005	0.008	0.007	0.007
R^2	0.98	0.92	0.88	0.95

Table 3-11 The calculated values of the constants a and b in the elimination capacity model, for a bed height of 0.66 m, in biofilters packed with palm shells and peanut shells and treating gases containing a VOC mixture.

Constant	Peanut		Palm	
	Methanol	Toluene	Methanol	Toluene
a	426.8	22.6	288.7	70.8
b	0.004	0.070	0.006	0.016
R^2	0.95	0.94	0.90	0.87

The above elimination capacity model was also applied to the experimental results of other biofilter researchers, using Excel Solver. The calculated values obtained for the constants a and b for each study are shown in Table 3-12. As would be expected, given that this is a macrokinetic model, the values of the constants depend on the experimental conditions and differ from one study to the next. With only one exception, the values of R^2 are high, confirming that for a given set of biofilter conditions, the elimination capacity model fits the experimental data well. A sample calculation showing how relevant information was used to develop the values for the constants is provided in Appendix C.3.

Table 3-12 Results obtained when applying the elimination capacity model to other biofiltration studies.

Researchers	H_{max}	a	b	R^2
Prado et al. (2005)	0.44	250.5	0.012	0.94
Zhang et al. (2007)	0.33	636.3	0.004	0.90
Delhoménie et. al. (2002a)	0.99	52.8	0.032	0.81
Liu et. al. (2002)	0.90	78.2	0.019	0.96
Torkian et al. (2003)	0.90	202.6	0.006	0.99
Chetpattananondh et al. (2005)	0.60	392.2	0.005	0.91
Rene et al. (2005)	0.70	140.6	0.011	0.94
Wright et al. (2005)	1.00	228.2	0.006	0.95
Xi et al. (2006)	0.40	148.2	0.021	0.97
Vergara-Fernández et. al. (2007)	0.75	534.8	0.002	0.97

Figures 3-72 through 3-75 show comparisons between elimination capacities calculated using the elimination capacity model and those calculated from the experimental data obtained in this study. The model can be used to predict the maximum elimination capacity. As shown in Table 3-13, these predicted values were generally very close to those obtained from the EC plots presented in section 3. This closeness between the model prediction and the experimental data confirms the suitability of this type of model for describing biofilter performance.

A number of experimentally derived EC values obtained when inlet loads were at their highest lie significantly below the predicted EC lines. These were all obtained at high air flow rates of 0.3 m^3/h under conditions where pressure drops were particularly high, presumably due to a build-up of excess biomass (see section 3.61). Nevertheless, because conditions within the biofilter were always changing (since biofilters are never at a steady state) it was decided to retain these points in the data base used to develop the elimination capacity model. Without their inclusion the R^2 value for the model would have been even higher.

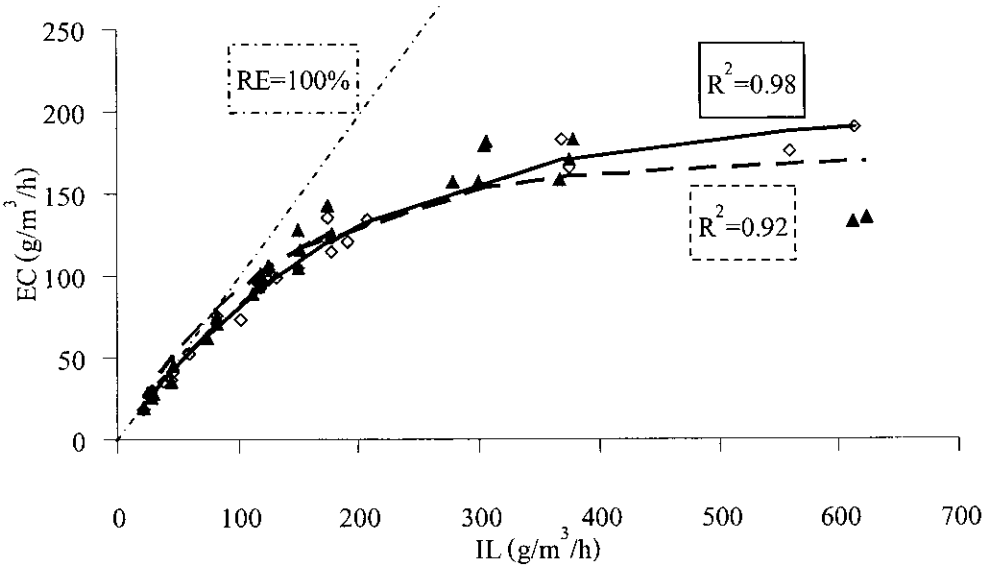


Figure 3-72 Measured and predicted elimination capacities as a function of inlet load for biofilters treating air flows containing methanol only: (◊) peanut shell (experiment), (-) peanut shell (model), (▲) palm shell (experiment), and (---) palm shell (model).

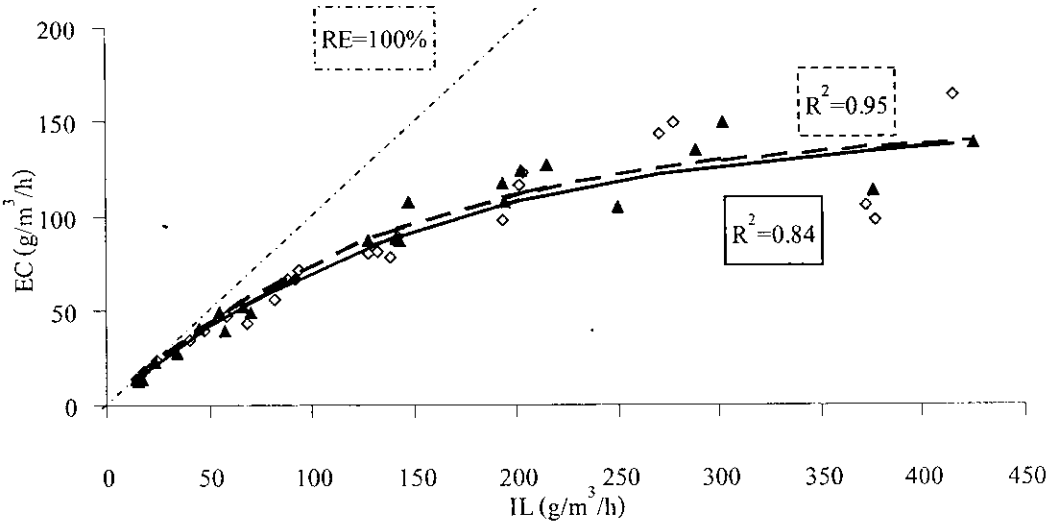


Figure 3-73 Measured and predicted elimination capacities as a function of inlet load for biofilters treating air flows containing toluene only: (◊) peanut shell (experiment), (-) peanut shell (model), (▲) palm shell (experiment), and (--) palm shell (model).

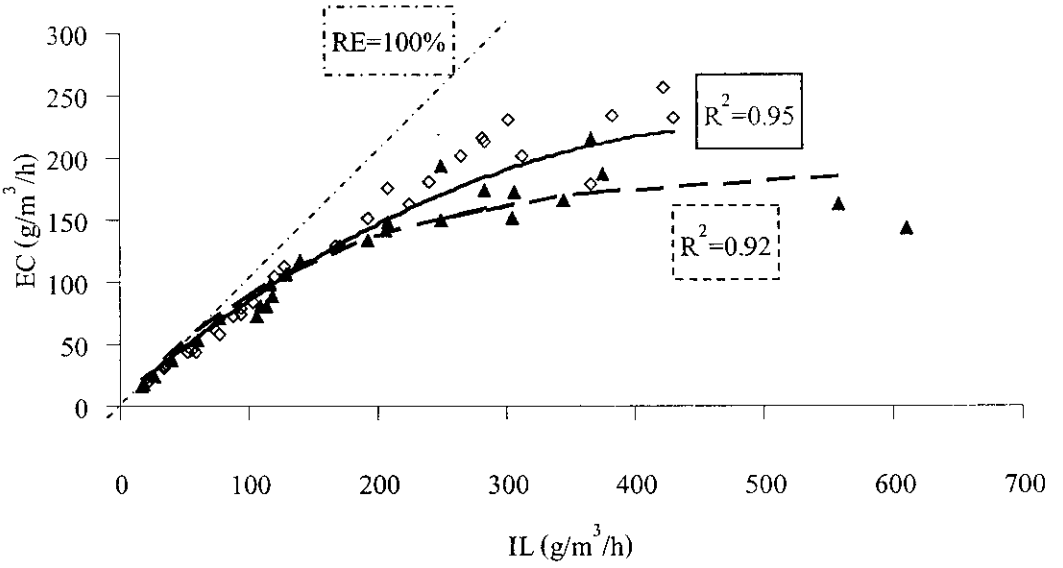


Figure 3-74 Measured and predicted elimination capacities of methanol as a function of inlet load for biofilters treating air flows containing methanol and toluene: (◊) peanut shell (experiment), (-) peanut shell (model), (▲) palm shell (experiment), and (--) palm shell (model).

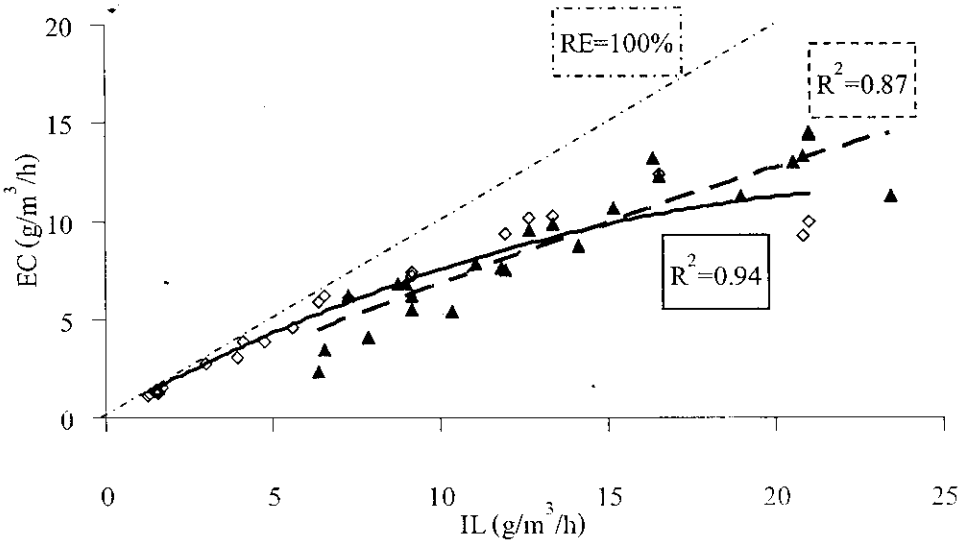


Figure 3-75 Measured and predicted elimination capacities of toluene as a function of inlet load for biofilters treating air flows containing methanol and toluene: (◊) peanut shell (experiment), (-) peanut shell (model), (▲) palm shell (experiment), and (--) palm shell (model).

Table 3-13. Comparison of maximum elimination capacity values from experimental data plots and the model.

Biofilter media	EC_{max} from trend line	EC_{max} from model
Pure methanol system		
- Peanut shells	198	195
- Palm shells	168	169
Pure toluene system		
- Peanut shells	141	137
- Palm shells	133	139
Methanol in mixed system		
- Peanut shells	215	222
- Palm shells	185	185
Toluene in mixed system		
- Peanut shells	6.6	11.3
- Palm shells	8.8	14.5

Chapter 4

Conclusions and Recommendations

4.1 Overall Performance

4.1.1 Biofilters Treating Gases Containing a Single VOC Component

The biofilters should be started with the gas flow rate at a very low level (0.06 m^3/h) and the VOC concentration also at a low level (1 g/m^3) to acclimatize the microorganisms to the VOC. This project has shown that biofilters containing either peanut shells or palm shells as packing materials are effective in removing methanol or toluene from waste air streams when these solvents are the sole VOCs in the gas stream. This was true over the entire range of gas phase concentrations studied, namely 1-9 g/m^3 for methanol and 0.1-6 g/m^3 for toluene, and over a range of flow rates of 0.06-0.3 m^3/h. Patterns of behavior in biofilters packed with peanut shells are remarkably similar to those in biofilters packed with palm shells, which means that on the basis of VOC degradation capacity neither has a clearcut advantage over the other. Elimination capacities for methanol are greater than for toluene since methanol is hydrophilic and toluene is hydrophobic, in addition methanol has a simpler structure making it easier to biodegrade than toluene. As would be expected, removal efficiencies (RE) were higher at low loading rates than at high loading rates. When the gas flow rate was kept constant, the RE decreased each time one of a series of stepwise increases in inlet concentration was applied. RE values were independent of VOC concentration and gas flow rate levels, as were elimination capacity (EC) values. The closeness of the EC values for the two VOCs is, to some extent, unexpected. This finding is useful for practitioners since it means that industries that need to treat gases containing a variety of VOCs may not have to use custom-designed biofilters for each VOC of concern. Even though the EBRT decreases from 252 seconds to 50 seconds as the gas flow rate is increased from 0.06 m^3/h to 0.3 m^3/h there seems to be no apparent effect on limiting EC values. This suggests that microbial degradation processes rather than mass transfer processes between the gas and liquid phases are the rate controlling step in the overall VOC removal process.

4.1.2 Biofilters Treating a Mixture of Methanol and Toluene

For biofilters treating gases containing a mixture of methanol and toluene, the EC values for methanol were comparable to the EC values obtained in biofilters treating gases containing methanol as the only VOC. Introducing toluene into the system had no discernible effect on methanol treatment efficiency in either the peanut shells or palm shells biofilters. However, the EC values for toluene in the biofilters treating gases containing a mixture of methanol and toluene were very different from those in biofilters treating gases containing toluene alone; the maximum elimination capacities for toluene in the mixed systems were less than 10 $g/m^3/h$ while in single component systems values as high as 133 $g/m^3/h$ were recorded. It can be inferred from these results that in the mixed system biofilters the methanol-degrading community became so well established during the initial 54 day period before toluene was introduced into the gases being treated that toluene-degrading organisms found it very hard to establish themselves in the biofilm. These observations contrast strongly with those made during a previous study (Nitipavachon, 2005) in which methanol and toluene were present together in the waste gases from the beginning of the experimental period. In this latter study the extent of toluene removal was much greater, suggesting that the microorganism community that had developed in the biofilm contained a large and viable population of toluene-degrading organisms. Together, these observations point up the importance of the biofilm development process in determining the treatment capabilities of the final biofilm. They also show that any VOC expected to be present in the gases to be treated in any particular biofilter should be present in the gases supplied to the biofilter during the biofilter start-up period. Therefore, where mixtures of VOCs are expected in waste gas streams the microbial community should be exposed to all the expected VOCs from the beginning.

4.1.3 Random Shock Loading Period

During this period the EC values observed in all 4 of the biofilters treating gases containing a single VOC component were consistently low and independent of the nature of the packing media involved. No discernible dependence of EC values on air flow rate or VOC concentration was evident, implying that the rates of VOC removal and degradation were controlled by the processes occurring within the biofilm. The very low EC values observed may have resulted from the rapid changes of inlet loading applied during this period. However, it is

more probable that they are due to a build-up of biomass within the biofilters that has limited the area of gas/biofilm contact. Therefore, it is very important to prevent excess biomass accumulation in the biofilters.

4.2 Influence of the Choice of Packing Media on Biofilter Performance

Under comparable operating conditions, the efficiencies obtained in both the peanut shell and palm shell systems are quite similar. Hence either could be used in industrial applications and the choice of one packing media over another should depend on local availability and cost efficiency of the materials. For example, the low bulk density of peanut shells may well make the cost of a peanut shell filter bed lower than that of a palm shell bed. However, peanut shells appear to degrade more rapidly than palm shells and would need to be replaced more often than palm shells.

4.3 Comparison of VOC Removals in Pure Component and Mixed Systems

4.3.1 Methanol

Patterns of change in air flow rate and inlet methanol concentration in the single component biofilter systems (M1 and M2) and the mixed systems (X1 and X2) were very similar and so were the observed EC values for methanol. The similarities between the EC values of single component systems and mixed systems show that adding the toluene into the incoming gas had no effect on the capacity of these biofilters to remove and degrade methanol.

4.3.2 Toluene

No direct comparisons of EC values for toluene in single component systems (T1 and T2) and mixed systems (X1 and X2) are possible since the mixed systems were only able to remove toluene at levels well below those treated effectively in the single component systems. It can be inferred that the toluene-degrading microorganisms found it hard to establish an effective presence in a biofilm dominated by an active community of methanol degrading organisms.

4.4 Removal Capabilities of Individual Bed Sections

In general the extent of VOC removal diminished slightly along the biofilter, with the most VOC being removed in the first section of the biofilter bed, where gas phase VOC concentrations are highest, and the least in the third section, where gas phase concentrations are lowest. This

implies that although there was no discernible effect of gas phase concentration levels on overall EC values, mass transfer effects do have a small effect on rates of VOC removal in biofilters.

4.5 Elimination Capacity and Inlet Load

The maximum EC values for biofilters packed with peanut shells and treating a single VOC component system were 198 $g/m^3/h$ for methanol and 141 $g/m^3/h$ for toluene. The corresponding maximum EC values for biofilters packed with palm shells were 168 $g/m^3/h$ for methanol and 133 $g/m^3/h$ for toluene. The maximum EC values for biofilters treating a mixture of methanol and toluene were 215 $g/m^3/h$ for methanol and 6.6 $g/m^3/h$ for toluene, when peanut shells were used as the packing material, and 185 $g/m^3/h$ for methanol and 8.8 $g/m^3/h$ for toluene when palm shells were the packing material. The EC values for methanol, and for toluene in a single VOC component system, are comparable with those obtained by other researchers in biofilters using more conventional packing materials. Hence both peanut shells and palm shells are suitable for use as packing media for a high performance biofilter, and since both are easily obtainable and cost effective in Thailand (cost of peanut shell is 7 Baht/kg (Tong Garden Co., Ltd., 2009); cost of palm shells is 6 Baht/kg (Suratthani Oil Palm Research Center, 2009) they appear to be well suited for use by Thai industries emitting substantial quantities of VOCs, such as paper and pulp industries and color industries.

4.6 The Other Parameters

4.6.1 Pressure Drop

The experiments demonstrated the importance of controlling pressure drop during biofilter operation. Major pressure drop increases occurred at the mid-stage of a number of runs due to biomass accumulation while more gradual increases occurred towards the end of most runs. Such increases can be caused by increases in gas flow rate, by accumulations of biomass on the packing media, or by combinations of both factors. In the present project, pressure drop increases attributable to a build-up of biomass caused a deterioration in EC values in the middle stages of the experimental runs. In order to restore EC values to their former high levels, the columns needed to be washed, and then the air flow rate was reduced from 0.3 to 0.06 g/m^3 to help the

biomass remaining on the packing to re-acclimatize. After this treatment a rapid return to good EC levels was observed.

4.6.2 The Other Parameters (temperature, relative humidity and pH)

Ambient air temperatures ranged from 24 to 31°C and the inlet gas temperatures were within the range of 25-29°C. Ambient relative humidity ranged from 51% to 90%; after passage through the humidifiers, the humidity of gases entering the biofilter was kept at a level higher than 90%. The pH within the column was controlled and kept in the range of 6-7 in all biofilters throughout the experimental runs. Very little variation was observed in the values of the above parameters within the biofilter; therefore, the influence of these parameters on biofilter performance was minimal.

4.7 Characteristics of Packing Materials

Combining the observations of changes in bed height, BET surface areas and pore volume distributions suggests that both packings are to some extent susceptible to attack by the VOCs themselves, and possibly also by intermediates formed in the course of biodegradation (such as benzoic acid in the case of toluene). In the case of palm shells, and of peanut shells exposed to toluene, the structural integrity of the packings does not seem to be compromised to any significant extent. With peanut shells exposed to methanol, though, the reduction in macropore volume coupled with the 0.5 cm decrease in bed height points to a more serious level of structural breakdown. Clearly, when using agricultural products as packing materials attention needs to be paid on the types of VOC involved before packing materials are selected.

4.8 Biofilm Characteristics

4.8.1 Biofilm Thickness

Mean biofilm thicknesses differed significantly between the two packing materials, being in the range 100-150 μm for the palm shells and 200-230 μm for peanut shells.

4.8.2 Microbial Fauna

On day 93, the surfaces of packing materials from all biofilters were dominated by rod shaped microorganisms. At this stage no differences related to the nature of the VOC involved were apparent. By day 147 the numbers of microorganisms present on the surfaces had increased

considerably and the nature of the microbial fauna was very different. Peanut shell surfaces appeared to be dominated by mycelial mats, with a scattering of cocci. Mycoflora or fungi develop easily on the peanut shells in moist atmospheres (Hanlin, 1968; Fonseca, et al. 1994); therefore, given the moist aerobic conditions under which peanut shells exist in the biofilters, it is not surprising that fungal mats became established on their surfaces. The microbial fauna on the palm shell surfaces was very different from those on the peanut shells.

4.9 Macrokinetic Models

A macrokinetic model of the following form was used to describe the results obtained in this project:

$$EC = aH_{max}(1 - e^{-bIL})$$

This equation was found to fit well the results for individual biofilters as well as the results obtained by other researchers.

4.10 Recommendations for Further Work

During the course of this project a number of areas were identified where further research should be undertaken:

4.10.1 It is evident that much remains to be learned about the way that biofilms develop on biofilter packings and how this development is affected by the nature and gas phase concentrations of the VOCs to which the developing biofilm is exposed. Of particular relevance to industrial biofilter applications is the impact that excluding a VOC from the mixture of VOCs introduced into the biofilter at start-up may have on the biofilter's subsequent capability to remove and degrade that particular VOC.

4.10.2 More needs to be learnt about the microbial species composition of biofilms and how this changes during the course of biofilm development and biofilter operation.

4.10.3 Whilst it appears that both palm shells and peanut shells can be used as packing media in biofilters, they do undergo change while in use; in order to determine the optimum intervals between bed replacements under various conditions, long term studies of changes in the properties of these packings during exposure to VOCs of various kinds are needed.

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Appendix A

Calibration Curve

Calibration Curve

Calibration of the gas chromatograph for analysis of the samples was carried out as follows. Several different known volumes of pure methanol solvent (or toluene) were injected into 1 litre sample bottles. This was done using liquid syringes inserted through the silicone rubber septa used to seal the sample bottles. After 4 hours, the solvent had completely evaporated. By regulating the amount of liquid solvent injected, various standard gas concentrations of methanol (or toluene) were created. The known initial solvent concentrations were plotted against the corresponding peak areas from the GC output to create a standard concentration curve as shown in Figures A-1 and A-2.

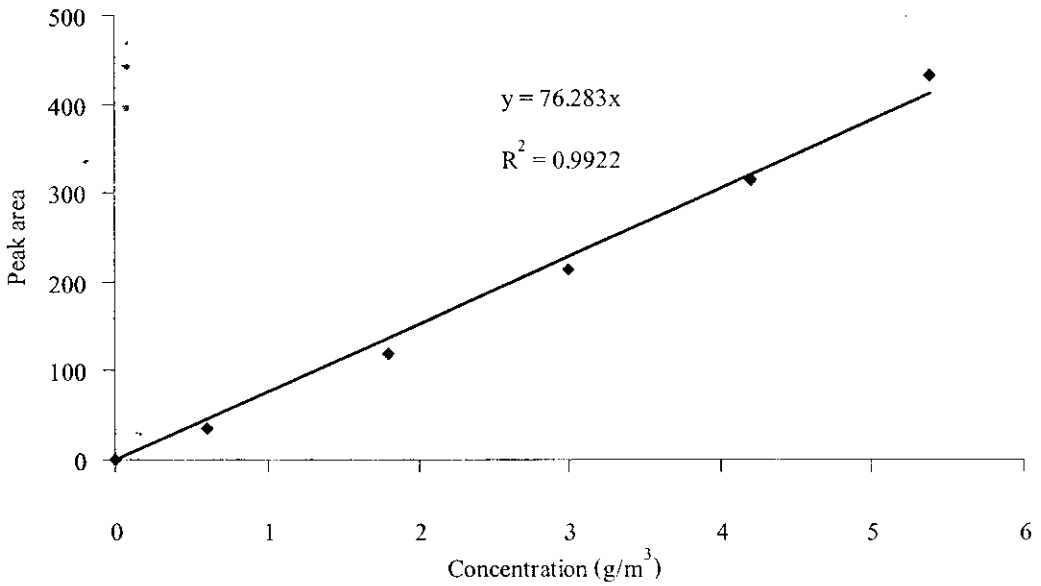

Figure A-1 Calibration curve for methanol.

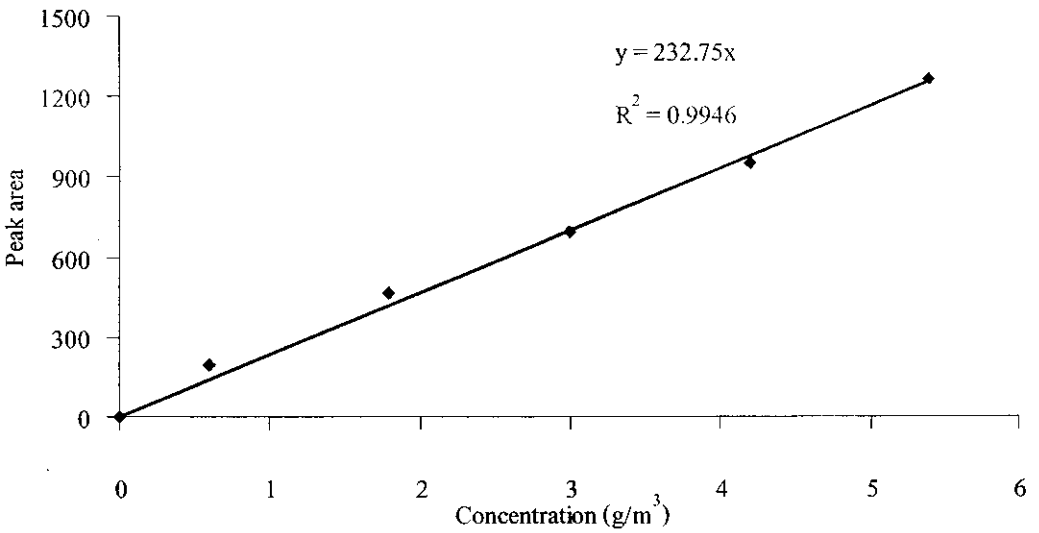

Figure A-2 Calibration curve for toluene.

Appendix B

The Elimination Capacity and Inlet Load

The Elimination Capacity and Inlet Load

The Elimination Capacities and Inlet Loads for the biofilters M2, T1 and T2 are shown in Figures B-1 to B-6.

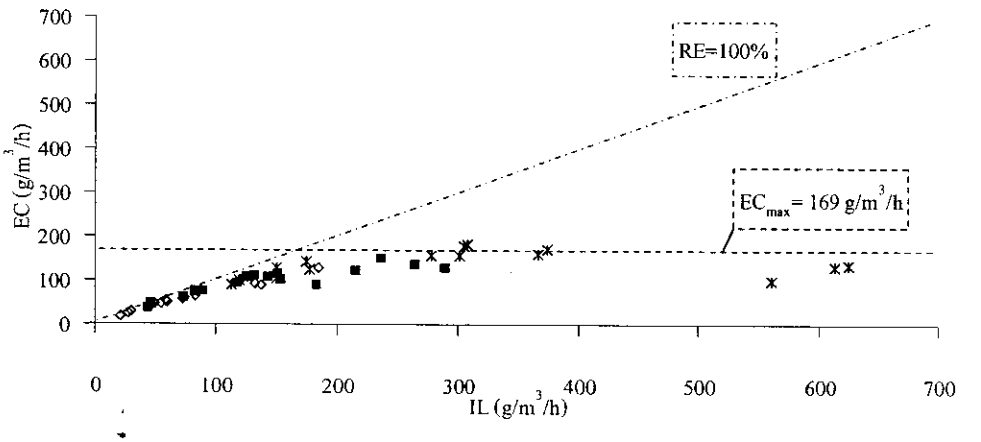

Figure B-1 Inlet load and elimination capacity for methanol in the biofilter packed with palm shells in the pure system (M2) at three ranges of concentration of: (◇) 1-3, (▪) 3-6, and (∗) 6-9 g/m^3.

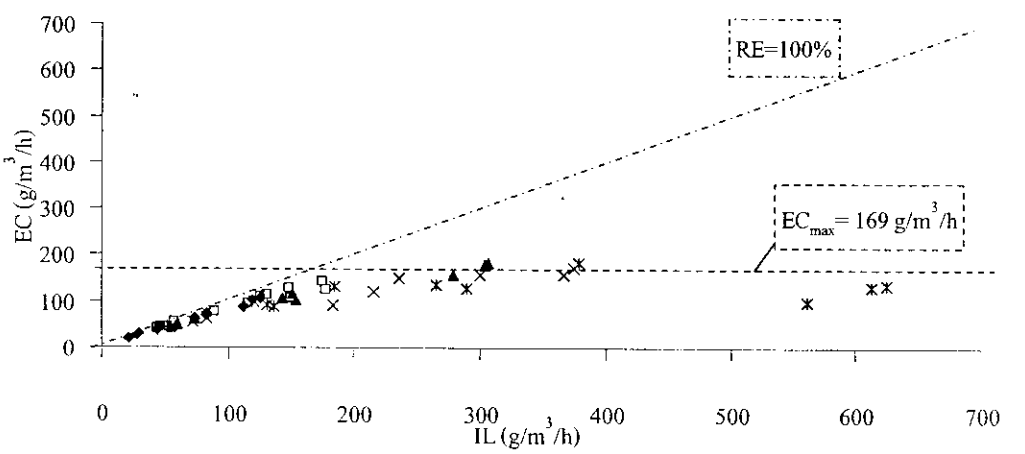

Figure B-2 Inlet load and elimination capacity for methanol in the biofilter packed with palm shells in the pure system (M2) at six air flow rate ranges of: (♦) 0.06, (□) 0.1, (▲) 0.15, (×) 0.2, and (∗) 0.3 m^3/h.

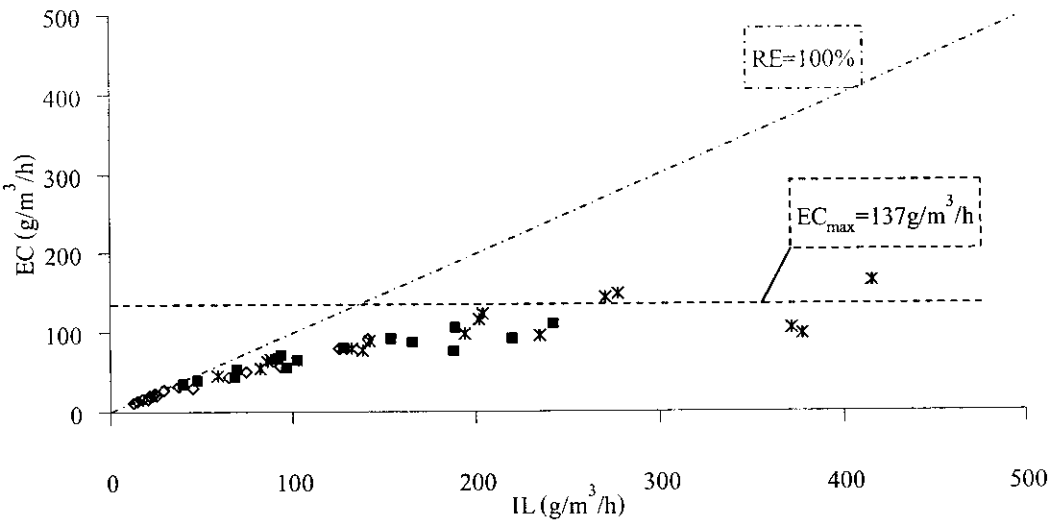

Figure B-3 Inlet load and elimination capacity for toluene in the biofilter packed with peanut shells in the pure system (T1) at three ranges of concentration of: (◇) 0.1-2, (▪) 2-4, and (∗) 4-6 g/m^3.

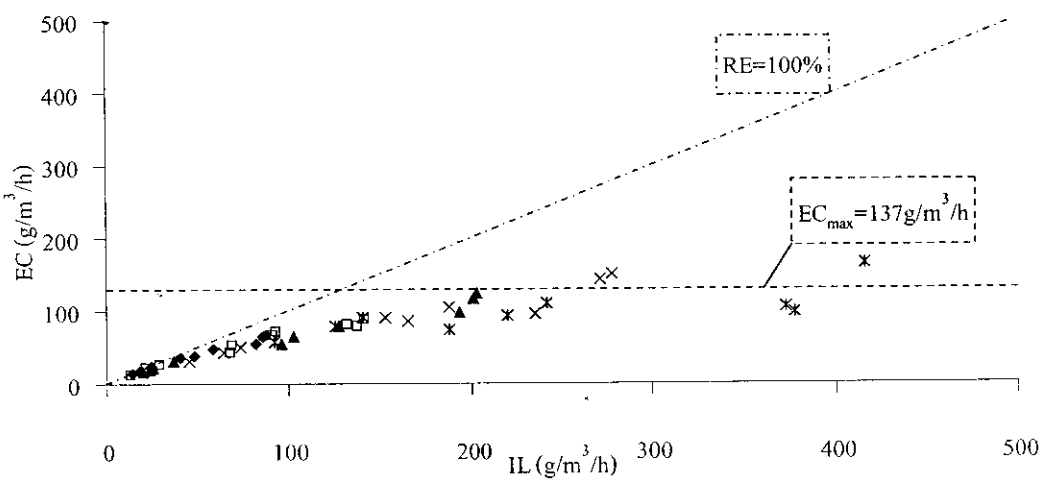

Figure B-4 Inlet load and elimination capacity for toluene in the biofilter packed with peanut shells in the pure system (T1) at six air flow rate ranges of: (♦) 0.06, (□) 0.1, (▲) 0.15, (×) 0.2, and (∗) 0.3 m^3/h.

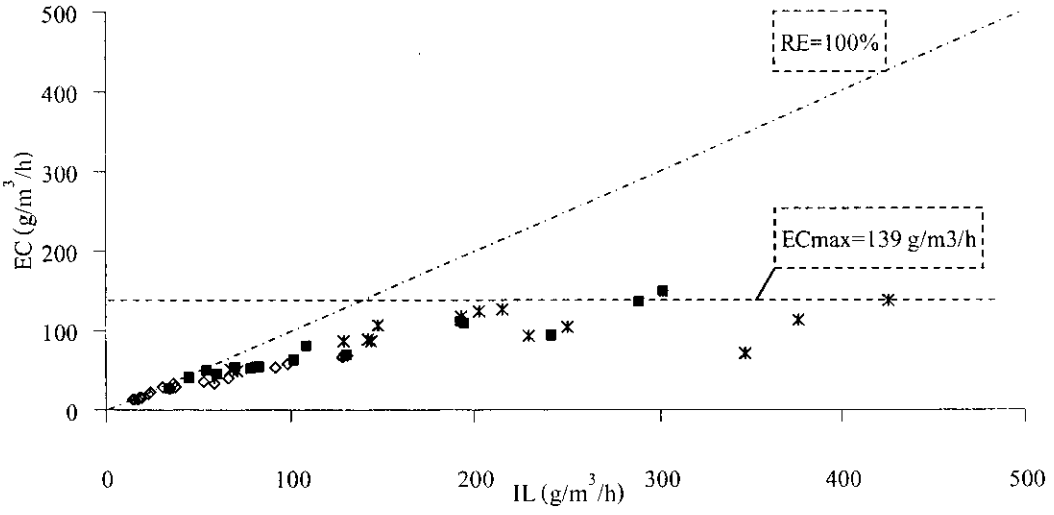

Figure B-5 Inlet load and elimination capacity for toluene in the biofilter packed with peanut shells in the pure system (T2) at three ranges of concentration of: (◇) 0.1-2, (▪) 2-4, and (∗) 4-6 g/m^3.

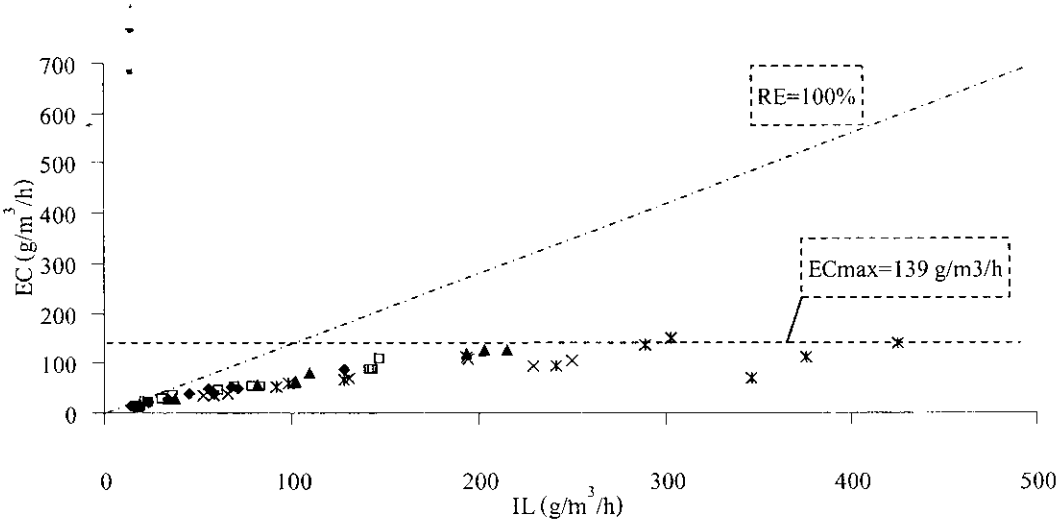

Figure B-6 Inlet load and elimination capacity for toluene in the biofilter packed with peanut shells in the pure system (T2) at six air flow rate ranges of: (♦) 0.06, (□) 0.1, (▲) 0.15, (×) 0.2, and (∗) 0.3 m^3/h.

Appendix C

Models

C.1 Macrokinetic Models

The macrokinetic model was developed using the Excel Solver tool in Microsoft Office to determine the constants in the model. The empirical model predicts elimination capacity as a function of inlet load and bed height. The parameters a and b were individually fitted to describe their relationship with the elimination capacity at different inlet load.

$$EC = aH_{\max}(1 - e^{-bIL}) \qquad \textbf{(3.1)}$$

where a and b are constant values, H_{max} is maximum bed height (m). This model is based on 8 options, such as Maximum time = 100 seconds, Precision = 0.000001, Tolerance = 5%, Convergence = 0.0001, tangent estimates, forward derivatives, and Newton search. After setting options in the Excel Solver, Solvers parameters also modified as shown in Table C-1. Initially, the the best values for the a and b constants are guessed by the researcher, and then the Excel Solver will operate itself for appropriate values.

Table C-1 The Relation between the Solver parameters and applied value.

Solver parameters	Applied value
Set Target Cell	The average total error between $EC_{experiment}$ and EC_{model}
Equal To	Min
By Exchanging Cell	a and b constants
Subject to the Constraints	EC_{model} <= IL

There are 3 equations which are calculated in this model before getting the constant values.

$$\text{Error} = (EC_{experiment} - EC_{model})^2 \qquad \textbf{(C.1)}$$

$$\bar{y} = \text{average } EC_{experiment} \qquad \textbf{(C.2)}$$

$$R^2 = \frac{\Sigma(EC_{experiment} - \bar{y})^2 - \Sigma(EC_{experiment} - EC_{model})^2}{\Sigma(EC_{experiment} - \bar{y})^2} \quad \textbf{(C.3)}$$

C.2 The experimental results and calculated values in this study

In this study, 6 biofilters were operated.

System: The removal of pure methanol in the biofilter packed with peanut shells (M1)

The maximum bed height: 0.66 m

Packing material: Peanut shells/ activated sludge

VOC: Methanol

Table C-2 EC from experiment and model in M1.

IL	$EC_{experiment}$	EC_{model}	Error	$(EC_{experiment}-\bar{y})^2$
20.6	18.6	20.6	4.1	5986.6
38.3	35.9	36.6	0.393	3605.4
27.6	25.7	27.1	2.1	4938.3
38.2	35.8	36.5	0.478	3618.9
46.7	41.5	43.6	4.537	2968.2
43.8	36.4	41.3	23.4	3544.9
82.8	75.1	70.7	19.1	436.5
58.9	52.9	53.4	0.245	1858.5
124.9	97.4	96.3	1.3	2.1
102.5	73.3	83.4	101.5	513.2
118.4	93.3	92.7	0.328	7.2
119.2	95.1	93.1	3.7	0.853
125.4	104.2	96.5	58.1	66.9
131.3	99.1	99.7	0.357	9.8
117.1	94.8	91.9	8.3	1.3
149.2	105.1	108.6	12.6	83.1
175.0	135.8	120.1	244.2	1582.2
177.4	114.4	121.1	45.1	340.5
190.9	121.3	126.4	26.9	639.6
208.3	133.8	132.8	1.1	1434.3
368.5	182.8	170.2	158.2	7544.6
375.9	165.7	171.3	31.8	4860.7
560.5	175.2	188.0	165.9	6269.3
613.7	190.2	190.5	0.069	8884.8
		Average total error	38.1	
		Σ	913.9	59198.0

The results of constant values: a = 300.0, b = 0.005, and $R^2 = 0.98$ where $\bar{y} = 96.0$

System: The removal of pure methanol in the biofilter packed with palm shells (M2)

The maximum bed height: 0.66 m

Packing material: Palm shells/ activated sludge

VOC: Methanol

Table C-3 EC from experiment and model in M2.

IL	$EC_{experiment}$	EC_{model}	Error	$(EC_{experiment} - \bar{y})^2$
29.4	27.6	34.2	43.4	6038.4
21.2	19.3	25.5	38.0	7403.4
21.1	18.9	25.3	40.7	7464.8
27.6	25.7	32.4	44.6	6336.0
46.7	44.9	51.1	37.9	3652.4
43.8	35.4	48.4	170.8	4893.2
73.3	62.1	73.1	120.8	1872.9
82.8	74.4	79.9	30.4	960.2
82.8	70.8	79.9	82.3	1193.4
119.2	101.3	101.8	0.240	16.1
125.2	105.6	104.9	0.491	0.058
112.1	88.7	98.0	86.8	278.0
117.1	94.4	100.7	39.0	118.6
149.2	128.0	115.9	146.5	512.6
175.0	142.8	125.6	293.7	1401.7
177.4	125.3	126.5	1.3	399.4
150.2	105.1	116.3	124.2	0.040
151.4	116.0	116.8	0.705	112.8
304.4	178.8	153.8	626.3	5404.5
278.1	157.7	150.1	58.0	2745.1
306.8	182.0	154.1	775.6	5875.7
300.4	157.6	153.3	18.0	2725.5
367.0	159.0	160.2	1.5	2877.6
374.7	171.0	160.8	103.7	4307.6
378.7	183.5	161.1	503.0	6110.7
613.4	133.5	169.0	1262.4	791.6
624.5	134.8	169.1	1179.8	867.1

IL	$EC_{experiment}$	EC_{model}	Error	$(EC_{experiment} - \bar{y})^2$
		Average total error	215.9	
		Σ	5830.1	74359.4

The results of constant values: a = 258.5, b = 0.008, R^2 = 0.92 where $\bar{y}$ = 105.3

System: The removal of pure toluene in the biofilter packed with peanut shells (T1)

The maximum bed height: 0.66 m

Packing material: Peanut shells/ activated sludge

VOC: Toluene

Table C-4 EC from experiment and model in T1.

IL	$EC_{experiment}$	EC_{model}	Error	$(EC_{experiment} - \bar{y})^2$
17.6	17.1	16.1	0.948	3662.2
14.4	13.3	13.4	0.002	4136.7
24.4	23.2	21.8	2.0	2958.8
40.4	34.5	34.4	0.032	1856.4
48.0	38.7	39.9	1.3	1513.1
58.8	46.7	47.2	0.323	959.3
87.9	66.4	64.6	3.1	127.0
85.8	64.2	63.5	0.495	180.9
82.1	55.4	61.4	35.1	492.5
93.8	71.2	67.7	11.7	41.9
92.1	66.2	66.8	0.388	130.4
68.4	42.8	53.4	111.2	1213.1
142.1	88.7	89.3	0.378	122.2
138.2	77.9	87.8	97.8	0.072
132.0	81.0	85.3	18.7	11.4
128.0	79.6	83.7	16.9	3.8
201.4	116.5	107.9	74.8	1513.0
193.3	97.9	105.7	61.6	410.6
203.5	122.8	108.4	208.6	2045.0
271. 3	143.3	122.2	444.8	4312.1
278.0	149.2	123.3	671.4	5118.0
372.2	105.4	134.1	823.8	770.3
415.7	163.6	137.2	693.9	7383.5
377.2	97.5	134.5	1366.9	395.8
		Average total error	193.6	
		Σ	4646.1	39358.1

The results of constant values: a = 222.1, b = 0.007, and R^2 = 0.88 where $\bar{y}$ = 77.6

System: The removal of pure toluene in the biofilter packed with palm shells (T2)

The maximum bed height: 0.66 m

Packing material: Palm shells/ activated sludge

VOC: Toluene

Table C-5 EC from experiment and model in T2.

IL	$EC_{experiment}$	EC_{model}	Error	$(EC_{experiment} - \bar{y})^2$
17.1	13.6	16.7	9.5	4204.8
15.0	12.6	14.8	4.7	4334.0
14.2	13.9	14.0	0.007	4162.7
23.7	22.4	22.6	0.074	3142.7
33.8	27.1	31.2	17.3	2638.2
45.1	39.8	40.1	0.126	1497.0
54.5	48.8	47.0	3.1	880.8
66.8	52.1	55.3	10.1	692.5
57.6	39.5	49.1	92.8	1515.6
70.6	48.8	57.7	80.8	881.2
127.9	87.2	87.5	0.073	76.8
147.4	107.2	95.1	146.0	826.8
141.3	88.2	92.8	20.9	96.3
143.2	86.8	93.6	45.4	70.4
214.7	126.9	114.8	146.5	2345.5
202.8	124.1	112.0	148.9	2088.4
193.3	117.2	109.5	59.6	1503.6
194.6	107.8	109.8	4.2	861.3
250.0	104.4	121.9	304. 3	676.6
302.4	149.5	129.7	393.2	5053.1
289.0	134.8	128.0	46.2	3171.9
376.0	112.8	136.7	571.0	1183.5
425.6	138.6	139.8	1.5	3615.1
		Average total error	91.6	
		Σ	2106.3	45518.9

The results of constant values: a = 222.9, b = 0.007, and R^2 = 0.95 where $\bar{y}$ = 78.4

System: The removal of methanol in a mixture of methanol and toluene in the biofilter packed with peanut shells (X1)

The maximum bed height: 0.66 m

Packing material: Peanut shells/ activated sludge

VOC: Methanol in mixed system

Table C-6 EC from experiment and model in X1 (methanol).

IL	$EC_{experiment}$	EC_{model}	Error	$(EC_{experiment} - \bar{y})^2$
21.6	19.8	21.6	3.1	10968.2
33.1	30.7	32.4	2.8	8803.4
34.2	32.4	33.5	1.0	8486.4
35.0	33.4	34.1	0.486	8304.5
76.4	70.4	69.3	1.2	2936.3
52.7	43.8	49.8	36.3	6526.7
72.2	63.4	66.0	6.5	3740.1
56.0	44.7	52.6	62.6	6376.3
58.9	42.9	55.1	148.7	6675.9
93.4	73.6	82.2	72.9	2595.5
103.8	84.7	89.7	25.4	1591.5
76.5	57.5	69.3	139.9	4496.6
127.4	113.4	105.7	58.6	124.8
87.8	71.8	78.0	38.9	2786.6
120.4	105.3	101.1	17.6	370.8
93.3	79.5	82.1	6.8	2029.1
171.4	129.6	132.1	6.5	25.0
208.2	176.5	151.1	.644.5	2696.6
168.2	129.4	130.4	0.890	23.5
193.0	151.2	143.6	58.1	711.3
240.2	181.3	165.7	244.0	3217.4
281.7	215.5	182.2	1113.6	8273.1
302.2	231.1	189.4	1739.2	11353.3
264.9	201.8	175.8	672.7	5957.9
282.7	212.6	182.6	900.2	7742.3
223.9	162.3	158.5	14.4	1423.1

IL	$EC_{experiment}$	EC_{model}	Error	$(EC_{experiment} - \bar{y})^2$
423.2	255.8	222.7	1094.3	17213.8
313.0	201.8	193.0	75.9	5957.9
382.4	233.5	213.1	418.5	11874.8
430.4	232.7	224.2	71.2	11685.0
365.5	179.2	208.7	868.8	2982.7
		Average total error	275.7	
		Σ	8545.6	167950.4

The results of constant values: $a = 426.8$, $b = 0.004$, and $R^2 = 0.94$ where $\bar{y} = 124.6$

System: The removal of toluene in a mixture of methanol and toluene in the biofilter packed with peanut shells (X1)

The maximum bed height: 0.66 m

Packing material: Peanut shells/ activated sludge

VOC: Toluene in mixed system

Table C-7 EC from experiment and model in X1 (toluene).

IL	$EC_{experiment}$	EC_{model}	Error	$(EC_{experiment} - \bar{y})^2$
6.5	6.2	5.5	0.549	1.2
6.3	5.9	5.3	0.320	0.621
4.1	3.9	3.7	0.032	1.5
3.0	2.8	2.8	0.001	5.6
1.5	1.4	1.5	0.003	13.8
1.5	1.3	1.5	0.068	14.8
1.7	1.5	1.7	0.031	13.3
1.4	1.3	1.4	0.018	14.7
1.3	1.1	1.3	0.017	16.0
1.3	1.2	1.3	0.006	15.1
1.5	1.3	1.5	0.015	14.3
1.5	1.3	1.5	0.041	14.4
9.1	7.4	7.0	0.152	5.3
9.2	7.2	7.1	0.031	4.5
12.7	10.2	8.8	1.941	25.4
11.9	9.4	8.4	0.834	17.9
3.9	3.1	3.6	0.230	4.1
7.2	6.1	5.9	0.021	0.909
5.6	4.5	4.8	0.083	0.348
4.7	3.8	4.2	0.143	1.7
13.3	10.3	9.1	1.493	26.6
16.6	12.4	10.2	4.755	53.3
21.0	10.0	11.5	2.284	23.6
20.9	9.3	11.5	4.703	17.4
		Average total error	0.740553	
		Σ	17.8	306.5

The results of constant values: a = 22.6, b = 0.070, and R^2 = 0.94 where $\bar{y}$ = 5.12

System: The removal of methanol in a mixture of methanol and toluene in the biofilter packed with palm shells (X2)

The maximum bed height: 0.66 m

Packing material: Palm shells/ activated sludge

VOC: Methanol in mixed system

Table C-8 EC from experiment and model in X2 (methanol).

IL	$EC_{experiment}$	EC_{model}	Error	$(EC_{experiment} - \bar{y})^2$
25.8	23.6	28.9	28.2	8500.1
18.2	17.1	20.9	13.9	9733.5
17.7	16.1	20.3	17.6	9930.4
40.2	37.2	43.1	35.0	6177.3
60.4	53.3	61.0	58.7	3904.4
77.6	71.2	74.5	10.5	1983.7
109.1	80.2	95.6	236.5	1264.9
114.5	81.1	98.8	313.8	1201.8
117.8	88.7	100.7	144.9	733.3
106.7	72.9	94.2	450.4	1836.4
117.1	98.7	100.3	2.7	293.1
139.7	117.1	112.4	21.3	1.6
128.6	107.2	106.7	0.230	73.4
193.0	134.0	135.0	1.0	330.9
205.7	142.5	139.3	10.3	715.4
208.2	149.1	140.1	80.6	1109.1
283.3	174.3	159.3	223.2	3420.3
306.3	173.4	163.6	95.6	3317.0
249.0	149.7	151.7	4.0	1149.0
248.7	193.6	151.6	1762.2	6051.9
304.5	150.9	163.3	152.5	1235.2
344.5	166.8	169.4	7.0	2601.6
376.0	187.3	173.3	197.5	5119.4
365.5	216.8	172.1	2003.8	10212.0
558.1	163.5	185.1	466.6	2280.9
611.1	144.0	186.7	1825.8	794.3

IL	$EC_{experiment}$	EC_{model}	Error	$(EC_{experiment} - \bar{y})^2$
		Average total error	314.0	
		Σ	8164.1	83970.9

The results of constant values: a = 288.7, b = 0.006, and R^2 = 0.90 where $\bar{y}$ = 115.6

System: The removal of toluene in a mixture of methanol and toluene in the biofilter packed with palm shells (X2)

The maximum bed height: 0.66 m

Packing material: Palm shells/ activated sludge

VOC: Toluene in mixed system

Table C-9 EC from experiment and model in X1 (toluene).

IL	$EC_{experiment}$	EC_{model}	Error	$(EC_{experiment} - \bar{y})^2$
7.9	4.1	5.5	2.0	22.5
10.3	5.3	7.1	3.0	12.0
6.5	3.5	4.6	1.2	28.3
6.3	2.4	4.5	4.5	41.8
9.1	6.2	6.3	0.007	6.7
9.2	5.5	6.3	0.741	11.2
12.7	9.5	8.5	1.0	0.504
11.9	7.5	8.1	0.334	1.8
7.2	6.1	5.1	1.1	7.1
13.3	9.8	8.9	0.820	1.0
16.6	12.3	10.8	2.1	12.0
21.0	14.5	13.3	1.4	32.1
14.1	8.8	9.4	0.420	0.003
9.0	6.8	6.2	0.362	4.0
8.7	6.8	6.1	0.489	4.3
11.1	7.8	7.5	0.052	1.1
11.8	7.6	8.0	0.164	1.5
21.0	14.4	13.3	1.4	31.6
15.2	10.7	10.0	0.385	3.4
16.4	13.2	10.7	6.1	19.1
20.9	13.3	13.2	0.020	20.4
20.6	13.0	13.0	0.001	17.5
19.0	11.3	12.2	0.850	6.0
23.4	11.3	14.5	10.5	6.1
		Average total error	1.6	
		Σ	39.1	291.9

The results of constant values: a = 70.8, b = 0.016, and R^2 = 0.87 where $\bar{y}$ = 8.82

C.3 The experimental results and calculated values for other studies.

The above elimination capacity model was also applied to the experimental results of other biofilter researchers, using Excel Solver. As would be expected, given that this is a macrokinetic model, the values of the constants depend on the experimental conditions and differ from one study to the next. With only one exception, the values of R^2 are high, confirming that for a given set of biofilter conditions, the elimination capacity model fits the experimental data well.

Researcher: Prado et al. (2005)

The maximum bed height: 0.44 m

Packing material: Lava rock/activated sludge

VOC: Toluene

Table C-10 EC from experiment and model of Prado et al.

IL	$EC_{experiment}$	EC_{model}	Error	$(EC_{experiment} - \bar{y})^2$
65	60	58.7	1.7	174.2
71	58	62.12	17.6	231.0
96	75	74.4	0.392	3.2
112	85	80.5	20.3	139.2
147	88	90.5	6.12	219.0
		Average total error	9.2	
		Σ	46.1	766.8

The results of constant values: a = 250.5, b = 0.012, and R^2 = 0.94 where $\bar{y}$ = 73.2

Researcher: Zhang et al. (2007)

The maximum bed height: 0.33 m

Packing material: Nova inert (silica)/specific microorganisms

VOC: Methanol

Table C-11 EC from experiment and model of Zhang et al.

IL	$EC_{experiment}$	EC_{model}	Error	$(EC_{experiment} - \bar{y})^2$
10	9	8.9	0.004	415.1
20	18	17.5	0.256	129.4
30	27	25.7	1.7	5.6
37	27	31.2	17.8	5.6
47	35	38.8	14.6	31.6
50	48	41.0	48.4	346.9
38	35	32.0	9.1	31.6
48	36	39.6	12.7	43.9
		Average total error	13.1	
		Σ	104.5	1009.9

The results of constant values: a = 636.3, b = 0.004, and R^2 = 0.90 where $\bar{y}$ = 29.4

Researcher: Delhoménie et al. (2002a)

The maximum bed height: 0.99 m

Packing material: Compost/ activated sludge

VOC: Toluene

Table C-12 EC from experiment and model of Delhoménie et al.

IL	$EC_{experiment}$	EC_{model}	Error	$(EC_{experiment} - \bar{y})^2$
60	48	44.5	12.3	25
50	42	41.6	0.172	1
36	32	35.6	12.9	121
102	48	50.2	5.0	25
56	45	43.44	2.4	4
		Average total error	6.6	
		Σ	32.8	176

The results of constant values: a = 52.8, b = 0.032, and R^2 = 0.813 where $\bar{y}$ = 43.0

Researcher: Liu et al. (2000)

The maximum bed height: 0.90 m

Packing material: Compost/ soil/lava rock

VOC: Toluene

Table C-13 EC from experiment and model of Liu et al.

IL	$EC_{experiment}$	EC_{model}	Error	$(EC_{experiment} - \bar{y})^2$
22	21.8	24.22835015	5.9	252.8
27	26.8	28.44794271	2.7	118.8
32	31.8	32.28137007	0.2	34.8
45	44.8	40.68545216	16.9	50.4
55	47	45.86409171	1.3	86.5
82	54	55.76180301	3.1	265.7
		Average total error	6.6	
		Σ	5.0	809.0

The results of constant values: a = 78.2, b = 0.019, and R^2 = 0.96 where $\bar{y}$ = 37.7

Researcher: Torkian et al. (2000)

The maximum bed height: 0.90 m

Packing material: Compost/ woodchip

VOC: Toluene

Table C-14 EC from experiment and model of Torkian et al.

IL	$EC_{experiment}$	EC_{model}	Error	$(EC_{experiment} - \bar{y})^2$
17	16.5	16.6	0.015	895.0
68	58	57.9	0.004	134.2
92	77	73.6	11.5	935.3
106	79	81.9	8.2	1061.7
39	38	35.9	4.4	70.8
16	10	15.7	32.4	1326.2
		Average total error	9.4	
		Σ	56.3	4423.2

The results of constant values: a = 202.6, b = 0.006, and R^2 = 0.99 where $\bar{y}$ = 46.4

Researcher: Chetpattananondh et al. (2005)

The maximum bed height: 0.60 m

Packing material: Palm shells/ activated sludge

VOC: Toluene

Table C-15 EC from experiment and model of Chetpattananondh et al.

IL	$EC_{experiment}$	EC_{model}	Error	$(EC_{experiment} - \bar{y})^2$
72.9	72.9	71.5	1.806	685.3
64.4	64.4	64.4	0.008	1204.0
55.9	55.9	57.0	1.46	1865.3
112.9	112.9	101.1	139.5	191.8
66.7	66.7	66.4	0.079	1044.5
59.3	59.3	60.1	0.631	1580.8
250.7	141.6	167.7	681.9	1805.5
222.3	166.7	157.4	86.6	4579.4
137.8	113.2	116.8	12.6	200.0
218.1	137.0	155.8	350.3	1443.3
		Average total error	127.5	
		Σ	1275.0	14599.9

The results of constant values: a = 392.2, b = 0.005, and $R^2 = 0.91$ where $\bar{y} = 99.1$

Researcher: Rene et al. (2005)

The maximum bed height: 0.70 m

Packing material: Compost/ceramic beads

VOC: Toluene

Table C-16 EC from experiment and model of Rene et al.

IL	$EC_{experiment}$	EC_{model}	Error	$(EC_{experiment} - \bar{y})^2$
25	20	22.8	7.8	2272.1
70	51	51.3	0.1	277.8
125	75	72.0	8.7	53.8
175	80	82.8	8.1	152.1
220	100	88.7	127.2	1045.4
233	80	90.0	99.3	152.1
		Average total error	41.8	
		Σ	251.2	3953.3

The results of constant values: a = 140.6, b = 0.011, and R^2 = 0.94 where $\bar{y}$ = 67.7

Researcher: Wright et al. (2005)

The maximum bed height: 0.70 m

Packing material: Diatomaceous earth

VOC: Toluene

Table C-17 EC from experiment and model of Wright et al.

IL	$EC_{experiment}$	EC_{model}	Error	$(EC_{experiment} - \bar{y})^2$
25	20	31.6	133.5	14042.3
75	60	82.2	491.8	6162.3
125	120	119.8	0.053	342.3
230	200	170.2	889.9	3782.3
500	199	216.6	309.1	3660.3
1260	232	228.1	15.2	8742.3
		Average total error	306.6	
		Σ	1839.6	36731.5

The results of constant values: a = 228.2, b = 0.006, and R^2 = 0.95 where $\bar{y}$ = 138.5

Researcher: Xi et al. (2006)

The maximum bed height: 0.40 m

Packing material: Woodchip/ propylene spheres/activated sludge

VOC: Toluene

Table C-18 EC from experiment and model of Xi et al.

IL	$EC_{experiment}$	EC_{model}	Error	$(EC_{experiment} - \bar{y})^2$
20	18	20.0	4.1	282.2
40	37	33.3	13.8	4.8
60	40	42.1	4.3	27.0
100	52	51.7	0.068	295.8
30	27	27.3	0.1145	60.8
		Average total error	4.5	
		Σ	22.4	670.8

The results of constant values: a = 148.2, b = 0.021, and R^2 = 0.97 where $\bar{y}$ = 34.8

Researcher: Vergara-Fernández et. al. (2007)

The maximum bed height: 0.75 m

Packing material: Compost/ sea shells

VOC: Toluene

Table C-19 EC from experiment and model of Vergara-Fernández et al.

IL	$EC_{experiment}$	EC_{model}	Error	$(EC_{experiment} - \bar{y})^2$
46	43	42.52651425	0.224189	225
60	54	54.55138712	0.304028	16
63	54	57.07521478	9.456946	16
73	66	65.35598063	0.414761	64
79	73	70.22845996	7.681434	225
		Average total error	4.5	
		Σ	18.1	546.0

The results of constant values: a = 534.8, b = 0.002, and R^2 = 0.97 where $\bar{y}$ = 58.0

Appendix D

Publications

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Date: 07/12/2009

Dear Mr. Yada Nitipavachon,

This has reference to your paper titled "The Suitability of Peanut Shells and Palm Shells for Use as Bed Packing Media in Biofilters". We are glad to inform you that your paper is accepted for publication and in all likelihood, it may be published in Vol. 2 No.1 of the Icfai University Journal of Chemical Engineering.

Looking forward to more contributions from you,

Warm regards,

Sincerely,

G R K Murty

Consulting Editor

The Icfai University Press

The suitability of peanut shells and palm shells for use as bed packing media in biofilters

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Abstract

The characteristics of peanut shells and palm shells used as packing media in biofilters treating air contaminated with methanol, toluene or mixtures of methanol and toluene for over 200 days were investigated. Although the characteristics of the two packings are different they both appear suitable for use as media in biofilters treating air contaminated with methanol or toluene since their maximum elimination capacity (EC_{max}) values are comparable to those obtained using other media. The EC_{max} values for peanut shells are slightly higher than those for palm shells, and the peanut shells have a much lower bulk density, which would certainly have cost advantages. However, the results also show that palm shells could retain their structural integrity better than peanut shells and so require replacing less frequently. This means that local availability and costs of the two materials are likely to determine which should be selected. Use of peanut shells or palm shells should be of considerable benefit to Thai industries considering installing biofilters to remove VOCs as it makes the cost of bed packing materials much more affordable than if more conventional packing materials had to be used.

Keywords: Biofiltration; Methanol; Toluene; Peanut shells; Palm shells

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1. Introduction

Volatile organic compounds or VOCs are organic compounds that evaporate readily at room temperature. They are discharged with waste gas streams to the atmosphere by a wide range of industries, and many VOCs are not only significant air pollutants but also harmful to human health. Although the amounts of VOCs emitted in individual waste gas streams are often quite low, the cumulative impact on the atmosphere of the emissions of VOC is substantial. Hence many industrialized countries have introduced regulations requiring industries, even quite small ones, to remove most of the VOCs from their waste gases before these are discharged to the atmosphere.

In many developing countries, such as Thailand, industrial discharges of air pollutants, such as VOCs, are less strictly regulated. However, more stringent regulations similar to those in developed countries are expected and will be introduced in due course. In Thailand, this will have an impact on industries like the printing industry, where the majority of the printing inks are solvent-based and the solvents evaporate during the printing process. The rate of expansion of the Thai printing industry is rapid, as can be inferred from the fact that for label printing alone the number of items printed rose from 9.26×10^8 pieces in 2000 to 15.9×10^8 pieces in 2008 (The office of industrial economics, 2009); hence substantial increases in VOC generation can be expected from this industry alone.

Many current technologies for controlling VOCs (e.g. thermal incineration, wet scrubbing, and adsorption onto activated carbon) are costly, especially in cases where pollutant concentrations in the waste gases are low (Mohseni and Allen, 2000). Since the VOCs are biodegradable, another possible alternative treatment is biofiltration. Biofiltration is inexpensive compared with the techniques mentioned

above and very effective for treating large volumes (up to 10^5 m^3/h) of moist air streams with low concentrations (less than 5 g/m^3) of biodegradable pollutants (Devinny *et al.*, 1999). Furthermore, the technology is comparatively environmentally friendly, as the process operates at ambient temperature; therefore, energy inputs to the process are small.

In a biofilter, the waste gas is passed through a shallow bed packed with some suitable inorganic or organic material. A microbial biofilm grows on the surface of the packings. As the gas passes through the bed, pollutants diffuse from the gas phase into the biofilm where they are converted by microorganisms into carbon dioxide, water and new biomass (Deshusses, 1997).

A number of requirements have to be met to make sure that the biofilter will work effectively. A critical requirement is to have a well established community of aerobic microorganisms that is well adapted to conditions in the bed and to the nature of the VOC(s) present in the waste gases being treated. Typical sources of such microbial consortia are compost (Torkian *et al.*, 2003; and Rene *et al.*, 2005), soil (Delhoménie *et al.*, 2002a), and sludge from sewage treatment plants (Krailas and Tuan, 2002; Ng *et al.*, 2004; and Prado *et al.*, 2005). In a few cases specially cultured microorganism colonies have also been used (Zilli *et al.*, 2002; Park and Jung, 2006; and Garcia-Pena *et al.*, 2008). Usual practice is to inoculate the bed with microbial source material and expose it to increasing quantities of the VOCs concerned until a well acclimatized microorganism community has become established. To achieve this, the bed moisture content needs to be maintained within a range (typically 40% to 60%) that enables VOC biodegradation to occur aerobically.

It is essential to choose suitable packing materials for the bed in order to keep the biofilter operating well for extended periods. These materials should facilitate the

attachment of the microbial biofilm and should have a high specific surface area in order to promote mass transfer of VOCs between the gas phase and the biofilm (Devinny *et al.*, 1999). The density of the packing material should be low so as to keep down the mass of the bed and the pressure at the base of the bed. If the operating pressure is high, the packing may disintegrate, hindering the passage of gas through the bed. A near neutral pH, and a good water holding capacity are also important (Barona *et. al.*, 2004; Delhoménie *et al.*, 2002a; and Dumont *et al.*, 2008). Commonly used packing materials include natural materials such as wood chips (Torkian *et al.*, 2003; and Xi *et al.*, 2006) and sea shells (Vergara- Fernández *et al.*, 2007), as well as manufactured products such as granular activated carbon (Aizpuru *et al.*, 2003), extruded diatomaceous earth pellets (Wright, 2005), and ceramic beads (Rene *et al.*, 2005).

The cost of bed packing materials is an important component of the biofilter capital cost. In addition, bed replacement should be scheduled on a regular basis, and the associated costs contribute substantially to plant operating expenses. Consequently, the attractiveness of biofiltration as a VOC removal technology will increase greatly if cheap but effective packing materials can be obtained locally. In Thailand, agricultural production is high and a number of waste agricultural products are available very cheaply. Two with potential for use as biofilter bed packing materials are peanut shells and oil palm shells. Ramírez-López *et al.* (2003) has previously suggested that peanut shells are good packing media since they have a large specific surface area, a low bulk density, a neutral pH, large water holding capacity, and sufficient nutrients for microbial growth. Peanut shells and oil palm shells are both available in Thailand. In 2007, the domestic production of peanuts and palms were 5.4×10^4 ton (Department of Agricultural Extension, 2009) and 6.39×10^6

ton, respectively (Suratthani Oil Palm Research Center (pdf), 2009). The shells have to be removed before these crops are processed into finished goods; hence large amounts of waste peanut and palm shells are produced. On average, the price of assorted size peanut shells and palm shells are 7 baht/kg (Tong Garden Co., Ltd., 2009) and 6 baht/kg (Suratthani Oil Palm Research Center, 2009), respectively. It should be noted that, although peanut shells and palm shells are both locally available materials, their respective centres of production are different. Peanut shells are most easily available in the north and northeast of Thailand while palm shells are more widely available in the south and centre of Thailand.

These costs of peanut shells and palm shells are very much less than those for more conventional packing media such as suitably sized granular activated carbon, which costs up to 85 baht/kg in Thailand (C.Gigantic Carbon Co., Ltd., 2009). This price differential was large enough to warrant further investigation of the suitability of peanut shells and palm shells as biofilter packing materials. Therefore a laboratory scale project was initiated to characterize the performance of peanut shells and palm shells as packing media in biofilters. Since industrial biofilters can be exposed to hydrophilic VOCs, hydrophobic VOCs and VOC mixtures this had to be allowed for in the investigation. The VOCs selected for use in the study were methanol, toluene and a mixture of methanol and toluene. Methanol, which has a high water solubility of 1000 g l^{-1} at 25°C, was used as a representative of the hydrophilic class of VOCs while toluene, which has a much lower water solubility of 0.53 g l^{-1} at 25°C (Chetpattananondh *et al.*, 2005) was used as the representative hydrophobic solvent. This paper describes the characteristics of the packing materials, how these altered over the course of the experimental program, and conclusions reached about the suitability of these materials for use as packing media in biofilters.

2. Materials and methods

2.1 Experimental set up

Six 1.2 m high laboratory scale biofilter columns were constructed for use in the study. Each consisted of a base section above which were three identical 290 mm lengths of 80 mm i.d. acrylic tube and a top section. The sections were connected by flanged joints, each fitted with O-rings to prevent gas leakage. Each of the three central sections was filled with packing material to an initial depth of 220 mm; a perforated plate at the base of each section provided support for the packing material while still allowing free passage of gases and liquids through the column. Waste gas was introduced at the bottom of the biofilter and withdrawn at the top. Each biofilter consists of three equal segments connected in series as seen in Figure 1.

Biofilters M1 and M2 were filled with peanut shells and palm shells respectively; throughout the operating period these received gas streams containing only methanol. Biofilters T1 and T2 were filled with peanut shells and palm shells respectively; throughout the operating period, these received gas streams containing only toluene. Biofilters X1 and X2 were filled with peanut shells and palm shells respectively; during the initial part of the operating period these received gas streams containing only methanol but after 54 days they started receiving gas streams containing a mixture of methanol and toluene.

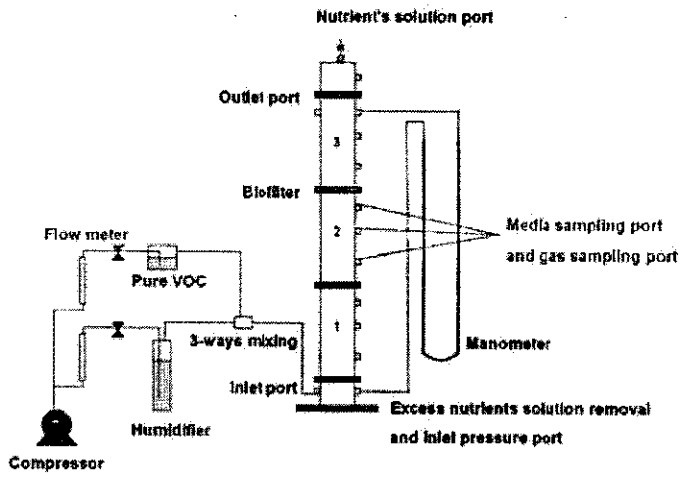


Figure 1. Experimental set up

2.2 Packing materials

The palm and peanut shells used were in the size range of 0.5-1 cm. The peanut shells were cut to size manually whereas the palm shells were selected from assorted palm shell wastes. Activated sludge was obtained from Man A Frozen Food Co. Ltd., a sea food manufacturing plant in Songkhla province. It was fed with the relevant VOC for 3 days in the ratio of VOC/nutrients/activated sludge 0.001/0.2/6.5 v/v/v. The peanut shells or palm shells were immersed in this activated sludge in a ratio of 1:2 v/v for 24 hours to become saturated, so that further particle swelling in the biofilter was avoided (Delhoménie *et al.*, 2002a). After that, these packing media were shaken to remove excess activated sludge and then transferred into the relevant column(s). Excess water was eliminated from the base of the biofilter columns using a peristaltic pump.

2.3 Analytical methods

Toluene and methanol concentration were analyzed by a gas chromatography unit (HP 6890, Hewlett Packard) equipped with a flame ionization detector (FID) using a 30-m capillary column (HP-1, crosslinked methyl siloxane). The temperature

of the injection port, the oven, and the detector were maintained at 180, 50, and 200°C, respectively.

The packing materials were characterized as follows. pH values were measured by AOAC method 973.04 (Helrich, 1990). This involves adding 3 g of shells to 50 ml of water, stirring the mixture gently for 30 minutes, and then measuring the pH. Packing density was found by determining the mass of shells that could be packed into a 250 ml flask (Ramírez-López *et al.*, 2003). Surface characteristics of the packing materials were also measured: small pieces (1x1mm) of peanut shell or palm shell were dried at 100°C for 12 hours, degassed at 120°C, and then Brunauer, Emmett, and Teller (BET) surface areas and the Barrett, Joyner, and Halenda (BJH) pore size distribution were measured using a SA3100 surface area analyzer (Coulter, USA). Ash content was obtained by heating the shells for 5 h at 600°C according to AOAC method 967.04 (Helrich, 1990). The physical appearance of packing media surfaces and of any microorganisms present was observed by scanning electron microscopy (SEM) (JSM-5800L V, JEOL).

2.4 *Performance Parameters*

The mass loading rate or inlet load (IL) is the mass of contaminant entering the biofilter per unit volume of filter material per unit time. Performance of the biofilter can be expressed in terms of the pollutant removal efficiency (RE) and the elimination capacity (EC). The definitions for three parameters are given by Equations 1 -3:

$$IL = \frac{C_{in} \times Q}{V} \qquad (1)$$

$$RE = \frac{C_{in} - C_{out}}{C_{in}} \times 100 \qquad (2)$$

$$EC = \frac{C_{in} - C_{out}}{V} \times Q \qquad (3)$$

where C_{in} and C_{out} are the inlet and outlet concentration (g/m^3), Q is air contaminated flow rate (m^3/h), and V is volume of packing media (m^3).

3. Results and discussion

Characteristics of raw peanut shells and palm shells, and of peanut shell and palm shell packings recovered from the biofilters at the end of the experimental runs, are shown in Table 1. The biofilters were operated continuously for 267 days for pure methanol systems and mixed systems, and for 214 days for pure toluene systems.

3.1 The characteristics of packing media

The palm and peanut shells used were in the size range of 0.5-1 cm. The size of the bed pellets is a very important bed characteristic. Whilst a small pellet size provides a large specific surface area, which is favorable for essential gas/biolayer exchanges, it also increases resistance to gas flow, and hence the pressure drop across the bed. On the other hand, if the pellet size is too large, resistance to gas flow is low but the number of potential sites for establishment of microbial activity decreases (Delhoménie *et al.*, 2002b). Leson and Winer (1991) have suggested a minimal pellet size of 4 mm in order to minimize pressure drop through the bed. However, most authors working in the biofiltration field have adopted pellet sizes greater than this proposed threshold value (Corsi and Seed, 1995; Cardenas-Gonzalez *et al.*, 1999; and Delhoménie *et al.*, 2001).

Table 1 shows that there were some substantial differences between the two packings studied in this project. The pH was slightly acidic (6.1) for raw peanut shells but significantly more acidic (4.9) for raw palm shells. In addition the raw peanut shells have a much lower packing density (71 kg/m^3) than the raw palm shells (490 kg/m^3), which suggests that structurally stronger and more robust filter bed supports

would be needed if using the latter material. This difference in packing density had little effect on the structural integrity of the packings. In most cases bed heights had dropped by only 0.1 cm after over 113 days of continuous operation; only in the case where peanut shells were being used in an experiment to remove methanol was a greater decrease in bed height (0.5 cm) observed. Some organic media (e.g. compost, peat or wood chips), by their nature, tend to decay easily, which leads to bed compaction (Jin *et al.*, 2008). Many researchers have reported that in order to minimize the bed compaction and extend the lifetime of the organic packing media, adding large size inert materials, such as glass beads, polystyrene spheres and lava rocks, into the organic packing media could decrease the bed compaction and avoid clogging and significant pressure drop (Jin-Ying *et al.*, 2005). However, most inert media are more expensive than natural organic media (Kennes *et al.*, 2002).

Table 1 also shows that the raw peanut shells have higher void fractions than the raw palm shells. Generally, biofilter media with a high void fraction are preferred (Shareefdeen and Singh, 2005) as this enables microorganisms to attach to much of the packing surface under low shear conditions, even though the gas is moving through the bed quite rapidly (Malhautier *et al.*, 2005). According to Tampion and Tampion (1987), the maximum accumulation of biomass occurs when pore sizes are one to five times the bacterial size (Cohen, 2001). Over time, decreases in void fraction were observed, for both packings, in all the experimental biofilter systems in our study. This behavior, which was not unexpected, resulted from accumulation of biomass on the packing media, which has been observed in other studies (Abumaizar *et al.*, 1998; Torkian *et al.*, 2003; and Iliuta and Larachi, 2004).

Table 1. The characteristics of peanut shells and palm shells.

Characteristics	Peanut shells		Palm shells	
	Before packing	After packing	Before packing	After packing
Pellet size (cm)	0.5-1	0.5-1	0.5-1	0.5-1
pH	6.1		4.9	
Packing density (kg/m^3)	71		490	
Void fraction (%)	80		65	
Methanol system		48.0		44.8
Toluene system		58.0		58.7
Mixed system		42.2		49.4
BET surface area (m^2/g)	1.23-1.31		0.17-0.34	
Methanol system		0.81-1.04		0.29-0.42
Toluene system		1.29-1.64		0.31-0.64
Mixed system		0.79-1.23		0.33-0.44
Moisture content (%)	3.2		8.9	
Methanol system		73.9		30.3
Toluene system		84.6		49.7
Mixed system		82.6		34.6
Ash content (%)	6.6		2.8	
Methanol system		1.3		1.2
Toluene system		-		1.2
Mixed system		1.2		1.7

For both packings the ash content is very low. Moisture contents were 73.9-84.6% for peanut shell packing and 30.3-49.7% for palm shell packing. Severe drying was not observed in any of the systems during the operational periods. The moisture content required for optimal performance of a compost biofilter is generally between 20 to 60% (Nikolaidis *et al.*, 1999). Biological activity ceases if the moisture content of an organic material is too low. In addition, cracks open in a dry bed and channeling occurs, further limiting performance (Ottengraf *et al.*, 1983). Maintaining an adequate moisture content can be difficult; for example, in one case where a biofilter was packed with compost/ground tire rubber for toluene removal, severe drying was

observed even though the inlet air stream was humidified and additional water was supplied directly to the bed on a daily basis (Oh *et al.*, 2009).

The BET surface areas of peanut shells and palm shells at the beginning and end of the experimental runs were different. The raw palm shells have much lower BET surface areas than the raw peanut shells. In the case of palm shells an increase in BET surface areas occurred no matter which VOC was being removed. A small increase also occurred when peanut shells were used in experiments to remove toluene. However, in biofilters packed with peanut shells and used for removal of methanol, whether present on its own or in a mixture with toluene, measured BET surface areas decreased significantly. Decreases in BET surface areas over time have been observed for other packing materials, for example when hydrogen sulfide was being removed in a biofilter packed with activated carbon (Ng *et al.*, 2004). In the latter case the decrease was attributed to biofilm developing on some of the pore surfaces in the carbon. However, in the present project the decrease could also be linked to chemical reaction of methanol with the surface of the peanut shells; the BET surface area of raw peanut shells immersed in methanol for three days was 0.89 m^2/g, which is around 30% lower than the value obtained for the untreated raw peanut shells, and this contrasts strongly with the 10% *increase* in BET surface area observed after palm shells had been immersed in methanol for three days. However, packing media immersed for three days in pure solvents experience conditions very different from those they are exposed to in operating biofilters. Therefore the relevance of the BET changes given above to what occurs in actual biofilter packing media remains uncertain. In the case where the packing materials were immersed for three days in toluene rather than methanol, decreases in BET surface areas of around 8% and 69%

were observed for peanut shells and palm shells respectively; this trend is opposite to that observed in the operating biofilters

Further evidence of the different impacts that methanol and toluene have on the peanut shell and palm shell packings is provided by pore size distribution measurements made at the beginning and end of the experimental runs. The volumes of both mesopores (2-50 nm in size) and macropores (>50 nm in size) were measured. Figure 2 shows the relationships between pore size and pore volume for both packing media when treating gas streams containing methanol or toluene separately. For palm shells there is an increase in both the mesopore volume and the macropore volume over the course of the experiments using methanol and those using toluene. The increases in mesopore volume are similar for both VOCs but a substantially greater increase in macropore volume occurred when using toluene. For the peanut shells, however, VOC-related differences are much greater. When experiments were conducted using methanol, small decreases in pore volume occurred across the entire range of pore sizes. In experiments involving toluene, however, marked increases in pore volume occurred in the macropore and larger mesopore range; only in the smaller mesopores was a small decrease in pore volume observed.

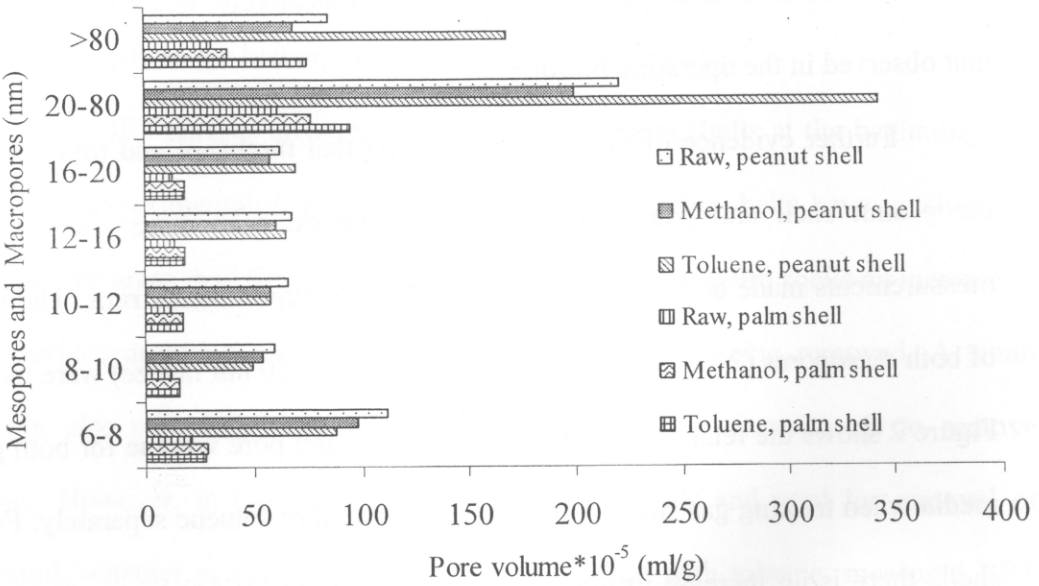
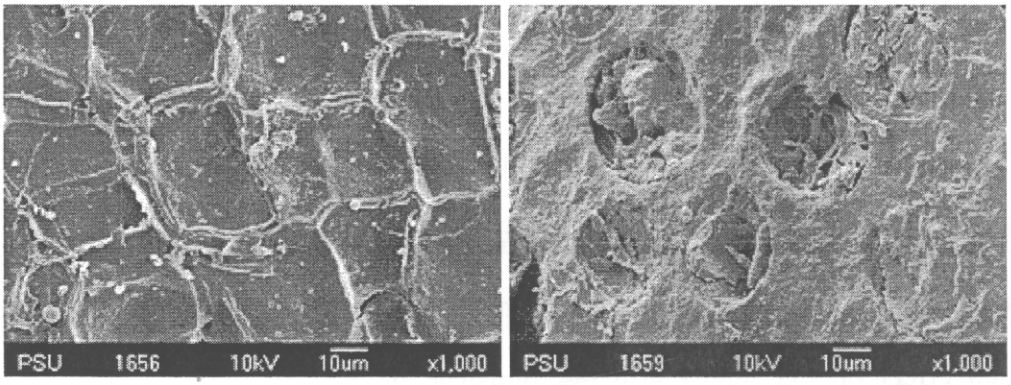


Figure 2. The BJH pore size distributions in single VOC systems.

Combining the observations of changes in bed height, BET surface areas and pore volume distributions suggests that both packings are to some extent susceptible to attack by the VOCs themselves, and possibly also by intermediates formed in the course of biodegradation (such as benzoic acid in the case of toluene). In the case of palm shells, and of peanut shells exposed to toluene, the structural integrity of the packings does not seem to be compromised to any significant extent. With peanut shells exposed to methanol, though, the reduction in macropore volume coupled with the 0.5 cm decrease in bed height points to a more serious level of structural breakdown. Clearly, when using agricultural products as packing materials attention needs to be paid to the types of VOC involved before packing materials are selected.

Scanning electron microscope (SEM) studies of both the raw and the used packing materials were also undertaken. Figure 3 shows SEM micrographs of the surfaces of raw peanut shell and raw palm shell at 1000x magnification. The surfaces of both packing media contain depressions 20-40 μm across and appear sufficiently

irregular to facilitate attachment of microorganisms during biofilm formation. SEM pictures of packing media samples taken on days 93 and 147 confirm that the surfaces were readily colonized by microorganisms. On day 93, the surfaces of packing materials from all biofilters were dominated by rod shaped microorganisms, as shown in Figure 4. At this stage no differences related to the nature of the VOC involved were apparent.



(a) (b)

Figure 3. SEM images of a raw peanut shell (a) and a raw palm shell (b).

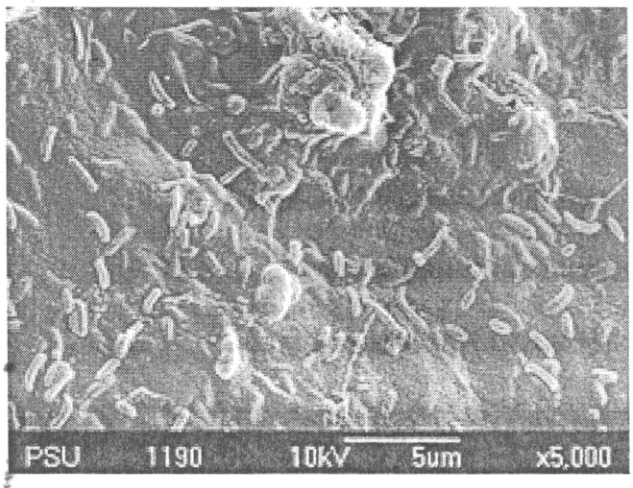
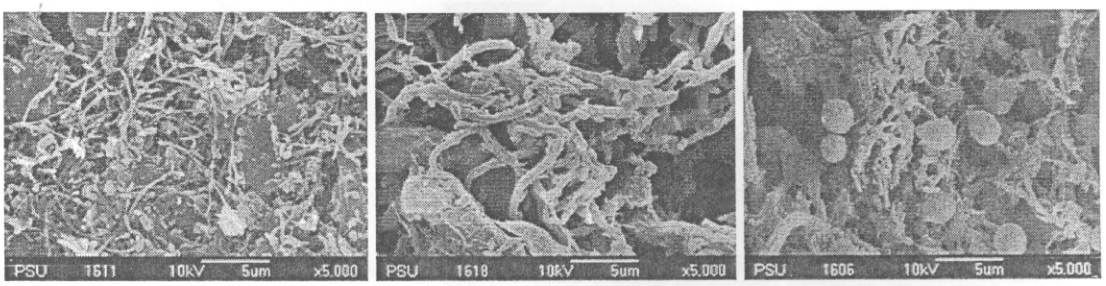


Figure 4. Microorganisms typical of those found on packing materials sampled after 93 days (5000x magnification).

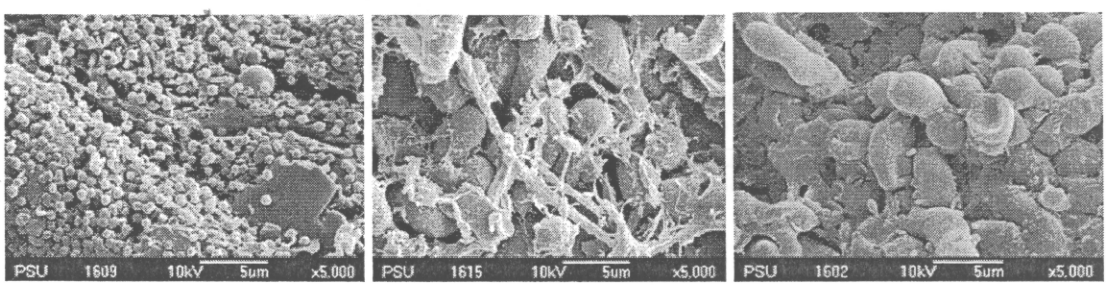
By day 147 the numbers of microorganisms present on the surfaces had increased considerably and the nature of the microbial fauna was very different. As illustrated in Figure 5, peanut shell surfaces appeared to be dominated by mycelial mats, with a scattering of cocci. Fungal mycelia are known to cause damage to peanut crops in the field (Nalim *et al.*, 1995; and Okabe and Matsumoto, 2000). Mycoflora or fungi develop easily on the peanut shells in moist atmospheres (Hanlin, 1968; Fonseca *et al.*, 1994); therefore, given the moist aerobic conditions under which peanut shells exist in the biofilters it is not surprising that fungal mats have become established on their surfaces. These mats were present on all peanut shell surfaces, irrespective of the VOC(s) to which they had been exposed, so that they do not seem to be implicated in the changes to BET surface areas and pore distributions experienced by peanut shells exposed to methanol. The methanol does seem to have had an effect on the fungal growths, however, as the mycelial strands found on packings exposed to methanol (images (a) and (c) in Figure 5) are very much finer than those present on the surfaces exposed only to toluene (image (b) in Figure 5).



(a) (b) (c)

Figure 5. SEM images (5000x magnification) of peanut shell packings sampled on day 147 from biofilters treating (a) methanol, (b) toluene, and (c) a methanol/toluene mixture.

As Figure 6 shows, by day 147 the microbial fauna on the palm shell surfaces was very different from that on the peanut shells. Here coccus-shaped microorganisms predominate, with only a small amount of mycelial growth apparent. Again, the methanol appears to have an impact on the size of the organisms. As Figure 6(a) shows, on the surface exposed solely to methanol there is only one coccus-shaped organism of the same size as those in Figure 6(c); the remaining organisms are only 20% as large, with a diameter of less than 1 μm. Not only was the microbial composition of the biofilm affected by the choice of VOC but also its color. The original raw peanut shells and palm shells were light brown and dark brown, respectively. In biofilters exposed to methanol, either alone, or in a mixture with toluene, the biofilm that developed was reddish brown in color; this was the case for both peanut shells and palm shells. In systems exposed only to toluene, however, the biofilm that developed was a distinctively different blackish brown color.



(a) (b) (c)

Figure 6. SEM images (5000x magnification) of palm shell packings sampled on day 147 from biofilters treating (a) methanol, (b) toluene, and (c) a methanol/toluene mixture.

3.2 The performance of biofilters

3.2.1 The removal efficiency

After acclimation period was finished (stage A), the performances of biofilters were determined. For biofilters M1, M2, T1, and T2, the first segment of the main experimental program comprised three stages, denoted stages B and C, during which the gas flows to the biofilters were successively increased from 0.1 m^3/h (stage B) to 0.2 m^3/h (stage C). Empty bed residence times (EBRT) for each of these stages were 151 and 76 seconds respectively. Several step changes in VOC concentration were made during each of the previous stages. Typical concentration ranges used were: 1-3, 3-6, and 6-9 g/m^3 for methanol and 0.1-2, 2-4, and 4-6 g/m^3 for toluene. It was originally intended to increase concentrations progressively so as to determine the limits of biofilter performance. However, measured removal efficiencies and calculated elimination capacities often fluctuated unpredictably and it was sometimes necessary to reduce VOC concentrations in the incoming gas. During stage C pressure drops through the biofilters began to increase and reached levels many times those measured at the start of the experiments. These pressure drop changes appeared to be contributing to the erratic performance of the biofilters.

The biofilters were restarted with the gas flow rate at a very low level (0.06 m^3/h) (stage D) and the VOC concentration also at a low level (1 g/m^3). The biofilters then performed much better and their performance was monitored during a sequence of successive increases in gas flow rate to 0.1 m^3/h (stage E), 0.15 m^3/h (stage F), 0.2 m^3/h (stage G), and 0.3 m^3/h (stage H). EBRTs for each of these stages were 151, 101, 76, and 50 seconds respectively. Stage H was terminated on day 267 in the case of M1 and M2 and on day 214 in the case of T1 and T2. These observations are in good accord with those of Barona et al. (2004) who found that the performance of

microbial communities in biofilters soon recovered after brief periods of starvation. During each of the above stages, the VOC concentration was raised stepwise several times, as was done in earlier stages.

The patterns of change followed by the RE values are quite similar for all four biofilters (M1, M2, T1, and T2). Patterns of behavior in biofilters filled with peanut shells are remarkedly similar to those in biofilters filled with palm shells, which means that on the basis of VOC removal efficiency neither has a clearcut advantage over the other. Figures 7 and 8 show the removal efficiency for removal of toluene in the biofilter packed with peanut shells and palm shells, respectively.

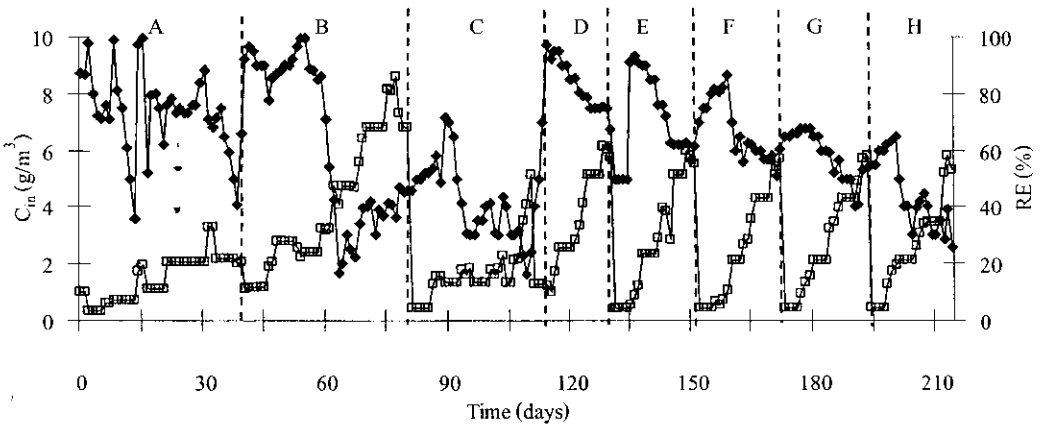


Figure 7. The overall performance in terms of removal efficiency for removal of toluene in the biofilter packed with peanut shells (T1): (♦) the removal efficiency, and (□) the inlet concentration.

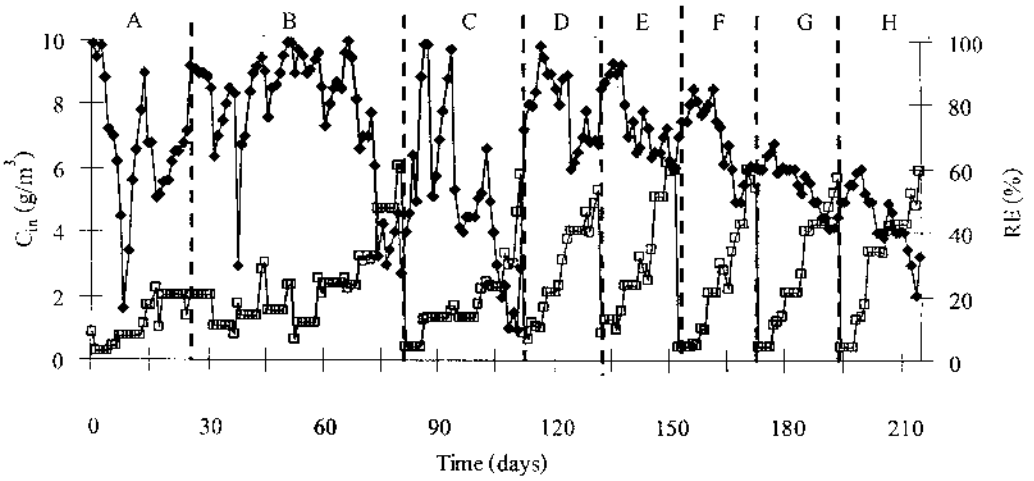


Figure 8. The overall performance in terms of removal efficiency for removal of pure toluene in the biofilter packed with palm shells (T2): (♦) the removal efficiency, and (□) the inlet concentration.

3.2.2 The elimination capacity

The effectiveness of biofilters is often expressed in terms of the elimination capacity (EC), which is the mass of VOC removed per hour in a cubic meter of packing. Figure 9 shows observed EC values for methanol in the biofilters treating gas streams containing methanol alone or methanol/toluene mixtures while ECs for toluene in biofilters containing toluene alone or methanol/toluene mixtures are shown in Figure 108. These are presented as a function of the inlet load (IL), the mass of VOC delivered to the biofilter per hour per cubic meter of packing. Maximum elimination capacity (EC_{max}) values for toluene were around 60% of those for methanol; according to Devinny *et al.* (1999), this is because toluene has a more complex structure than methanol and its degradation is a more energy intensive process. The maximum elimination capacities obtained in this study are compared with those of other researchers in Table 2. It can be seen that, with the exception of the anomalously low values obtained for toluene in the system treating a mixture of

methanol and toluene, these values are comparable to those obtained in other studies. These results suggest that both peanut shells and palm shells are suitable for use as packing media in biofilters. Neither of these materials appears to have a clear advantage over the other. The EC_{max} values for peanut shells are perhaps marginally greater than those for palm shells and the peanut shells have a much lower bulk density, which would certainly have cost advantages; however, indications are that palm shells could retain their structural integrity better than peanut shells and so require replacing less frequently.

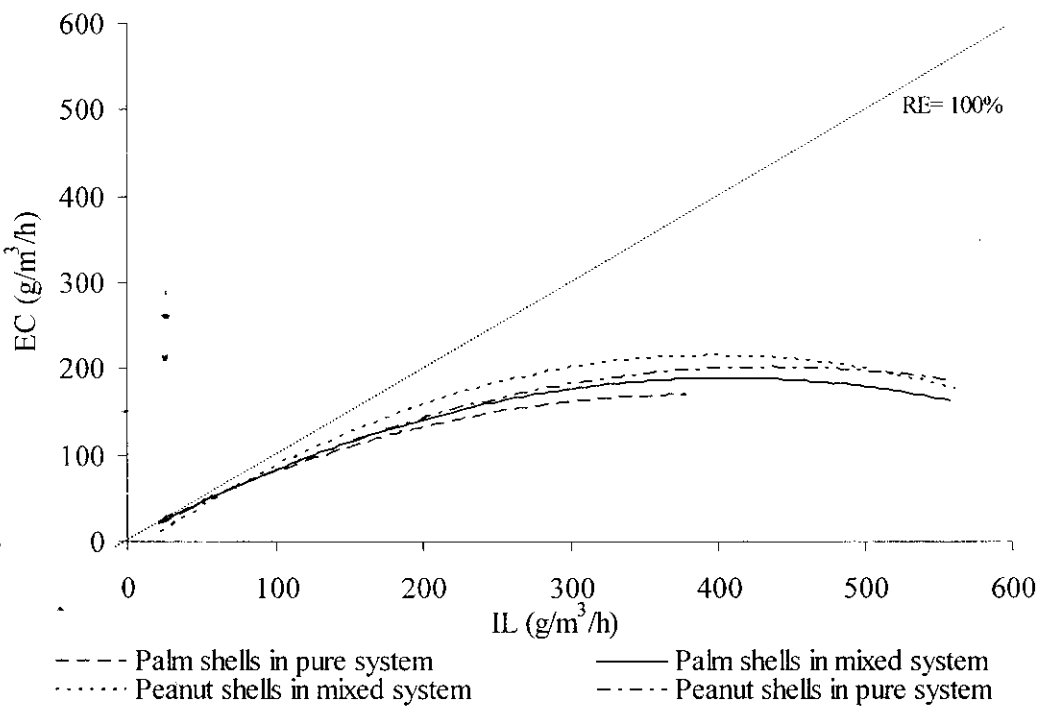


Figure 9. Elimination capacity and inlet load curve for removal of methanol from air contaminated with pure methanol or methanol/toluene packed with palm shells or peanut shells.

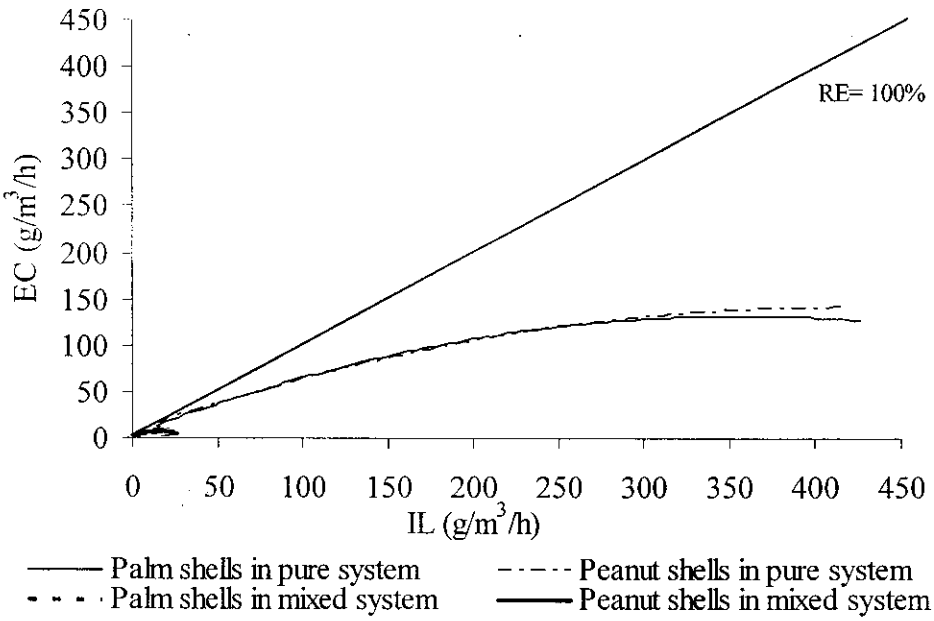


Figure 10. Elimination capacity and inlet load curve for removal of toluene from air contaminated with pure toluene or methanol/toluene packed with palm shells or peanut shells.

Table 2 Comparison of maximum elimination capacity values from biofiltration studies.

Researchers	Substance	Packing media	EC_{max}
Prado et al., 2005	Methanol	Lava rock	173
This study	Methanol	Peanut shells	198
		Palm shells	168
	Methanol*	Peanut shells	208
		Palm shells	190
Zilli et al., 2001	Toluene	Peat/glass beads	242
Delhoménie *et al.*, 2002a	Toluene	Compost based	55
Chetpattananondh et al., 2005	Toluene	Palm shells	190
Rene et al., 2005	Toluene	Compost/ceramic beads	128
Wright et. al., 2005	Toluene	Diatomaceous earth	232
Vergara-Fernández et. al., 2007	Toluene	Compost/sea shells	82
This study	Toluene	Peanut shells	145
		Palm shells	129
	Toluene*	Peanut shells	6.6
		Palm shells	8.8

* in the mixed system

4. Conclusions

The results of this study show that both peanut shells and palm shells are suitable for use as packing media in biofilters even though the nature of the microbial fauna that develops on each is quite different. This should be of considerable benefit

to Thai industries considering installing biofilters to remove VOCs as it makes the cost of bed packing materials much more affordable than if more conventional packing materials had to be used. The elimination capacities measured in this study are comparable to those reported by other researchers working with a range of different packing materials. Neither of the materials studied shows a clear-cut advantage over the other, which means that local availability and costs of the two materials are likely to determine which should be selected.

Acknowledgements

This research was financially supported by Prince of Songkla University and the National Research Council of Thailand (NRCT), budget year 2007. The Graduate School at Prince of Songkla University also provided partial funding. The authors are grateful to the Department of Chemical Engineering and the Faculty of Engineering, Prince of Songkla University for other support.

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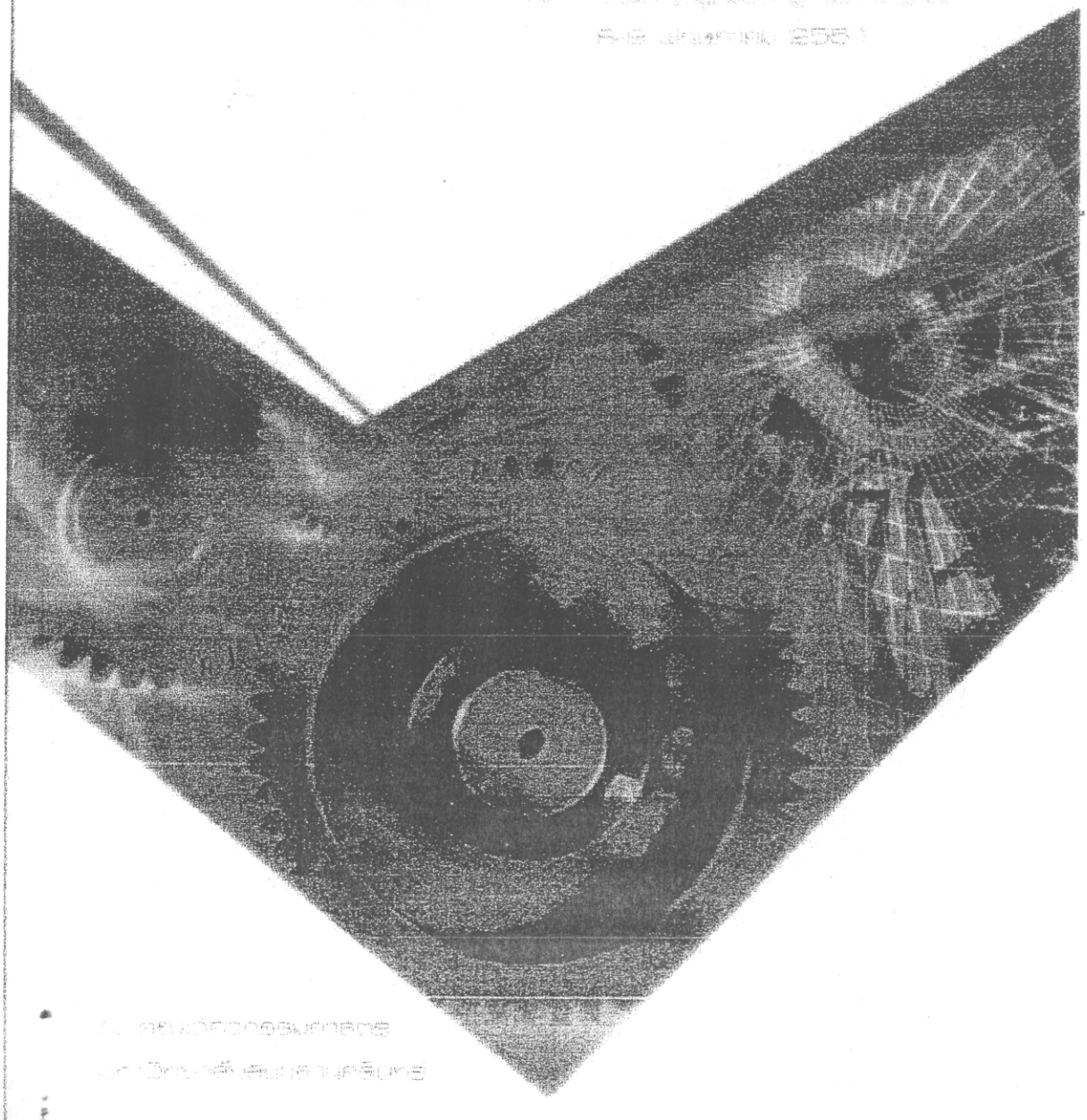

Treatment of Air Contaminated with Methanol by Biofilter Packed with Palm shells or Peanut Shells

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Abstract
Air contaminated with methanol was treated by two biofilter systems. One was packed with mixture of palm shells and activated sludge and another was packed with mixture of peanut shells and activated sludge. The peanut shell has a larger porosity and BET surface area than the palm shell while a bulk density is lower. The pH is closed to neutral for peanut shell while acid for palm shell. The experiments were carried out with methanol inlet concentration in the range of 1-10 g/m^3 at air flow rate of 0.1 m^3/h. The critical elimination capacities of the palm shell system and peanut shell system were 32 and 60 g/m^{3}h, respectively. The maximum elimination capacity of the two systems was not reached yet. Removal efficiency was predominantly influenced by inlet concentration and height of media than ambient temperature and relative humidity in the air. Performances of the two biofilters were fitted to the simple equations in relation to inlet concentration and height of media.

Keywords: biofilter, biofiltration, methanol, palm shells, peanut shells

1. INTRODUCTON

Volatile organic compounds (VOCs) are substances which easily vapor at ambient temperature and pressure. They are widely used in chemical, petroleum, color, paint, coating and printing industries [1,2,3,4]. Waste gas streams from these sources are often characterized by high flow rates and low pollutant concentrations of less than 2000 ppm [1]. Methanol is grouped as hazardous air pollutants in the 1990 Clean Air Act Amendments [5,6]. Methanol may cause skin irritation, central nervous system depression, kidney damage and possible death due to respiratory failure [7]. Therefore, it is vital to control the amount of methanol in air to preserve human health and environment.

VOCs can be treated by many technologies, for instance incineration, adsorption, absorption and condensation [1,8]. However, these technologies are not economically effective for the treatment of gases with low concentration of pollutants.

Alternatively, biofiltration is a lower cost and more environmental friendly technology accepted recently [5]. Any porous materials capable of adsorbing gaseous compounds and supporting biological growth can possibly be used as packing media in biofilter. The packing materials commonly used include natural materials such as peat, compost, soil, and sludge from sewage treatment plants and synthetic materials such as vermiculite, granular activated carbon, and extruded diatomaceous earth pellets [2]. Ramirez-Lopez et al. [9] studied the characteristics of five different agricultural by-products; rice husk, maize stubble, bagasse, coconut shells and peanut shells for their potential use as biofilter carriers and peanut shells were reported to be the suitable carriers without any validation by biofiltration experiment.

In this study, the palm shell biofilter and peanut shell biofilter for treatment of air contaminated with methanol were compared. The experiments were operated at methanol concentration of 1-10 g/m^3 and air flow rate of 0.1 m^3/h.

2. MATERIALS AND METHODS

2.1 VOC

Methanol (99.5%) was obtained from Merck, Germany.

2.2 Packing Materials

Palm shells and peanut shells were sized in the range of 0.5-1 cm. The biofilter media were a mixture of palm shells or peanut shells and activated sludge from food manufacturers in Songkla province in the proportion of 1:2 by volume.

2.3 Biofiltration Experiments

Two bench-scale biofilters made of acrylic were used. Each biofilter consists of three equal segments connected in series (Figure 1). Each segment has a diameter of 9 cm and a height of 30 cm (being filled to a height of 20 cm with equal amounts of the prepared filter-bed media).

The artificial waste gas fed to the biofilter was produced by mixing two different air streams, one passing through a humidifier and the other passing through a column containing methanol.

The concentration of methanol was varied by modifying the flow rate of air passing through that column. Water was occasionally sprayed to the biofilter to control the bed moisture content and air relative humidity.

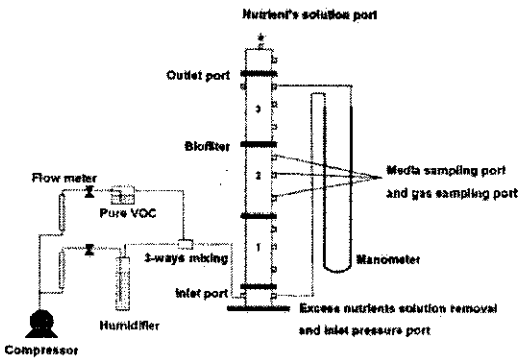

Figure 1. Experimental set up

2.4 Analytical Methods

Gas samples were taken by vacuum glass bottle (0.01 liter) at different ports of the biofilter. Toluene concentration was analyzed by a gas chromatography unit (HP 6890, Hewlett Packard) equipped with a flame ionization detector (FID) using a 30-m capillary column (HP-1, crosslinked methyl siloxane). The temperature of the injection port, the oven, and the detector were maintained at 180, 50, and 200°C, respectively.

Temperature and relative humidity were monitored via AP-104 (Sila Research Co., Ltd., Thailand). BET surface area was measured by SA3100 surface area analyzer (Coulter, USA) while pH was measured by adding 1 g of packing material in 30 ml of DI water and shaking for 30 minutes following by detecting pH with a pH meter.

2.5 Performance Parameters

Biofiltration studies was performed on the level of the VOC inlet load (IL) while the performance of the biofilter can be expressed in terms of the pollutant removal efficiency (RE) and the elimination capacity (EC). The definitions for these three parameters are given by Equations 1-3:

$$IL = \frac{Q \times C_i}{V} \quad (1)$$

$$RE = \left(1 - \frac{C_o}{C_i}\right) \times 100 \quad (2)$$

$$EC = \frac{Q \times (C_i - C_o)}{V} \quad (3)$$

3. RESULTS AND DISCUSSION

3.1 Characteristics of the Packing Materials

The peanut shell has a larger porosity and BET surface area than the palm shell while a bulk density is lower. The pH is closed to neutral for peanut shell while acid for palm shell as shown in Table 1. From these characteristics the peanut shell would be considered a more suitable packing material for biofiltration.

Table 1. The physical characteristics of palm shells and peanut shells.

Characteristics	Palm shells	Peanut shells
Pellet size (cm)	0.5-1	0.5-1
BET surface area (m^2/g)	0.338	0.959
pH	4.94	6.1
Bulk density (kg/m^3)	490	71
Porosity (%)	65	80

3.2 The Overall Performance

At the initial time, the biofilters packed with palm shells and peanut shells could remove methanol closed to 100%. This state was predominant by adsorption and absorption mechanisms. After that, it was bacterial acclimatization and desorption periods, which the removal efficiency decreased. These four mechanisms are included in start up period, which were about 20 days for the palm shell system (Figure 2) and 23 days for the peanut shell system (Figure 3). Three ranges of inlet concentration were carried out; stage A for inlet concentration less than 2 g/m^3, stage B for inlet concentration of 2-4 g/m^3, and stage C for inlet concentration of 4-8 g/m^3. At stages A and B both biofilter systems could remove methanol up to 99%, while at stage C average removal efficiency of 67% was observed for the palm shell system and 79% was observed for the peanut shell system. Then, the biofilters might need more time to be acclimatized with the inlet concentration higher than 4 g/m^3.

In addition, the efficiency of system can express by elimination capacity [3]. At low inlet load the elimination capacity was equal to the inlet load (RE 100%) while at high inlet load the elimination capacity was less than the inlet load (RE < 100%). The point generating removal efficiency less than 100% is called the critical load or critical elimination capacity (EC_{crit}) which was 32 $g/m^3.h$ for the palm shell system (Figure 4) and 60 for the peanut shell system (Figure 5). The performance of biofilter packed with palm shells or peanut shells was comparable to the biofilter packed with compost or compost and perite (Table 2). The maximum elimination capacity was not reached yet for our biofilters as EC still increased with increasing of IL.

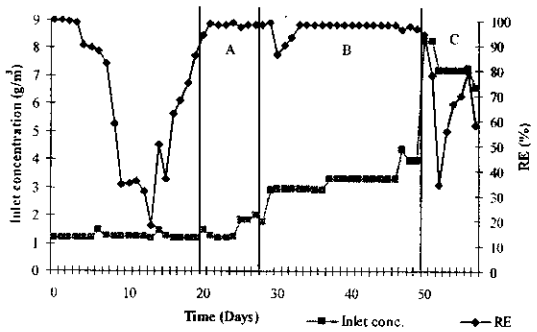

Figure 2. The overall performance of the biofilter packed with palm shells.

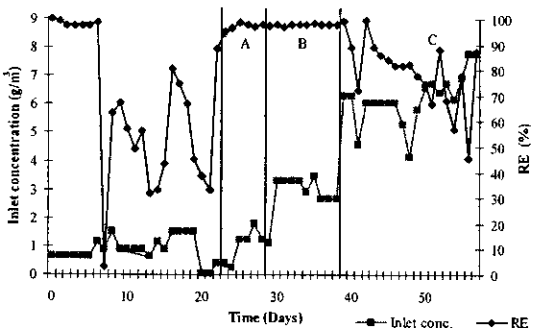

Figure 3. The overall performance of the biofilter packed with peanut shells.

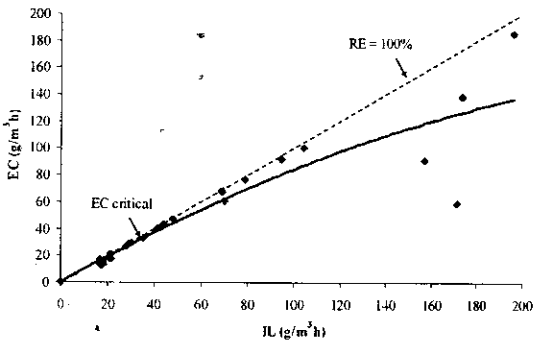

Figure 4. Inlet load and Elimination capacity of the biofilter packed with palm shells.

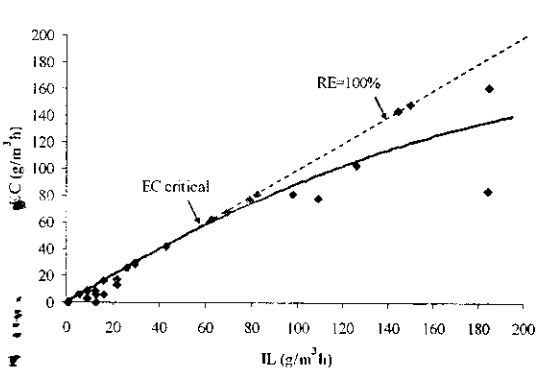

Figure 5. Inlet load and Elimination capacity of the biofilter packed with peanut shells.

Table 2. Performance comparison between this work and other biofiltration studies.

Study	Biofilter media	EC_{crit} (g/m^3h)
Shareefdeen *et al.* [10]	Compost/perite	50-80
Lee *et al.* [11]	Compost/perite	10-20
Briggs [12]	Compost	42
Johnson & Deshusses [13]	Compost	30-35
This study	Palm shell	32
	Peanut shell	60

3.3 Influence of Inlet concentration and Height of Media on Removal Efficiency

Removal efficiency in each stage of the biofilter (height of media at 20, 50, and 80 cm) was evaluated over the 3 ranges of inlet concentration. It can be seen that RE increased with increasing of height of media for both palm shell system (Figure 6) and peanut shell system (Figure 7). At a height of 80 cm, RE in the range of concentration 1-2 and 2-4 g/m^3 was 97% averagely for both biofilters. At concentration higher than 4 g/m^3, RE was down to 64.5% for the biofilter packed with palm shells and 72% for the biofilter packed with peanut shells. Thus, the RE decreased with increasing of inlet concentration.

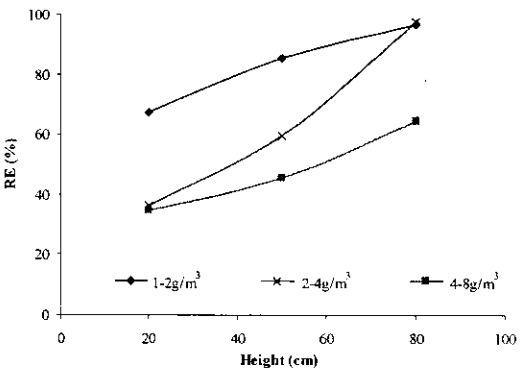

Figure 6. Variation in the removal efficiency of the biofilter packed with palm shells for each range of inlet concentration in a function of height of media.

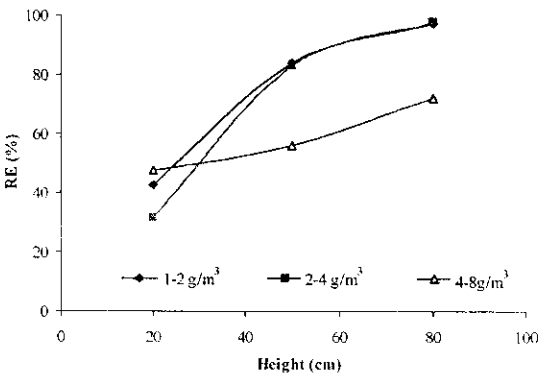

Figure 7. Variation in the removal efficiency of the biofilter packed with peanut shells for each range of inlet concentration in a function of height of media.

The influence of inlet concentration and height of media on RE was further investigated. All trend lines of experimental data were best fitted to polynomial equations with order of 3. For the palm shell system (Figure 8), similar trend lines of height at 50 and 80 cm were observed, while the trend line of height at 20 was opposite side. The RE50 was closed to RE80. This implies that a height of 50 cm of palm shells was probably enough for treating methanol at inlet concentration less than 5 g/m^3. For the biofilter packed with peanut shells (Figure 9), removal efficiencies at height of 80 cm were clearly higher than the height of 50 cm.

The empirical equations in relation to inlet concentration (IC) and height of media (H) for performance of the two biofilters were generated by Excel Solver in Microsoft Office and can be presented as in Equation 4 where a, b, c, d, e, and f are the constant values as shown in Table 3.

$$RE = aIC^3 + bIC^2 + cIC + dH^2 + eH + f \qquad (4)$$

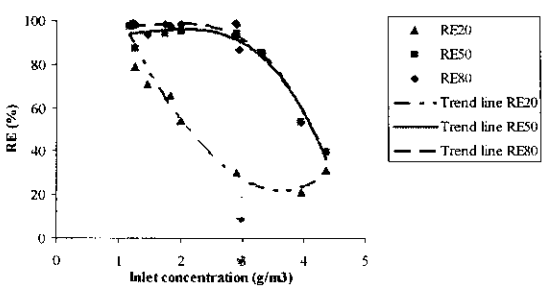

Figure 8. Variation in the removal efficiency of the biofilter packed with palm shells for each height of media in a function of inlet concentration.

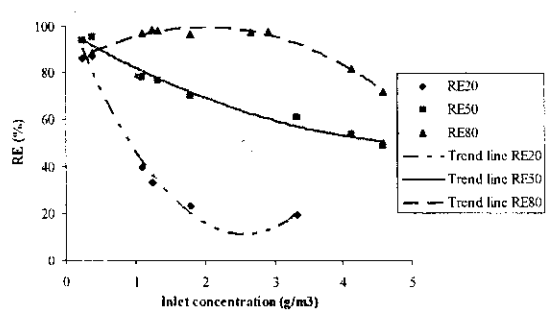

Figure 9. Variation in the removal efficiency of the biofilter packed with peanut shells for each height of media in a function of inlet concentration.

3.4 Influence of Temperature, Relative Humidity and Other Parameters

In our experiments, ambient temperature was not controlled. So, influence of the ambient temperature on performance of the biofilters was investigated. Over the study period of 57 days the ambient temperatures were varied in the range of 24-30°C. The inlet temperatures were depended up on the ambient temperatures. The outlet temperatures were a bit higher than the ambient and inlet temperatures as shown in Figures 10 and 11, which indicates the activity of the microorganisms in the biofilters.

Table 3. The constant values of empirical equations for performance of biofilters packed with palm shells and peanut shells.

Constant value	The palm shells system	The peanut shells system
a	-5.30	-0.08
b	37.18	2.87
c	-90.4	-21.08
d	-0.01	-0.13
e	1.64	1.89
f	112.83	71.53
R^2	0.84	0.79

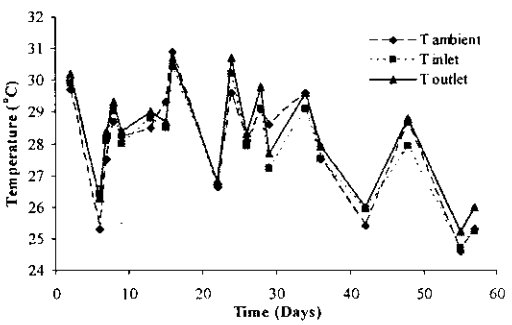

Figure 10. Ambient temperature, inlet temperature and outlet temperature measured for the palm shell system.

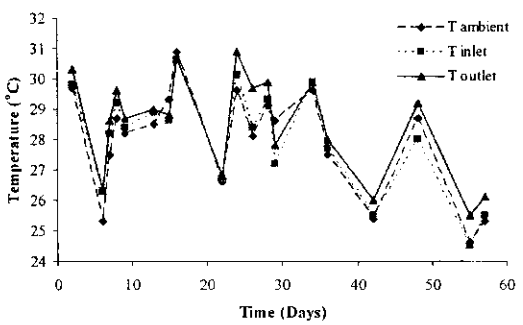

Figure 11. Ambient temperature, inlet temperature and outlet temperatures measured for the peanut shell system.

The relation of outlet temperature and elimination capacity was presented in Figures 12 and 13. In general it may be observed that elimination capacity increased with increasing of outlet temperature. However, the influence of outlet temperature was less affected to elimination capacity compared with inlet concentration and height of media.

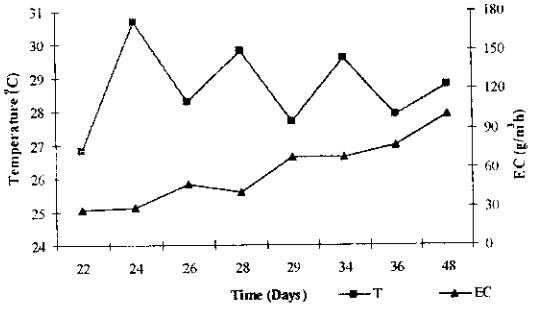

Figure 12. Outlet temperature (T) and the elimination capacity (EC) in the palm shells packing system.

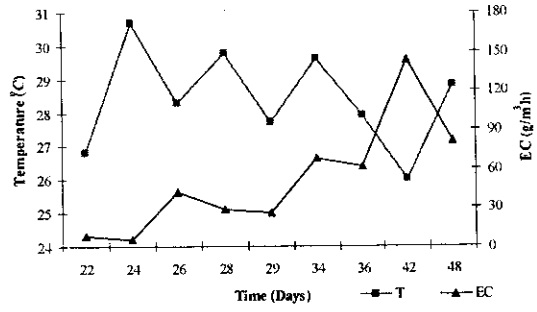

Figure 13. Outlet temperature (T) and the elimination capacity (EC) in the peanut shells packing system.

Relative humidity at the inlet and each section of biofilter was also measured. Relative humidity at the inlet was kept higher than 90% to minimize drying effect reported by Morales et al. [14]. The relative humidity in the biofilters was observed to be higher than the relative humidity at the inlet (Figure 14 and 15). This points out that our biofilters were in saturation condition. The biofilm was developed and covered all sections of the biofilters with probably most plenty at the top section (height of media 80 cm). This is because the inlet was fed from the bottom section leaded to high loading of methanol, which may suppress the growth of biofilm at the bottom section of biofilters.

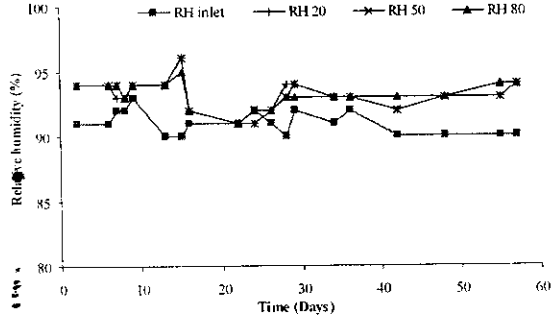

Figure 14. Relative humidity (RH) at the inlet and each section of the biofilter packed with palm shells.

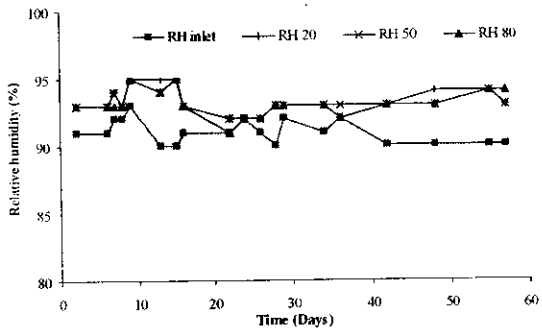

Figure 15. Relative humidity (RH) at the inlet and each section of the biofilter packed with peanut shells.

For all over the operating period of 57 days, pressure drops of both biofilter systems were still zero mmH_2O (Figure 16). Similarly, pH of both packing media was maintained at 7. These values of pressure drops and pH were proper for microorganism growth. Adding of chemical to adjust pH or washing step to reduce the pressure drop was not necessary yet.

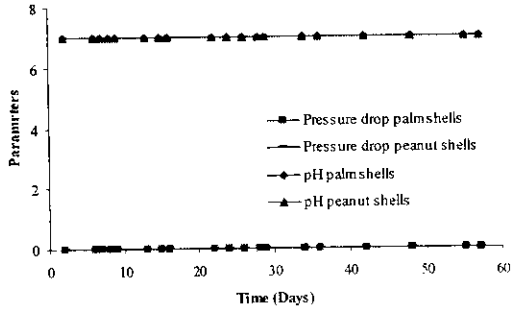

Figure 16. Pressure drop (P) and pH in the palm and peanut shells packing system.

5. Conclusion

Air contaminated with methanol at concentration less than 4 g/m^3 could be treated with the biofilter packed with palm shells or peanut shells with removal efficiency up to 99%. Removal efficiency and elimination capacity decreased with increasing of inlet concentration. From physical characteristics peanut shells may considered as more suitable packing media for biofilter. In addition, the critical elimination capacity of the biofilter packed with peanut shells was higher. However, when considering the removal efficiency for each section of the biofilter only 50 cm height of palm shell packing was required to treat methanol at low concentration of less than 3 g/m^3, while 80 cm of peanut shell packing was needed. Therefore, palm shells may be more proper used when the air was contaminated with very low concentration of methanol. For both biofilter systems the maximum elimination capacity was not reached. Therefore, higher flow rate of air or higher inlet concentration of methanol will be possibly treated.

Acknowledgments

This research has been financially supported by Prince of Songkla University and the National Research Council of Thailand (NRCT), budget year 2007. The Department of Chemical Engineering and the Faculty of Engineering, Prince of Songkla University are gratefully acknowledged for other supports.

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PURE AND APPLIED CHEMISTRY
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BIOFILTRATION USING PEANUT SHELLS OR PALM SHELLS FOR REMOVAL OF AIR CONTAMINATED WITH METHANOL OR TOLUENE

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Abstract: Air contaminated with volatile organic compound (VOC), methanol or toluene, was treated by two biofilter systems. One was packed with mixture of palm shells and activated sludge and another was packed with mixture of peanut shells and activated sludge. The BET surface area of peanut shell was about 1.27 m^2/g, which is larger than the palm shell (0.26 m^2/g). The pH was closed to neutral for peanut shell (6.1) while acid for palm shell (4.94). The experiments were carried out with VOC inlet concentrations in the ranges of 1-9 g/m^3 at air flow rates of 0.06-0.3 m^3/h. The maximum elimination capacities of the palm shell system and peanut shell system were 168 and 198 g methanol/m^3h and 129 and 145 g toluene/m^3h, respectively. Although, the maximum elimination capacities of the peanut shell biofilters were higher than the palm shell biofilters, in the long term operation, palm shells may be considered as more suitable packing media because of their stability property. After 100 operating days of toluene removal, the organic carbon content in the packing media reduced from 52 % to 7 % for peanut shells and from 51 % to 28 % for palm shells. The media height loss was about 0.5 cm for peanut shell biofilter and 0.1 cm for palm shell biofilter. The primary microorganisms in the peanut shell systems were different from those in the palm shell systems.

Introduction

Volatile organic compounds are generally emitted by chemical manufacturing, food processing, furniture manufacturing, and petroleum industry [1]. Methanol and toluene are met in these sources and grouped as hazardous air pollutants in the 1990 Clean Air Act Amendments [2-3]. Methanol may cause skin irritation, central nervous system depression, kidney damage and possible death due to respiratory failure. In the long term in contacting, toluene cause damage liver and kidney. Therefore, it is vital to control the amount of methanol and toluene in air to preserve human health and environment.

Biofiltration is currently the most used biological gas treatment technology because it is suitable for the treatment of polluted airstreams with high volumetric rates and low pollutant concentrations [4-6]. In proceeding, contaminants are transferred from an air stream into a biofilm immobilized on a packing material and then, microorganisms biodegrade contaminants into environmentally acceptable end products including CO_2, water, and biomass.

Any porous organic materials capable of adsorbing gaseous compounds and supporting biological growth can possibly be used as packing media in biofilter, such as yellow straw, peanut shell, rice husk and coconut shell [7]. Biofilter performance is highly dependent on the nature of the carrier material, such as specific surface area, porosity, density, water holding capacity and the nutrients availability [8-9].

An objective of this work is to study the performances of peanut shell biofilter and palm shell biofilter on removal of methanol or toluene. Physical and chemical characteristics of peanut shells and palm shells were investigated. The biofilter experiments were operated at concentrations of 1-9 g/m^3 and the air flow rate of 0.06-0.3 m^3/h.

Materials and Methods

Packing Materials: Palm and peanut shells were sized in the range of 0.5-1 cm. The biofilter media were a mixture of palm shells or peanut shells and activated sludge from food manufacturers in Songkla province in the proportion of 1:2 by volume.

Biofiltration Operation: Four bench-scale biofilters made of acrylic were used for the removal of pure methanol or toluene. Each biofilter consists of three equal segments connected in series (Figure 1). Each segment has a diameter of 9 cm and a height of 30 cm (being filled to a height of 22 cm with equal amounts of the prepared filter-bed media). The artificial waste gas at ambient temperature fed to the based of biofilter was produced by mixing two different air streams, one passing through a humidifier and the other passing through a column containing VOC. The concentrations of VOCs were varied by modifying the flow rate of air passing through that column. Water was occasionally sprayed to the biofilter to control the bed moisture content and air relative humidity.

Measurement of variables and parameters: Gas samples were taken by vacuum glass bottle (0.01 liter) at different ports of the biofilter. Toluene and methanol concentration were analyzed by a gas chromatography unit (HP 6890, Hewlett Packard) equipped with a flame ionization detector (FID) using a 30-m capillary column (HP-1, crosslinked methyl

siloxane). The temperature of the injection port, the oven, and the detector were maintained at 180, 50, and 200°C, respectively.

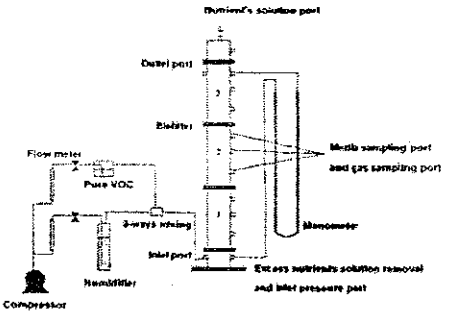

Figure 1. Experimental set up

Temperature was monitored via AP-104 (Sila Research Co., Ltd., Thailand). Particle sizes were determined by direct measurement. pH was measured by adding 1 g of packing material in 30 ml of DI water and shaking for 30 minutes following by detecting pH with a pH meter. Packing density was determined by filling a 250 ml flask with the material and weighting it before and after. The void fraction of the packing material was determined by submerging it in a known volume of water, the volume of water added per volume of material gives directly the void fraction [7]. BET surface areas were analyzed by SA3100 surface area analyzer (Coulter, USA). Organic carbon was calculated from Eq. 1

$$Organic\_carbon = 100 - (\%ash + \%moisture) \times 0.58 \quad (1)$$

The physical characteristic of packing media and microorganisms was observed by scanning electron microscopy, SEM (JSM-5800L V, JEOL).

Performance Parameters: The mass loading rate or inlet load (IL) is the mass of contaminant entering the biofilter per unit volume of filter material per unit time. Performance of the biofilter can be expressed in terms of the pollutant removal efficiency (RE) and the elimination capacity (EC). The definitions for four parameters are given by Eq. 2-4:

$$IL = \frac{C_{in} \times Q}{V_f} \quad (2)$$

$$RE = \frac{C_{in} - C_{out}}{C_{in}} \times 100 \quad (3)$$

$$EC = \frac{C_{in} - C_{out}}{V} \times Q \quad (4)$$

where C_{in} and C_{out} are the inlet and outlet concentration (g/m^3), Q is air contaminated flow rate (m^3/h), and V is volume of packing media (m^3).

Results and discussion

Characterization of the Packing Materials: The peanut shell has a larger porosity and BET surface area than the palm shell while a bulk density is lower. The pH is closed to neutral for peanut shell while acid for palm shell as shown in Table 1. From these characteristics the peanut shell would be considered a more suitable packing material for biofiltration, however, it should be validated with the biofilter performance.

The BET surface areas of filtering materials before packing in the biofilter and after operating were compared. After operating in the biofilters for removal of methanol the BET surface areas of peanut shells decreased, while the BET surface areas of palm shells increased (Table 1). Dissimilarly, the BET surface areas after operating in the biofilters for removal of toluene increased for both peanut and palm shells. However, after operating the BET surface areas of peanut shells were still higher than those of palm shells. The BET surface area should be a dominant parameter when adsorption is a major mechanism, when biodegradation takes place the effect of BET surface area on biofilter performance is doubted. This will be discussed further in the next section.

The organic carbon content in peanut shell before packing in the biofilters is closed to its content in palm shell. After operating, the organic carbon content in both packing media reduced, especially for the peanut shells used for removal of toluene. These results imply that the microorganisms also consumed organic carbon in the packing material beside VOC and toluene was less preferred to take in than methanol as its structure is more complex.

Table1. The physical and chemical characteristics.

Characteristics	Palm shells	Peanut shells
Particle size (cm)	0.5-1	0.5-1
pH	4.94	6.1
Packing density (kg/ m^3)	490	71
Void fraction (%)	65	80
BET surface area (m^2/g)		
Before packing	0.17-0.34	1.23-1.31
Methanol system	0.29-0.42	0.81-1.04
Toluene system	0.31-0.64	1.29-1.64
Organic carbon (%)		
Before packing	51	52
Methanol system	40	14
Toluene system	28	7

Response to step loading: After acclimation period (concentration of 1 g/m^3 and air flow rate of 0.06 m^3/h), the air flow rates in all biofilter systems were gradually increased to 0.1, 0.15, 0.2, and 0.3 m^3/h with methanol concentrations of 1-3, 3-6, and 6-9 g/m^3 (called as stages C1, C2, and C3, respectively) or toluene concentrations of 0.1-2, 2-4, and 4-6 g/m^3. From Figure 2 it can be seen that the removal efficiencies decreased with increasing of methanol concentration and also air flow rates. At low air flow rates (0.06-0.1 m^3/h) the removal efficiencies of two packing materials were not significantly different, but at higher air flow rates the peanut shell system

represented higher efficiencies. This is probably because of larger BET surface area of peanut shells.

The high impact of flow rate on removal efficiency is shown again in Figure 3, which the concentrations were maintained at stage C2. More accurately, it should be stated that the removal efficiency declined with rising of inlet load. Figure 4 shows removal efficiencies of toluene with air flow rates. At the same inlet load the toluene removal efficiencies were lower than the methanol removal efficiencies by the reason of more complex structure and lower water solubility of toluene (0.53 g/l at 25°C for toluene and 1,000 g/l at 25°C for methanol).

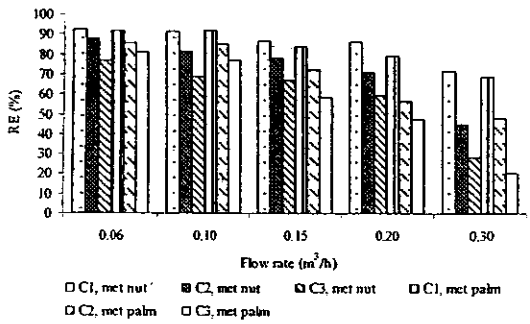

Figure 2. The overall performance of the biofilters for removal of methanol (met); nut = the biofilter packed with peanut shells and palm = the biofilter packed with palm shells.

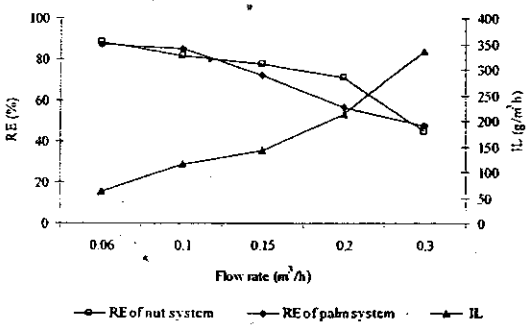

Figure 3. The removal efficiencies of the biofilters for removal of methanol at concentration of 3-6 g/m^3.

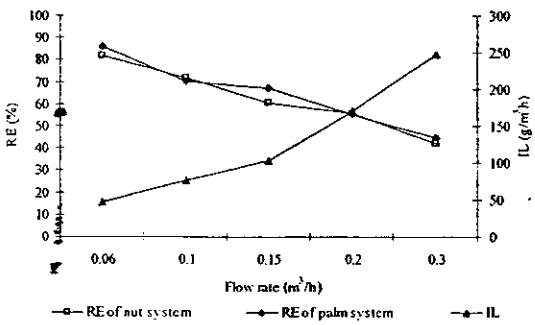

Figure 4. The removal efficiencies of the biofilters for removal of toluene at concentration of 2-4 g/m^3.

Elimination capacity and inlet load: The efficiencies should be expressed by elimination capacity as it allows for direct comparison of the results of different biofilter systems because the volume and flow are normalized by definition. At low inlet load, the elimination capacity was equal to the inlet load (RE 100%) while at high inlet load the elimination capacity was less than the inlet load. The maximum elimination capacities were 198 g methanol /m^{3}h and 145 g toluene /m^{3}h for peanut shell system and 168 g methanol /m^{3}h and 129 g toluene /m^{3}h for palm shell system (Figure 5). These confirm that the peanut shells with larger BET surface areas possess higher efficiencies than the palm shells. However, the stability of filtering media should be taken into account. The media bed heights of all systems were observed. For removal of methanol, the media bed height loss was about 0.5 cm for peanut shell system and about 0.1 cm for palm shell system. As the results of less organic carbon content reduction and less media bed height loss, the palm shells may be considered as more suitable packing media for a long term operating biofilter.

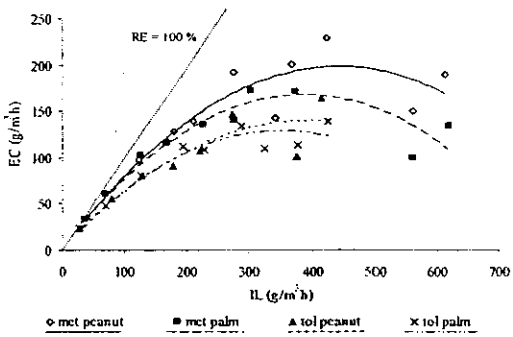

Figure 5. The inlet loads and elimination capacities of all biofilter systems. (tol nut = the removal of toluene in biofilter packed with peanut shells).

The performances of our biofilter systems are compared with other studies as shown in Table 3. The maximum elimination capacities in this study were comparable to the results obtained by other researchers as shown in Table 2. This suggests that peanut shells and palm shells, which are agricultural waste, can also be used as the packing media for an efficient biofilter.

Table 2. Performance comparison between this work and other biofiltration studies.

Study	Packing material	VOC	IL	EC_{max}
[10]	Palm shell	Methanol	780	230
[11]	Lava rock	Methanol	182	173
This study	Peanut shell	Methanol	410	198
	Palm shell	Methanol	380	168
[12]	Activated carbon	Toluene	263	128
[13]	Compost/seashell	Toluene	100	82
[14]	Compost-based	Toluene	N/A	180
This study	Peanut shell	Toluene	415	145
	Palm shell	Toluene	355	129

Influence of Temperature: Over the study period of 100 days the inlet temperatures were in the ranges of 25-30°C depended on the ambient temperatures. The temperatures in the biofilter were higher than the inlet temperatures (Figure 6). The temperatures at media heights of 50 and 80 cm were about the same, while lower at the height of 20 cm. These results could be implied that there were more active microorganisms in the sections 50 and 80 cm. Figure 7 presents the outlet temperatures and elimination capacities. There is no distinctive relation between them.

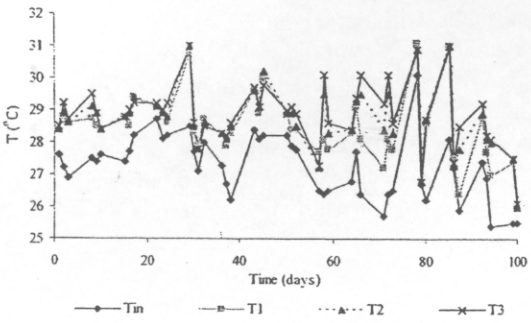

Figure 6. The inlet temperatures (Tin) and temperatures of each section in the peanut shell biofilter for methanol removal; T1, T2, and T3 = the temperatures at media heights of 20, 50, and 80 cm, repectively).

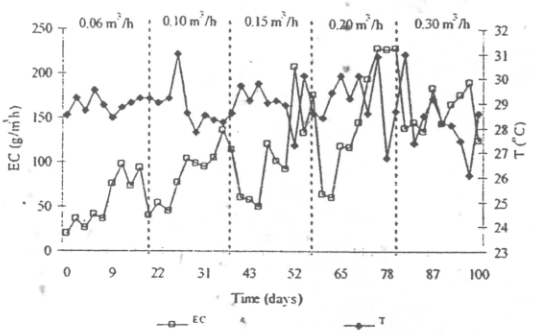

Figure 7. The outlet temperatures (T) and the elimination capacities (EC) in the peanut shell biofilter for methanol removal.

SEM analysis: From SEM microphotographs (Figure 8), higher microbial density was shown for the biofilters packed with peanut shells. The dominant microorganisms in the peanut shell system were coccus colonies while mycelial structures in the palm shell system. In addition, the primary microorganisms for removal of methanol seem different from those observed for removal of toluene. The microorganisms in palm shell biofilter observed for removal of methanol in this study looks similar to our previous work [10]. These suggest that the types of predominant microorganisms also depend on a type of packing material beside a type of VOC.

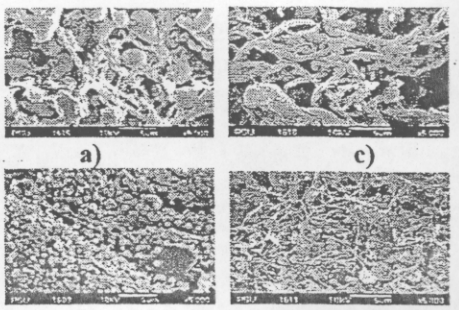

Figure 8. The SEM microphotographs of the peanut shells in a) methanol system and b) toluene system and palm shell in c) methanol system and d) toluene system.

Conclusions

The industrial application of biofilter systems requires the high efficient filtering materials, which, apart from being cost effective, are their stability. The biofilter packed with peanut and palm shells could treat methanol up to 198 and 168 g/m^{3}h, respectively and could remove toluene 145 and 129 g/m^{3}h, respectively. Although the elimination capacities of biofilter packed with palm shells were little lower than peanut shells, the palm shells are more suitable for the long term operating biofilters.

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