Promotor	Prof. dr. ir. Herman Van Langenhove Vakgroep EnVOC
Decaan	Prof. dr. ir. Guido Van Huylenbroeck
Rector	Prof. dr. ir. Anne De Paepe

UNIVERSITEIT
GENT

Faculty of Bioscience Engineering

Diëgo Volckaert

Evaluation of conventional and innovative air treatment biotechnologies for VOC mixtures

Thesis submitted in fulfillment of the requirements for the degree of Doctor (PhD) of Applied Biological Sciences

2014

Dutch translation of the title:

Evaluatie van conventionele en innovatieve biologische luchtzuiveringstechnieken voor VOC mengsels.

The cover was coloured by Lonne Volckaert (2 years), as the research of today is to improve the life quality of the future generation.

ISBN: 978-90-5989-718-2

Dankwoord

Een dankwoord schrijven… Het lijkt op het eerste zicht een verplicht nummertje waarbij je simpelweg iedereen bedankt die ook maar enige inbreng had bij het verwezenlijken van deze scriptie, maar eenmaal je eraan moet beginnen blijkt het allemaal niet zo eenvoudig. Terugdenkend aan de afgelopen 4 jaar, lijkt het me quasi onmogelijk om mijn dankbaarheid naar zoveel mensen toe slechts in enkele alinea's te omschrijven. Laat mij dus eerst en vooral beginnen met me te verontschuldigen dat ik het zo kort moet houden, maar weet dat alles wat ik hier neerpen zeker niet als een verplichting aanvoelt en slechts een kleine indruk geeft van hoe dankbaar ik jullie allemaal ben.

In de eerste plaats wil ik mijn promotor Professor Herman Van Langenhove bedanken. Toen je mij opbelde om mee te delen dat ik aan jouw vakgroep mocht doctoreren, zie ik mezelf nog steeds ronddansen in huis. Een droom die uitkwam… Bedankt Herman dat je mij de kans gaf om die droom te verwezenlijken. Je gaf mij de vrijheid en de ruimte om zelf mijn onderzoeksonderwerp uit te werken en ondanks je drukke agenda, had je steeds tijd om naar mijn vragen, absurde ideeën en verzuchtingen te luisteren.

Daarnaast een dikke merci aan alle collega's van EnVOC en dan in de eerste plaats mijn bureaugenoten op het 5e. De unieke groepssfeer zorgde ervoor dat ik iedere dag met plezier kwam werken. Bedankt voor jullie hulp, fijne babbels, geduld en het appreciëren van mijn flauwe humor. Een extra woordje dank aan Philippe voor de begeleiding en de vele interessante discussies en aan Patrick en Lore voor de technische ondersteuning als ik weer eens in de knoei zat met een meettoestel.

Special thanks to Javier, Raquel and Hector for all the help in the lab and to teach me some basic Spanish. Javier, your guidance at the beginning of my PhD was just the best gift a starting PhD student could wish for. Without your help, I would have never been able to start up my research. Of course I will never forget the enthusiastic Spanish girl, Raquel. Maybe this is the right time to confess that you were not "a real pain in the

behind", in fact it was a pleasure to work, laugh and argue with you. Hector, working with you was just big fun. If every Cuban guy is that cheerful, I definitely need to visit Cuba.

Thanks a lot to my master thesis students Tammy, Joren, Sander, Lucy and Elnaz for doing the hard lab work. I hope that I could encourage your interest for biological air treatment and that you have learned a lot during your thesis.

Een speciaal woord van dank ook aan mijn familie en schoonfamilie, die steeds interesse toonden (of toch wel zeer goed veinsden) in mijn onderzoek. In het bijzonder wil ik mijn ouders bedanken, die ALTIJD klaar staan voor mij en me alle kansen hebben gegeven die ik nodig had. Jullie inbreng in dit alles is gewoon onbeschrijfelijk en verdient veel meer dan een simpele dankjewel…

Uiteraard wil ik ook mijn twee lieve schatjes van kinderen bedanken! Lonne en Jiffe, zonder jullie onuitputtelijke enthousiasme, deugnieterij en speelsheid had ik het schrijven van mijn scriptie waarschijnlijk veel sneller kunnen afronden, maar dat doet er gewoon niet toe. Jullie zijn simpelweg prachtig en bieden mij zoveel levensvreugde, dat niets of niemand anders mij kan bieden.

Als laatste, maar zeker niet in het minst wil ik mijn vrouw Nele bedanken. Het is belangrijk om met plezier te kunnen gaan werken, maar het is nog belangrijker om thuis te kunnen komen bij iemand die je in alles steunt. Nele jouw hulp, liefde en medeleven maken alles mogelijk. Je bent er voor mij, altijd… Bedankt!!

Although it's only my name which is printed on the cover of this work, it would never have been realized without the help and support of all of you. So I'm not going to say "I made it", but "WE made it"!

Summary

Air pollution has a global impact on the environment and the human health, which has become more problematic during the last decades. Although emissions of many air pollutants substantially have decreased in Europe over the last decades, air quality problems persist. The continuous development and improvement of air treatment technologies and the search for new, innovative techniques is therefore of main importance.

A typical group of air pollutants, which causes damage to the environment even nowadays, is the group of the volatile organic compounds (VOC). One of the major problems of these VOC is their contribution in the formation of photochemical smog in urban areas with a high density population and industrial activity. Several air treatment technologies, both physical-chemical and biological, have already been implemented to reduce the industrial VOC point emissions (stationary emissions). The biological treatment technologies have gained more interest during the last years, due to their environmental friendly character and their lower operating cost. In spite of these advantages the performance of a biofilter to treat a mixture of VOC with different hydrophobicity is challenged, by the low mass transfer of the hydrophobic compounds and the inhibitory effect of the hydrophilic compounds on the degradation of hydrophobic compounds.

In the present thesis, the key operating parameters influencing the bioreactor performance are evaluated and a new analytical technique, Selected Ion Flow Tube Mass Spectrometry (SIFT-MS), is used to gain more information on the transient behaviour of a bioreactor when changing the working conditions or applying VOC pulse injections. Also the use of a non-aqueous phase (NAP) in order to reduce the mass transfer resistance of hydrophobic compounds is evaluated in different bioreactor set-ups.

In the first experimental part of this work, **chapter 2**, the performance of a biofilter filled with *Macadamia ternifolia* nutshells as a carrier material is evaluated when treating an air stream loaded with ethyl benzene (EB) under mesophilic conditions. During a period of 5 months the biofilter was continuously operated, while the influence of several operational

parameters, e.g. inlet load (IL), empty bed residence time (EBRT) and temperature, were determined. This resulted in a half-saturation constant, Km, and maximal volumetric elimination rate, $r_{m,}$ of respectively 0.28 ± 0.09 g m^{-3} and 89 ± 11 g m^{-3} h^{-1}, at an EBRT of 90 s and respectively 0.72 ± 0.18 g m^{-3} and 117 ± 15 g m^{-3} h^{-1} at an EBRT of 150 s, which indicates that higher Elimination Capacities (EC) for EB removal can be reached at a higher EBRT. At an EBRT of 90 s and an IL of 80 g m^{-3} h^{-1}, a maximal EC of 68.5 g m^{-3} h^{-1} was reached at a temperature of 312 K. The obtained data demonstrates that a biofilter filled with *Macadamia ternifolia* nutshells as a carrier material is a good option for air treatment in tropical areas with typical temperatures varying from 292 to 313 K, using EB as a test substrate.

In a second experimental part, **chapter 3**, SIFT-MS is used to determine the performance, the biokinetic parameters and the porosity of a biofilter in a short period of time, ± 60 hours. The transient behaviour of the biofilter on VOC pulse injections is used to obtain more information about mass transfer resistance and reaction limitation. These online analyses were performed on a biofilter packed with a mixture of compost and wooden dowels, treating an air stream contaminated with dimethyl sulphide (DMS), hexane and toluene. The measurements were performed in less than three days at EBRT of 35, 60 and 90 s, which resulted in a Km and r_m value of respectively 0.028 ± 0.002 g m^{-3} and 7.23 ± 0.11 g m^{-3} h^{-1} independent of the applied EBRT. Based on the pulse injection experiments, the porosity of the biofilter, 40.2 ± 0.3 %, could be determined online. These measurements also indicate that mass transfer resistance becomes significant at lower gas velocities for compounds with a high Henry law coefficient.

In **chapter 4** a NAP was applied in four different biotechnologies for air treatment in order to improve the mass transfer of hydrophobic compounds.
The first evaluated biotechnique using a NAP was a two -phase partitioning bioreactor (TPPB), which was used for the removal of a mixture of DMS, n-hexane and toluene. The reactor contained 25 V% silicone oil as NAP and 75 V% water and mineral medium and was first inoculated with activated sludge under continuous feeding conditions. GC-FID and SIFT-MS measurements were performed in order to determine the reactor performance and to compare both measuring techniques. SIFT-MS and GC-FID both recorded the same performance, but with SIFT-MS it was possible to obtain this information in 3 days, while the GC-measurements took several weeks. At an IL of 350 g m^{-3} h^{-1} with hexane as single compound, EC values of 138.9, 163.8 and 241.6 g m^{-3} h^{-1} are reached at EBRT of respectively 30, 60 and 120 s. Feeding the TPPB with a mixture of DMS, hexane and toluene at an EBRT of 60 s, results in EC of respectively 45, 45 and 75 g m^{-3} h^{-1} for the different compounds at an IL of 100 g m^{-3} h^{-1} per compound. These results indicate that a TPPB is a good option to treat air pollution emissions containing

hydrophobic and hydrophilic compounds. Pulse injection experiments were performed in order to obtain the net residence time (NRT) of the compounds online. This NRT is related to the aeration and dispersion within the reactor, as decreasing aeration and dispersion will lead to a lower NRT. As excessive biomass growth can lead to deteriorated aeration and a decrease in reactor performance, the NRT can be used as a parameter indicating when biomass needs to be purged or when the aqueous medium needs to be refreshed in order to maintain a good reactor performance.

In a second part of **chapter 4**, a NAP phase was applied in a two-liquid-phase biofilter and a two-liquid-phase biotrickling filter. During this experiment waste air contaminated with a mixture of acetone, DMS, toluene, limonene and hexane was first continuously fed to a biofilter, filled with compost (40 V%) and wooden dowels (60 V%), and a two-liquid-phase biofilter, filled with wooden dowels saturated with silicone oil, in series. In order to decrease the mass transfer resistance for hydrophobic compounds even more, a 40/60 V% silicone oil/water emulsion was recirculated over the second biofilter in a second part of the experiment, resulting in a two-liquid-phase biotrickling filter. Adding a NAP to a biofilter (two-liquid-phase biofilter) or recirculating a silicone oil/water emulsion (two-liquid-phase biotrickling filter) increases the removal of hydrophobic compounds and reduces the inhibitory effect when a mixture of hydrophilic and hydrophobic compounds is fed to the reactor. A two-liquid-phase biotrickling filter shows a better degradation for hydrophobic compounds than a two-liquid-phase biofilter, but consumes more energy, due to the higher pressure drop and the need of a recirculation pump.

In a last part of **chapter 4**, a NAP was applied on a flat sheet composite membrane bioreactor (MBR) for air treatment, resulting in a new type of MBR, the two-phase partitioning membrane bioreactor (TPPMB). In the TPPMB a 60/40 V% water/silicone oil emulsion inoculated with activated sludge was used as recirculation liquid in order to obtain an acceptable removal for both hydrophobic and hydrophilic compounds. A mixture of DMS, n-hexane and toluene was first continuously fed to a MBR and in a second part fed to a TPPMB in order to compare the performance of both reactor types. Removal efficiencies (RE) of respectively 76.8 ± 7.7, 77.6 ± 13.0 and 12.1 ± 12.3 % were reached for toluene, DMS and hexane inlet concentrations ranging up to 2.6 g m^{-3} for each compound (IL ≤ 312 g m^{-3} h^{-1}) in a MBR. This indicates that a MBR is suitable to treat DMS and toluene, but unreliable to treat hexane, when feeding the bioreactor with a mixture of these compounds. In a TPPMB RE of 85 ± 5, 62 ± 5 and 53 ± 6 % were reached for respectively toluene, DMS and hexane inlet concentrations ranging up to 2.8 g m^{-3} for each compound (IL ≤ 336 g m^{-3} h^{-1}). The RE for hexane is significantly higher in a TPPMB, than in a MBR and shows less variation, so a TPPMB is more suitable and reliable for treating air emissions containing hydrophobic compounds or a mixture of compounds with different hydrophobicity.

In general the results of this work illustrate that a biofilter is reliable to treat a single VOC like EB, but is less suitable to treat more hydrophobic compounds like hexane. When feeding a mixture of VOC with different hydrophobicity, the more hydrophilic compounds can have an inhibitory effect on the degradation of the more hydrophobic compounds. SIFT-MS can be used in order to measure the performance and the biokinetic parameters of a bioreactor in a short period of time. By using the SIFT-MS it is possible to obtain more information about the transient behaviour of a bioreactor when applying VOC pulse injections. This information indicates that mass transfer resistance becomes significant at lower gas velocities for compounds with a high Henry law coefficient. By applying pulse injections it is also possible to measure the NRT of a compound in a bioreactor online. In a biofilter, a higher Henry law coefficient, defined as the concentration in the gas phase over the concentration in the liquid phase ($(g\ m^{-3})_{gas}/(g\ m^{-3})_{liquid}$), will result in a lower retention time. The NRT of an inherent compound (RE ≈ 0 %) can be used to determine the online porosity of a biofilter. In a TPPB the NRT can be used as a parameter indicating when biomass needs to be purged or when the aqueous medium needs to be refreshed in order to maintain a good reactor performance. Applying an NAP in a bioreactor decreases the mass transfer resistance for hydrophobic compounds and the inhibitory effect of the hydrophilic compounds on the degradation of hydrophobic compounds, which makes the biotechniques more reliable to treat an emission which contains a mixture of hydrophilic and hydrophobic compounds.

Samenvatting

Luchtverontreiniging heeft een wereldwijde impact op het milieu en de gezondheid van de mens wat de laatste decennia steeds problematischer is geworden. Hoewel de emissies van veel luchtverontreinigende stoffen gedurende de laatste decennia aanzienlijk gedaald zijn in Europa, blijven er problemen met de luchtkwaliteit bestaan. De continue ontwikkeling en verbetering van bestaande luchtbehandelingstechnieken en het zoeken naar nieuwe, innovatieve technologieën is daarom van cruciaal belang.

Een typische groep van luchtverontreinigende stoffen die tot op de dag van vandaag schade veroorzaakt aan het milieu, is de groep van de vluchtige organische componenten (VOC). Eén van de belangrijkste problemen van deze VOC is hun bijdrage aan de vorming van fotochemische smog in verstedelijkte gebieden met een hoge populatiedichtheid en industriële activiteit. Verschillende luchtzuiveringstechnieken, zowel fysisch-chemisch als biologisch, zijn al toegepast om industriële VOC puntemissies (stationaire emissies), te reduceren. Gedurende de laatste jaren wint de biologische behandeling van afvalstoffen aan interesse als gevolg van het milieuvriendelijke karakter en de lagere operationele kosten. Ondanks deze voordelen blijft het een uitdaging om een mengsel van VOC met verschillende hydrofobiciteit te behandelen met een biofilter, vanwege de lage massaoverdracht van de hydrofobe verbindingen en het inhibitie effect van de hydrofiele verbindingen op de afbraak van hydrofobe verbindingen.

In dit proefschrift worden de belangrijkste operationele parameters geëvalueerd die de reactorprestatie beïnvloeden en wordt er een nieuwe analyse techniek, Selected Ion Flow Tube mass Spectrometry (SIFT-MS) toegepast, om meer informatie in the winnen over het overgangsgedrag van een bioreactor bij het veranderen van de operationele parameters of bij het aanbrengen van VOC pulsinjecties. Daarnaast wordt het gebruik van een niet-waterige fase (NAP), om de weerstand tegen de massaoverdracht van hydrofobe verbindingen te verminderen, in verschillende types bioreactoren geëvalueerd.

In het eerste experimentele deel van dit werk, **hoofdstuk 2**, wordt de prestatie geëvalueerd van een biofilter, gevuld met *Macadamia ternifolia* nootschalen als draagmateriaal, die instaat voor de zuivering van een met ethylbenzeen (EB) beladen luchtstroom onder

mesofiele omstandigheden. De biofilter werd continu bediend gedurende een periode van 5 maanden, terwijl de invloed van verschillende operationele parameters, zoals de inlaatbelasting (IL), de lege bed verblijftijd (EBRT) en de temperatuur, op de werking van de biofilter werd bepaald. Dit resulteerde in een half verzadigingsparameter, Km, en maximale volumetrische eliminatiesnelheid, r_m, van respectievelijk 0.28 ± 0.09 g m^{-3} en 89 ± 11 g m^{-3} h^{-1}, bij een EBRT van 90 s en respectievelijk 0.72 ± 0.18 g m^{-3} en 117 ± 15 g m^{-3} h^{-1} bij een EBRT van 150 s wat aantoont dat een hogere eliminatiecapaciteit (EC) kan worden bereikt voor het verwijderen van EB bij een hogere EBRT. Bij een EBRT van 90 s en een IL van 80 g m^{-3} h^{-1} werd een maximale EC bereikt van 68.5 g m^{-3} h^{-1} bij een temperatuur van 312 K. De verkregen experimentele data toont aan dat een biofilter, gevuld met *Macadamia ternifolia* nootschalen als dragermateriaal en met EB als test substraat, een goede optie is voor het zuiveren van lucht in tropische gebieden met typische temperaturen variërend tussen 292 en 313 K.

In een tweede experimenteel gedeelte, **hoofdstuk 3**, is SIFT -MS gebruikt om de prestatie, de biokinetische parameters en de porositeit van een biofilter te bepalen in een korte tijd, ± 60 uur. De respons van de biofilter op VOC pulsinjecties wordt gebruikt om meer informatie te verkrijgen over massatransfer weerstand en reactiebeperkingen. Deze online analyses werden uitgevoerd op een biofilter gepakt met een mengsel van compost en houten deuvels voor het behandelen van een luchtstroom vervuild met dimethylsulfide (DMS), hexaan en tolueen. De metingen werden uitgevoerd in minder dan drie dagen bij een EBRT van 35, 60 en 90 s, resulterend in een Km en r_m waarde van respectievelijk 0.028 ± 0.002 g m^{-3} and 7.23 ± 0.11 g m^{-3} h^{-1}, onafhankelijk van de toegepaste EBRT. Gebaseerd op de pulsinjectie experimenten, kan de porositeit van de biofilter, 40.2 ± 0.3 %, online bepaald worden. Deze metingen gaven ook aan dat massatransfer weerstand significant wordt bij lagere gassnelheden voor componenten met een hoge Henry coëfficiënt.

In **hoofdstuk 4** werd een NAP toegepast op vier verschillende biotechnieken voor luchtbehandeling teneinde de massaoverdracht van hydrofobe verbindingen te verbeteren. De eerste biotechniek die werd geëvalueerd en die gebruik maakt van een NAP was een twee fasen partitie bioreactor (TPPB) die werd gebruikt voor het verwijderen van een mengsel van DMS, n-hexaan en tolueen. De reactor bevatte 25 V% siliconenolie als NAP en 75 V% water en mineraal medium en werd eerst geïnoculeerd met geactiveerd slib onder continue voedingsomstandigheden. GC-FID en SIFT-MS metingen werden uitgevoerd om de prestatie van de reactor te bepalen en om beide meettechnieken met elkaar te vergelijken. Zowel met SIFT-MS als GC-FID werd dezelfde prestatie waargenomen, maar met SIFT-MS was het mogelijk om dezelfde informatie te verkrijgen in 3 dagen, terwijl de GC-metingen enkele weken in beslag namen. Bij een IL van 350 g

m^{-3} h^{-1} met hexaan als enige component, werden EC waarden van 138.9, 163.8 en 241.6 g m^{-3} h^{-1} bereikt bij een EBRT van respectievelijk 30, 60 en 120 s. Wanneer de TPPB werd gevoed met een mengsel van DMS, hexaan en tolueen bij een EBRT van 60 s, resulteerde dit in een EC van respectievelijk 45, 45 and 75 g m^{-3} h^{-1} voor de verschillende verbindingen en dit bij een IL van 100 g m^{-3} h^{-1}per component. Deze resultaten geven aan dat een TPPB een goede optie is om luchtvervuilende emissies te behandelen die zowel hydrofobe als hydrofiele componenten bevatten. Pulsinjectie experimenten werden uitgevoerd om online de netto verblijftijd (NRT) van een verbinding te bepalen. Deze NRT is gerelateerd aan de beluchting en de dispersie van de lucht in de reactor. Een vermindering in beluchting en dispersie van de lucht zal namelijk leiden tot een lagere NRT. Aangezien een overmatige groei aan biomassa kan leiden tot een slechtere beluchting en een vermindering in reactorperformantie, kan de NRT worden gebruikt als parameter die aangeeft wanneer er biomassa moet worden verwijderd of wanneer het waterige medium moet worden vernieuwd om een goede reactorperformantie te behouden.

In een tweede deel van **hoofdstuk 4** werd een NAP fase toegepast in een twee vloeistof fasen biofilter en een twee vloeistof fasen biotrickling filter. Tijdens dit experiment werd lucht, verontreinigd met een mengsel van aceton, DMS, tolueen, limoneen en hexaan, eerst continu gevoed aan een biofilter gevuld met compost (40 V%) en houten deuvels (60 V%) en een twee vloeistof fasen biofilter gevuld met houten deuvels die verzadigd werden met siliconen olie in serie. Om de weerstand tegen massaoverdracht van hydrofobe componenten nog verder te doen dalen werd in een tweede deel van het experiment een 40/60 V% siliconen olie/water emulsie gerecirculeerd over de tweede biofilter wat resulteerde in een twee vloeistof fasen biotrickling filter. Een NAP toevoegen aan een biofilter (twee fasen biofilter) of het recirculeren van een siliconen olie/water emulsie (twee fasen biotrickling filter) verhoogt de verwijdering van hydrofobe verbindingen en vermindert het inhibitie effect wanneer een mengsel van hydrofiele en hydrofobe verbindingen wordt toegevoerd aan de reactor . Een twee fasen biotrickling filter breekt beter hydrofobe verbindingen af dan een twee fasen biofilter, maar verbruikt meer energie door de hogere drukval en de nood aan een vloeistofcirculatiepomp.

In een laatste deel van **hoofdstuk 4** werd een NAP toegevoegd aan een vlak samengesteld membraanbioreactor (MBR) voor luchtbehandeling, resulterend in een nieuw type MBR, namelijk de twee fasen partitie membraanbioreactor (TPPMB). In de TPPMB werd een 60/40 V% water/siliconen olie emulsie, die geïnoculeerd werd met geactiveerd slib, gebruikt als recirculatievloeistof om een aanvaardbare verwijdering van zowel hydrofobe als hydrofiele verbindingen te verkrijgen. Een mengsel van DMS, n-hexaan en tolueen werd eerst continu gevoed aan een MBR en in een tweede deel gevoed aan een TPPMB, zodat de prestaties van beide reactortypes met elkaar kunnen worden vergeleken. In de MBR werden verwijderingsrendementen (RE) van respectievelijk 76.8 ± 7.7, 77.6 ± 13.0

and 12.1 ± 12.3 % bereikt voor tolueen, DMS en hexaan met inlaatconcentraties tot 2.6 g m^{-3} voor iedere verbinding afzonderlijk (IL ≤ 312 g m^{-3} h^{-1}). Dit geeft aan dat een MBR geschikt is voor het verwijderen van DMS en tolueen uit een afvalluchtstroom, maar onbetrouwbaar in het verwijderen van hexaan wanneer een mengsel van deze drie componenten wordt gevoed aan de MBR. In een TPPMB werden RE van 85 ± 5, 62 ± 5 en 53 ± 6 % bereikt voor respectievelijk tolueen, DMS, en hexaan met inlaatconcentraties tot 2.8 g m^{-3} voor iedere verbinding afzonderlijk (IL ≤ 336 g m^{-3} h^{-1}). De RE voor hexaan is significant hoger in een TPPMB dan in een MBR en vertoont minder variatie, waardoor kan geconcludeerd worden dat een TPPMB meer geschikt en betrouwbaarder is voor het behandelen van luchtemissies die hydrofobe verbindingen of een mengsel van verbindingen met verschillende hydrofobiciteit bevatten.

In het algemeen illustreren de resultaten van dit werk dat een biofilter betrouwbaar is voor het behandelen van VOC zoals EB, maar minder geschikt is om meer hydrofobe verbindingen zoals hexaan te behandelen. Bij het behandelen van een mengsel aan VOC met verschillende hydrofobiciteit kunnen de meer hydrofiele verbindingen een inhibitie effect hebben op de afbraak van de meer hydrofobe verbindingen. SIFT-MS kan worden gebruikt om de performantie en de biokinetische parameters van een bioreactor op te meten in een korte tijd. Met SIFT-MS is het mogelijk om meer informatie te verkrijgen over de respons van een bioreactor op VOC pulsinjecties. Uit deze informatie bleek dat de massatransfer weerstand significant wordt bij lagere gassnelheden voor componenten met een hoge Henry coëfficiënt. Door het toepassen van pulsinjecties is het ook mogelijk om de NRT van een verbinding in een bioreactor online op te meten. Een hogere Henry-coëfficiënt, gedefinieerd als de concentratie in de gasfase over de concentratie in de vloeistoffase ($(g\ m^{-3})_{gas}/(g\ m^{-3})_{liquid}$), leidt tot een lagere retentietijd in een biofilter. De NRT van een inherente verbinding (RE ≈ 0 %) kan worden gebruikt om de online porositeit van een biofilter te bepalen. In een TPPB kan de NRT worden gebruikt als parameter om aan te geven wanneer biomassa moet worden verwijderd of wanneer het waterige medium moet worden vernieuwd om een goede reactorperformantie te behouden. De toepassing van een NAP in een bioreactor vermindert de diffusie weerstand voor hydrofobe verbindingen en het inhibitie effect van de hydrofiele verbindingen op de afbraak van de hydrofobe verbindingen wat de biotechnieken betrouwbaarder maakt voor het behandelen van luchtemissies die een mengsel aan hydrofiele en hydrofobe verbindingen bevat.

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Symbol list

A	Surface area (m^2)
C	Concentration ($g\ m^{-3}$)
$C_{CO2,in}$	Inlet CO_2 concentration ($g\ CO_2\ m^{-3}$)
$C_{CO2,in}$	Outlet CO_2 concentration ($g\ CO_2\ m^{-3}$)
C_g	Concentration in the gas phase ($g\ m^{-3}$)
C_{in}	Inlet concentration ($g\ m^{-3}$)
C_l	Concentration in the liquid phase ($g\ m^{-3}$)
COD	Chemical oxygen demand ($mg\ l^{-1}\ O_2$)
C_{out}	Outlet concentration ($g\ m^{-3}$)
CPS	Counts per second (cps)
C_{top}	Concentration at the peak top ($g\ m^{-3}$)
EBRT	Empty bed residence time (s)
EC	Elimination capacity ($g\ m^{-3}\ h^{-1}$)
$EC_{i;calc}$	Elimination capacity based on calculated data ($g\ m^{-3}\ h^{-1}$)
$EC_{i;exp}$	Elimination capacity based on experimental data ($g\ m^{-3}\ h^{-1}$)
EC_{max}	Maximal elimination capacity ($g\ m^{-3}\ h^{-1}$)
F	Mass flux through the membrane ($g\ s^{-1}$)
H	Air - water partition coefficient or Henry law coefficient ($g\ m^{-3}$ / $g\ m^{-3}$)
IL	Inlet load ($g\ m^{-3}\ h^{-1}$)
k_b	Biofilm transfer coefficient ($g\ s^{-1}$)
k_g	Gas transfer coefficient ($g\ s^{-1}$)
k_l	Liquid transfer coefficient ($g\ s^{-1}$)
Km	Half-saturation constant ($g\ m^{-3}$)
k_m	Membrane transfer coefficient ($g\ s^{-1}$)
Km'	Net half-saturation constant ($g\ m^{-3}$)
K_{ov}	Overall mass transfer coefficient ($m\ s^{-1}$)
m_{ash}	Mass ash (g)
m_{BN}	Mass bottle filled with nutshells (g)
m_{BNW}	Mass bottle filled with nutshells and water (g)
m_{DN}	Mass dried nutshells (g)

m_N	Mass nutshells at ambient conditions (g)
m_{NW}	Mass nutshells after pouring water over them (g)
m_W	Mass water (g)
N	Number of data points (-)
NEC	Net elimination capacity (g m^{-3} h^{-1})
NIL	Net inlet load (g m^{-3} h^{-1})
NRT	Net residence time (s)
Q	Gas flow rate (m^3 h^{-1})
r	Rate of VOC utilization at any point in the biofilm (g m^{-3} h^{-1})
RE	Removal efficiency (%)
r_m	Maximal volumetric elimination rate (g m^{-3} h^{-1})
r_m'	Net maximal volumetric elimination rate (g m^{-3} h^{-1})
RT	Response time (s)
T	Temperature (K)
t	Time (s)
t_{end}	Time last point of the peak (s)
t_{start}	Time first point of the peak (s)
t_{top}	Time peak top (s)
μ	Growth rate (g new cells per g cells per day)
u_{EB}	Empty bed velocity (m h^{-1})
μ_m	Maximal growth rate (g new cells per g cells per day)
V	Volume reactor (m^3)
V_B	Volume bottle (l)
V_W	Volume water (l)
X	Biomass concentration (g m^{-3})
Y	Biomass yield coefficient (g g^{-1})
Y_{XS}	Yield coefficient (g dry biomass per g compound degraded)
ρ_{H2O}	Density water (g l^{-1})
$\rho_{nutshells}$	Density nutshells (g ml^{-1})

Abbreviations index

BAT	Best available techniques
BF	Biofilter
BTEX	Benzene, toluene, ethyl benzene and xylene
DMS	Dimethyl sulphide
EB	Ethyl benzene
EU	European Union
GC	Gas chromatography
GC-FID	Gas chromatography - flame ionization detector
GC-MS	Gas chromatography - mass spectrometry
Hex	Hexane
MBR	Membrane bioreactor
MEK	Methyl ethyl ketone
NAP	Non-aqueous phase
NMVOC	Non-methane volatile organic compound
PDMS	polydimethylsiloxane
SIFT-MS	Selected ion flow tube - mass spectrometry
TLPBF	Two-liquid-phase biofilter
TLPBTF	Two-liquid-phase biotricklingfilter
TPPB	Two-phase partitioning bioreactor
TPPMB	Two-phase partitioning membrane bioreactor
Tol	Toluene
VOC	Volatile organic compound
VOSC	Volatile organic sulphur compound
VP	Vapour permeation
WHO	World health organization

Introductory chapter Evaluation of conventional and innovative air treatment biotechnologies for Volatile Organic Compound mixtures

AIM OF THE STUDY

Biological waste gas treatment technologies like biofiltration, biotrickling filtration and bioscrubbing have already been used for several decades to remove Volatile Organic Compounds (VOC) out of industrial gas emissions, but they still encounter analytical, process and microbial limitations. This work mainly focuses on finding solutions for the analytical and process limitations.

The first aim of this work is to reduce the analytical limitations, by exploring the possibilities of a new analytical technique, selected ion flow tube mass spectrometry (SIFT-MS). By using this technique, concentrations can in principle be measured much faster, ± 4 measurements per second, than in a conventional GC, so it should be possible to obtain more information concerning the transient behaviour of a bioreactor when changing the operational conditions.

Process limitations occur especially when dealing with stationary emissions containing a mixture of hydrophilic and hydrophobic compounds. To reduce these emissions, the residence time in a bioreactor needs to be sufficiently high due to the low mass transfer of the hydrophobic compounds and the inhibitory effect of the hydrophilic compounds on the degradation of hydrophobic compounds. Therefore the second aim of this work is to reduce the process limitations of bioreactors, e.g. shorter residence time for same performance, by optimizing existing techniques and by setting up new biotechniques at laboratory level.

OUTLINE OF THE STUDY

Chapter 1 provides a general literature review on the different types of air pollution, its sources and its effects. The environmental effects caused by VOC pollutants are described more in detail as well as the waste treatment techniques for stationary VOC emissions, with the focus on biotechnologies and the microbial ecology in bioreactors. As environmental problems caused by air pollution, e.g. smog, mostly occurs at places with a high population density, the focus of this thesis is the removal of anthropogenic VOC, more specifically on the reduction of VOC mixtures from stationary emission sources, as these emissions are the most easy to control by "end-of-pipe" technologies.

In **Chapter 2** the operation of a biofilter is explained more in detail by applying a case study in which ethyl benzene (EB) is fed to a biofilter filled with macadamia nutshells as packing material. In this study the influence of several operational parameters like inlet load (IL), empty bed residence time (EBRT) and temperature, on the reactor performance was investigated.

In **Chapter 3** the analytical limitations of a conventional GC were decreased by using a new analytical technique called SIFT-MS. SIFT-MS is a new and fast analysis apparatus which can be applied to determine the performance of a bioreactor, the biokinetic parameters and the net residence time in a bioreactor. SIFT-MS is also used to obtain more information about mass transfer resistance and reaction limitation which can occur in bioreactors by applying pulse injections on the reactor.

The research in **Chapter 4** describes the use of a non-aqueous phase (NAP) in order to decrease process limitations like the mass transfer resistance for hydrophobic compounds and so increasing the reactor performance for gas emissions containing a mixture of hydrophilic and hydrophobic compounds. This NAP was applied in a two-phase partitioning bioreactor, a two-liquid-phase biofilter and biotrickling filter and in a two - phase partitioning membrane bioreactor.

The VOC used in **Chapter 3 and 4** were chosen because of their different mass transfer (different hydrophobicity) and biodegradation properties.

Chapter 5 provides some general conclusions and perspectives for future research.

ACKNOWLEDGEMENTS

The author acknowledges the support of Ghent University under the GOA-project: Ugent BOF10-GOA010.

The research was conducted at:
Research Group Environmental Organic Chemistry and Technology (EnVOC),
Ghent University, Coupure Links 653, 9000 Ghent.
Tel: +32(0)9 264 59 50, Fax: +32(0)9 264 62 43,
URL: http://www.envoc.ugent.be

Chapter 1 Literature review: Air treatment technologies for VOC mixtures

1.1 AIR POLLUTION

Air pollution can be defined as any additional gas or particle, which is introduced or formed in the air and which destroys the natural balance in such a way that it becomes potentially harmful to humans, animals or the environment. The global impact on the environment, e.g. global warming, and the human and animal health, led to a growing interest in air treatment technologies during the last decennia. Therefore emissions of many air pollutants in Europe have been decreased substantially over the past decades, resulting in an improved air quality. However air pollutant concentrations are still too high and air quality problems persist (E-PRTR, 2014). Even atmospheric emission concentrations as low as ppm_v or even ppb_v level may still have significant effects on humans, plants and buildings (Kennes and Veiga, 2010). Therefore the continuous development and improvement of existing techniques and the search for new, innovative air treatment technologies, remains very important.

1.1.1 Waste air emission sources

Air pollution can result from both natural sources (biogenic emissions) and human sources (anthropogenic emissions).

1.1.1.1 Biogenic emissions

Natural air pollutant sources include emissions from plants, forest fires, volcanic eruptions, wind erosion, pollen dispersal, evaporation of organic compounds, microbiological decomposition of organic material, ... (Berenjian and Malmiri, 2012; Zemankova and Brechler, 2010) The emission rates of these pollutants are affected by a variety of factors, such as tree species, temperature, humidity, ...

1.1.1.2 Anthropogenic emissions

Anthropogenic emissions are mostly found at industrial areas and places with a high population density (Michulec et al., 2005). The sources of these emissions can be divided in two groups: mobile sources and stationary sources (Huang et al., 2011; Kennes and Veiga, 2010; Theloke and Friedrich, 2007). Mobile sources contain basically all the traffic emissions caused by the combustion process of the different vehicles. This includes particulate matter, benzene, toluene, ethyl benzene and xylene (BTEX) emissions and inorganic pollutants. Stationary sources contain solvent evaporation in industrial and non-industrial activities (surface coating, printing, dry cleaning), waste treatment and disposal processes (waste water treatment, incineration), food industries, paper pulp and polymer producing industries ... (Álvarez-Hornos et al., 2007; Kim and Kim, 2005; Lebrero et al., 2013a)

1.1.2 Typical air pollutants

Air pollutants can be classified as primary pollutant if it is emitted directly from a source, while a secondary pollutant, e.g. photochemical smog and ground level ozone, is not directly emitted but is formed when other pollutants (primary pollutants) react in the atmosphere. Some pollutants may be both primary and secondary as they can be emitted directly and can be formed from other primary pollutants. Five of the major primary pollutants or pollutant groups are CO, NO_x, SO_x, VOC and even particulate matter as the atmosphere is a good carrier for these pollutants (Michulec et al., 2005).

1.1.2.1 CO, NO_x and SO_x

Carbon monoxide (CO) is produced when carbon containing compounds, like fossil fuel, are burnt incompletely because of a shortage in oxygen. During this combustion, the carbon and hydrogen combine to form carbon dioxide, water and heat, but also carbon monoxide, due to partial oxidation. At proper combustion conditions (air/fuel ratio, temperature, turbulence, residence time), the fuel burns clean and produces only small amounts of carbon monoxide, but anything which disrupts the burning process or results

in a shortage of oxygen can increase the carbon monoxide production. Mobile sources are one of the major sources for CO formed due to incomplete combustion, but also natural sources like volcanoes and forest fires can lead to partial oxidation of carbon containing compounds. Next to incomplete combustion, carbon monoxide is also formed naturally, due to photochemical reactions in the troposphere (Hudman et al., 2008).

Like carbon monoxide, NO_x and SO_x emissions can originate as combustion by-products. At high temperatures, nitrogen and sulphur gases can react with oxygen gases to form respectively NO_x and SO_x. Next to anthropogenic emissions, NO_x can also be formed naturally by lightning. SO_x and in particular SO_2 can naturally be produced by volcanoes and hot springs.

1.1.2.2 Volatile organic compounds

VOC are very common air pollutants which can be defined as any organic compound having at 293.15 K a vapour pressure of 0.01 kPa or more, or having a corresponding volatility under the particular conditions of use (EU, 1999). This definition is based on a physical parameter and so VOC covers a whole group of different chemical compounds, such as alkanes, aromatic compounds, ketones, terpenes, sulphuric compounds... which all have different properties. Table 1.1 shows the overall point emissions of non-methane volatile organic compounds (NMVOC) from 15 countries of the European Union (EU), Norway and Switzerland from 2007 to 2011 (E-PRTR, 2014). In these countries the number of economic activities between 2007 and 2011 remained about stable.

Table 1.1: Non-methane volatile organic compound (NMVOC) point emissions from 15 countries of the European Union, Norway and Switzerland from 2007 to 2011 (E-PRTR, 2014).

Country	Emissions (10^3 kg)					Variation from 2007 and 2011 (%)
	2007	2008	2009	2010	2011	
Austria	3327	3068	2625	2994	3209	-3.5
Belgium	38171	36169	26863	27568	23531	-38.4
Bulgaria	4325	4210	3964	358	433	-90.0
Czech Republic	6110	6046	4969	6397	6170	1.0
France	90220	75471	60720	64043	60512	-32.9
Germany	45415	51528	40938	40905	40498	-10.8
Greece	5766	4394	5188	4585	4874	-15.5
Italy	51059	44227	40679	39145	38497	-24.6
Netherlands	17932	17332	15060	16204	15562	-13.2
Norway	83823	59406	52711	42785	37991	-54.7
Poland	9708	10119	6060	5870	5688	-41.4
Portugal	14678	12869	9795	9604	9423	-35.8
Slovakia	4535	3732	4654	2941	3673	-19.0
Spain	70776	60712	52722	46786	46656	-34.1
Sweden	25479	23774	23587	25083	24873	-2.4
Switzerland	2752	2986	2721	2203	1917	-30.3
United Kingdom	170934	124587	109680	101991	76061	-55,5
TOTAL:	645010	540630	462936	439462	399568	-38,1

Since 2007 the total emissions of NMVOC decreased in most of these countries. Only in Austria, the Czech Republic and Sweden, the total NMVOC emissions stayed about the same. The high decrease of NMVOC emissions in Bulgaria is mainly due to the emission decrease during the manufacture of refined petroleum products, which decreased from 4.08 kton in 2007 to 0.127 kton in 2011. In spite of the high reduction of NMVOC emissions in the United Kingdom and France between 2007 and 2011, they still remain the two countries with the largest absolute amount of NMVOC emissions in 2011. When the NMVOC emissions from 2011 are related per citizen, than the highest NMVOC emissions can be found in Norway (7.5 kg citizen^{-1}), Sweden (2.7 kg citizen^{-1}) and Belgium (2.1 kg citizen^{-1}), while all the other countries stay below 1.2 kg NMVOC emissions per citizen. The high amount of NMVOC emissions per citizen in Norway is due to the extraction of crude petroleum which covers 60 % of the Norwegian NMVOC emissions.

Figure 1.1 shows the overall NMVOC point emissions of 27 countries of the EU, Norway, Serbia and Switzerland divided in different industrial sectors. Although the total NMVOC emissions decreased with 38.5 %, from 705.2 kton in 2007 to 433.6 kton in 2011, the subdivision into the different industrial sectors remained about the same. The energy sector (41.3 % in 2007 to 38.9 % in 2011) and the chemical industry (19.3 % in 2007 to 21.3 % in 2011) remained the two industries with the largest share of NMVOC emissions, while the share of the paper and wood sector increased from 4.2 to 6.9 % becoming the sector with the third largest NMVOC emissions. The largest share of NMVOC emissions in the energy sector (70.2 % in 2011) is for the manufacture of refined petroleum products, which is overall the economic activity with the largest amount of NMVOC emissions.

Although VOC emissions in Europe decreased substantially over the past decades, the emission concentrations are still too high, causing serious damage to the air quality. Even in the last months Western Europe has been enveloped by dangerously high levels of air pollution which have rivalled with the levels in Beijing (EEB, 2014). Due to the high difference in VOC and the great number of stationary sources, it is very challenging to come up with one general solution to treat the whole range of VOC in a waste stream, therefore the focus of this thesis will is decreasing the process limitations of bioreactors in order to increase the performance for treating mixtures of VOC.

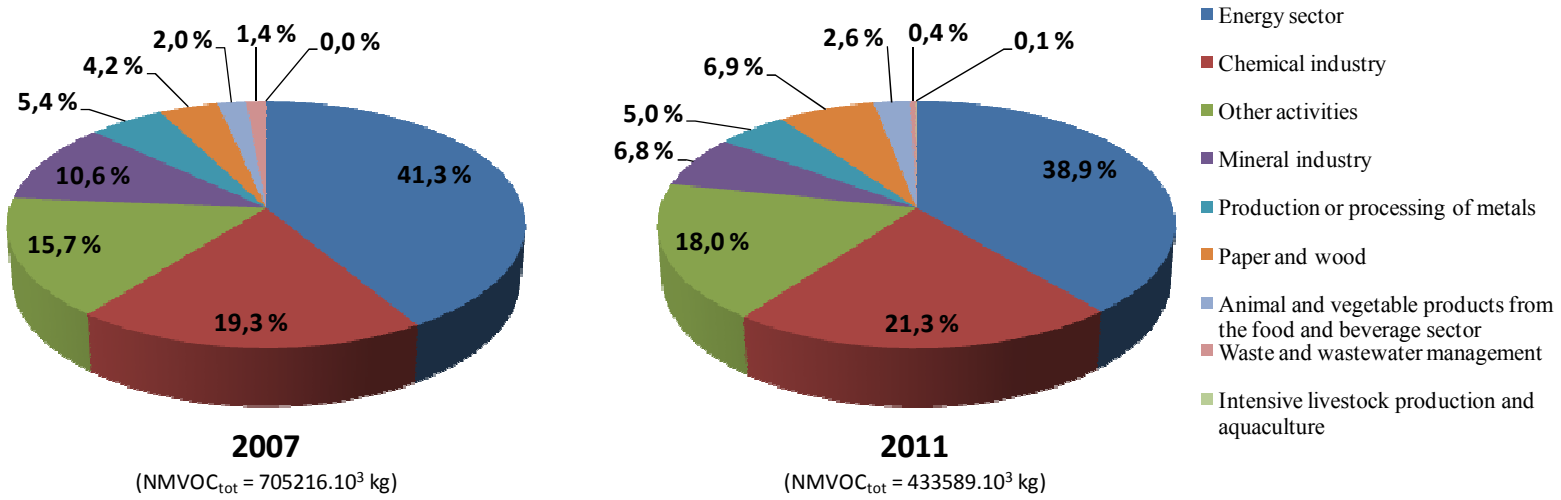


Figure 1.1: Overall non-methane volatile organic compound (NMVOC) point emissions of 27 countries of the EU, Norway, Serbia and Switzerland divided in different industrial sectors (E-PRTR, 2014).

1.1.2.3 Particulate matter

Particulate matters are tiny particles of solids or liquids suspended in a gas. The significant negative impact of these particulates on the human health, due to their morphological characteristics and their chemical composition, led to a growing interest (Walgraeve et al., 2010). Some particulates occur naturally, originating from volcanoes, dust storms, forest and grassland fires..., while others originate from human activities, such as the burning of fossil fuels in vehicles, power plants and various industrial processes.

1.1.3 Effects

At places with a high population density, e.g. cities, air quality standards are often exceeded, which makes it of main importance to know the effect of these air pollutant emissions on the human health and the environment. Data from the 2013 European Environment Agency (EEA) report indicated that up to 96 % of the urban population in the EU was exposed to fine particulate matter concentrations which were above the United Nations World Health Organization (WHO) guidelines. Even more, 98 %, were subject to concentrations of ground-level ozone above the levels recommended by the WHO (EEA, 2013).

1.1.3.1 Health

Indoor and outdoor air quality has a great influence on the human health (Qian et al., 2004; van Leeuwen, 2001). VOC are one of the major contributors to photochemical smog, which can cause respiratory problems such as eye irritation, headache, haze and damage to plant and animal life (Shareefdeen and Singh, 2005). Assumption of VOC by human beings can occur by inhalation, ingestion or even by skin contact. Frequent contact with VOC can disturb the central nervous system resulting in dizziness, headache, sleepiness, sickness and disturbance in the coordination and equilibrium system. Longer contact may even cause irreversible damage to the kidneys and liver. VOC like benzene and vinyl chloride causes cancer, birth defects, long term lung injuries, as well as brain and nerve damage. The WHO declared that air pollution causes more than 400 000 people a year to die prematurely and that it was a leading environmental cause of cancer deaths in 2013 (EEB, 2014).

1.1.3.2 Environment

Many air pollutants act as catalyst for the formation of photochemical smog, which is caused by the chemical reaction of sunlight NO_x and VOC in the atmosphere forming a harmful mixture of air pollutants including particulate matter, VOC, NO_x and tropospheric ozone. This dangerous ground level ozone is mainly produced during the summer, due to the increase of solar energy. Ozone is a strong oxidiser and readily reacts with animal and plant tissues, destroying trees, crops, animals... Next to tropospheric ozone, air pollutants can contribute to the depletion of the ozone layer in the stratosphere, leading to higher levels of UVB radiation reaching the earth's surface.

SO_2 and NO_x can react with the water molecules which are present in the atmosphere resulting in the formation of respectively sulphuric acid and nitric acid. These acids will cause a decrease in pH, resulting in acid rain, which is harmful for forests and other vegetation, soil, lakes and aquatic life. Acid rain can also damage monuments and buildings and increases the corrosion rate of metals.

The European Environmental Agency report of 2013 highlights that the natural environment continues to suffer from the air pollution impairing vegetation growth and harming biodiversity (EEA, 2013).

One of the major problems of VOC in the environment nowadays is their contribution in the formation of photochemical smog in big cities like Beijing, Ahvaz and Paris (DW, 2014; Phys.org, 2014; Qiu, 2014). Photochemical smog formation proceeds through a sequence of reactions, which all involve a free radical mechanism. Primary pollutants, including VOC and nitrogen oxides (NO_x), are introduced into the atmosphere through vehicular emissions (mobile sources) and emissions from industrial processes (stationary sources).When the nitrogen dioxide (NO_2) concentrations are well above clean air levels and in the presence of sunlight, NO_2 can be photo dissociated to form free radicals, which generates tropospheric ozone and oxygen atoms, see Eq. (1.1) and (1.2).

$$NO_2 + h\nu \rightarrow NO^{\bullet} + O^{\bullet\bullet}\ (^3P) \quad (1.1)$$

$$O^{\bullet\bullet}\ (^3P) + O_2 \rightarrow O_3 \quad (1.2)$$

O (3^P) is the oxygen atom in the triplet ground-state (1s2; 2s2; 2p(x)2; 2p(y)1; 2p(z)1 instead of 1s2; 2s2; 2p(x)2; 2p(y)2), which is very reactive and will react very fast with O_2 to form O_3.The ozone can be reduced with NO, see Eq. (1.3), but during day time, the production of ozone is larger than during the night and ozone concentrations will increase.

$$O_3 + NO^{\bullet} \rightarrow NO_2 + O_2 \quad (1.3)$$

The oxygen radicals react with water to form hydroxyl radicals, see Eq. (1.4).

$$O^{\bullet} + H_2O \rightarrow 2\ {}^{\bullet}OH \quad (1.4)$$

In the presence of these hydroxyl radicals, VOC can oxidise in order to form aldehydes, see Eq. (1.5).

$$RH + 2\ O_2 + 2\ NO + {}^{\bullet}OH \rightarrow R'CHO + H_2O + 2\ NO_2 + {}^{\bullet}OH \quad (1.5)$$

The aldehydes are oxidised further to form aldehyde peroxides and aldehyde peroxyacids, see Eq. (1.6) and (1.7), which are the compounds that cause irritation to sensitive biological tissues and cause most of the health problems associated with photochemical smog.

$$R'CHO + {}^{\bullet}OH + O_2 \rightarrow R'C(O)\ O_2^{\bullet} + H_2O \quad (1.6)$$

$$R'C(O)\ O_2^{\bullet} + NO_2 \rightarrow R'C(O)_2NO_2 \quad (1.7)$$

Like most air pollutions, VOC can originate from biogenic or anthropogenic sources, see 1.1.1. Most of the biogenic VOC (e.g. terpenes) are emitted by plants during their growth and biosynthesis, while anthropogenic VOC are emitted from mobile sources, like traffic, or stationary sources, like industrial plants.

1.1.3.3 Economic

The effect of air pollution on the economy may be derived from the effect of air pollution on the human health and the environment. Each day, air pollution causes illness leading to people staying off work because of health problems which leads to a huge economic cost, not only because of the restricted economic activity, but also due to the higher medical costs. Air pollution also reduces agricultural crop and commercial forest yields by billions of Euros each year. Also the increased corrosion of metals and the damage to buildings due to acid rain have a serious impact on the economy. Probably the largest impact on the global economy is the potential effect of global warming, which is very hard to estimate, but can cost billions of Euros.

1.2 WASTE GAS TREATMENT TECHNOLOGIES FOR VOC REDUCTION

1.2.1 Overview

Different waste gas treatment technologies are available to control VOC emissions from stationary sources. These technologies can be classified in two different groups. In the first group the VOC emissions are controlled by modifying the process equipment, the raw material or by changing the actual process in order to prevent or reduce VOC emissions. These technologies are the most effective but their applicability is limited (Khan and Ghoshal, 2000). The waste gas treatment techniques in the second group are "end-of-pipe" techniques where an additional unit process control method is added to the process in order to control the emissions. These "end-of-pipe" removal technologies can be biological and non-biological (i.e. physical-chemical). The biological techniques are destructive methods as the VOC will be degraded by the microorganisms. In the physical-chemical techniques the VOC can be destructed or recovered. An organizational tree diagram presenting the major VOC control techniques is shown in Fig. 1.2. The choice of the most economic "end-of-pipe" waste gas treatment technology for each specific VOC emission is influenced by the concentration range of the VOC, the air flow rates of the waste gas to be treated, the different physical properties of the VOC, the desired efficiency, the VOC sources...

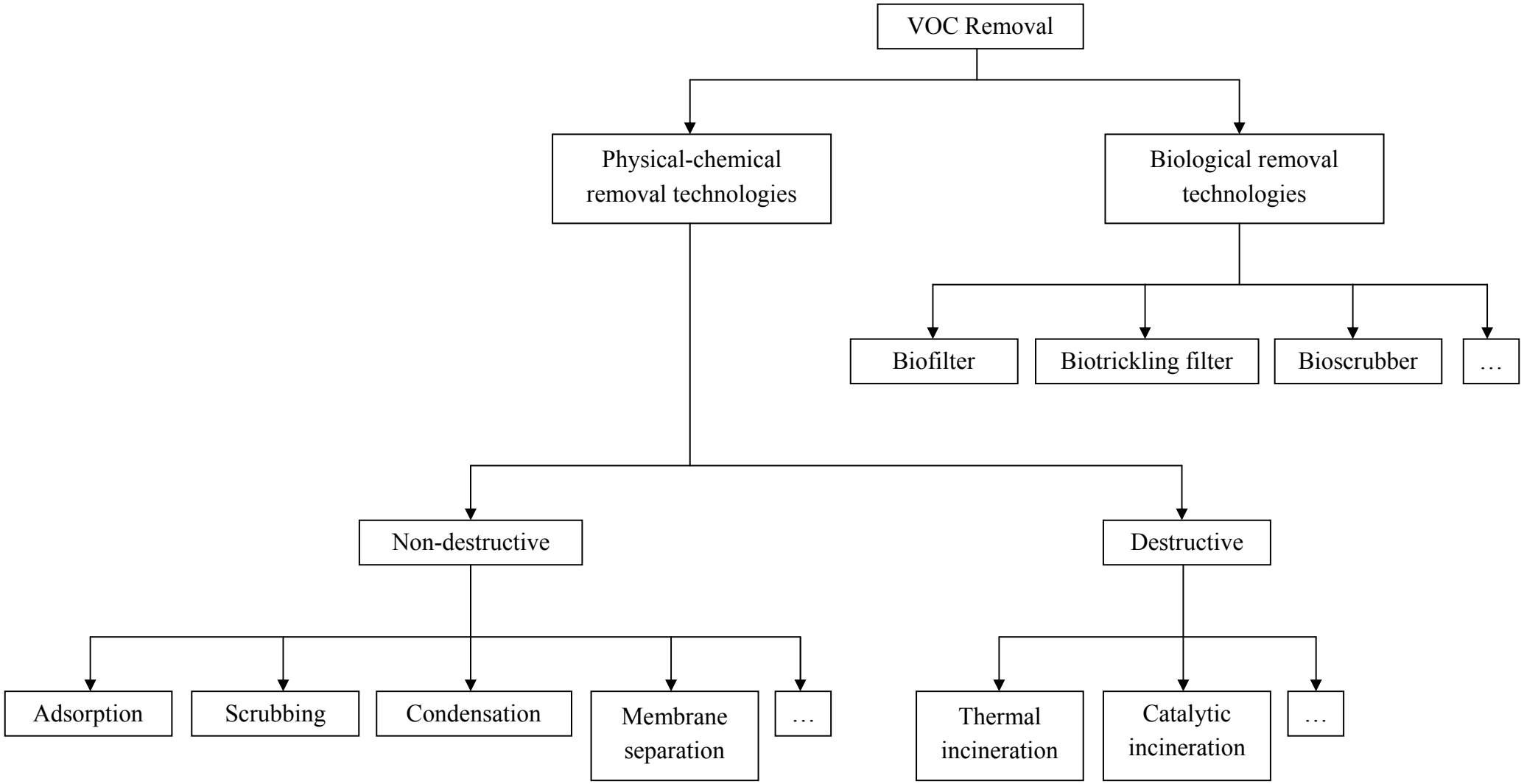


Figure 1.2: Classification of "end-of-pipe" VOC control techniques

1.2.2 Non-biological techniques

The most frequently used non-biological or physical-chemical methods are adsorption, scrubbing, condensation and combustion (Kennes and Thalasso, 1998). These typical non-biological removal technologies can be divided in two groups, i.e., the non-destructive or recovery technologies and the destructive technologies.

1.2.2.1 Non-destructive techniques

Non-destructive technologies such as adsorption and scrubbing are generally based on the transfer of the pollutants from the gas phase to respectively a solid (e.g. activated coal) or liquid phase. In this case, the pollutants can afterwards be recovered from or destroyed in a secondary treatment.

Another way to recover VOC is by condensation. In a condensation system the driving force is oversaturation which can be achieved by an increase in pressure, a reduction of temperature or both. When reducing the temperature, the vapour pressure of the pollutants in the gas flow is reduced. If the vapour pressure drops under the partial pressure of the pollutants, the substance will condense into a mist or droplets. The mist must afterwards be separated from the incondensable gases by a demister. To cool down the gas flow a cold medium (cold wall of a heat exchanger or fluid) can be used. This technique is used for pollutants with a boiling point lower than 40 °C and for concentration higher than 5000 ppm (Khan and Ghoshal, 2000).

During the last years, vapour permeation (VP) by using membrane technologies is well established for VOC removal from gas emissions (Bodzek, 2000; Li et al., 2009). Some types of membranes, e.g. polydimethylsiloxane (PDMS) membranes, can be highly selective and permeable to organic compounds relative to the main air compounds. The VP technique can be used in combination with a condenser to recover VOC from process plant emissions. In this process, the VOC containing air stream is compressed and sent to a condenser, where some of the organic vapour is collected as a liquid for reuse. The non-condensable fraction of the air stream is sent to the membrane module, where it is separated into a permeate stream, being solvent loaded air, and a retentate stream, being solvent depleted air. The permeate, which contains most of the remaining uncondensed VOC, is recycled to the compressor inlet. Compared to a conventional condensation process, this combination achieves higher recovery rates or can be used at higher temperatures, lower pressures, or both in order to obtain comparable recovery rates (less energy consumption).

1.2.2.2 Destructive techniques

In destructive techniques the VOC will be degraded to smaller compounds, mainly carbon dioxide and water. Thermal and catalytic incineration are two largely used destructive air treatment techniques with differences in operative temperature and in combustion chamber design. Thermal oxidation occurs in a combustion chamber at 700 - 1000 °C, while the presence of a catalyst in the catalytic oxidation reduces the reaction temperature to 350 – 500 °C. Both techniques can be applied for VOC inlet concentrations ranging between 100 to 2000 ppm. The efficiency of the destruction depends on the temperature, residence time and turbulence. An additional heat source (e.g. burning of natural gas or oil) is needed to reach the high temperatures in the combustion chamber for complete oxidation, since the combustion process cannot be self-maintained by the low amount of VOC in the polluted air stream. The main disadvantages of these combustion techniques are the possible production of toxic by-products (mainly with thermal oxidation) and the poisoning of the catalysts if sulphur compounds are present in the polluted air stream (with catalytic oxidation) (Busca and Pistarino, 2003; Smet et al., 1998). Also the additional CO_2 production due to the extra heat source is a major drawback.

1.2.3 Biotechniques

Biotechniques for VOC containing waste gas treatment have gained more and more attention, due to the several advantages they offer compared to the more traditional physical and chemical treatment technologies (Mudliar et al., 2010). Not only can these techniques be used at ambient temperatures and pressure, reducing the energetic requirements, they also require less chemicals and the absence of expensive adsorbent materials make the biological treatment technologies more cost-effective. Biological VOC removal technologies include bioreactors known as biofilters, biotrickling filters, bioscrubbers and newer technologies such as membrane bioreactors (MBR) and two-phase partitioning bioreactors (TPPB) (Cox and Deshusses, 1998; Deshusses, 1997a; Kennes et al., 2009). The operation mode for all these reactors is very similar. Polluted air is blown through the bioreactor where the contaminants transfer from the gas phase into the liquid phase. Microorganisms such as bacteria and fungi, which are present in the liquid phase, convert the absorbed biodegradable contaminants into innocuous compounds such as carbon dioxide, salt, water and biomass, which makes these biotechniques environment friendly (Deshusses and Johnson, 2000). In theory, all biodegradable pollutants could be removed in a bioreactor, but the efficiency and suitability is also influenced by non-biological parameter such as the solubility of the compound in the liquid medium (Kennes et al., 2009). Therefore the biological treatment of air polluted

with a mixture of different VOC with different non-biological parameters remains a challenging task.

Figure 1.3 presents the application limits of the major air pollution control technologies (Kennes et al., 2001). As is clear from Fig. 1.3, bioreactors are cost effective approaches to treat contaminated air with a high flow rate and low VOC concentrations on the condition that the compounds to be treated are biodegradable. At higher VOC concentrations, condensation becomes more interesting, as the driving force is oversaturation.

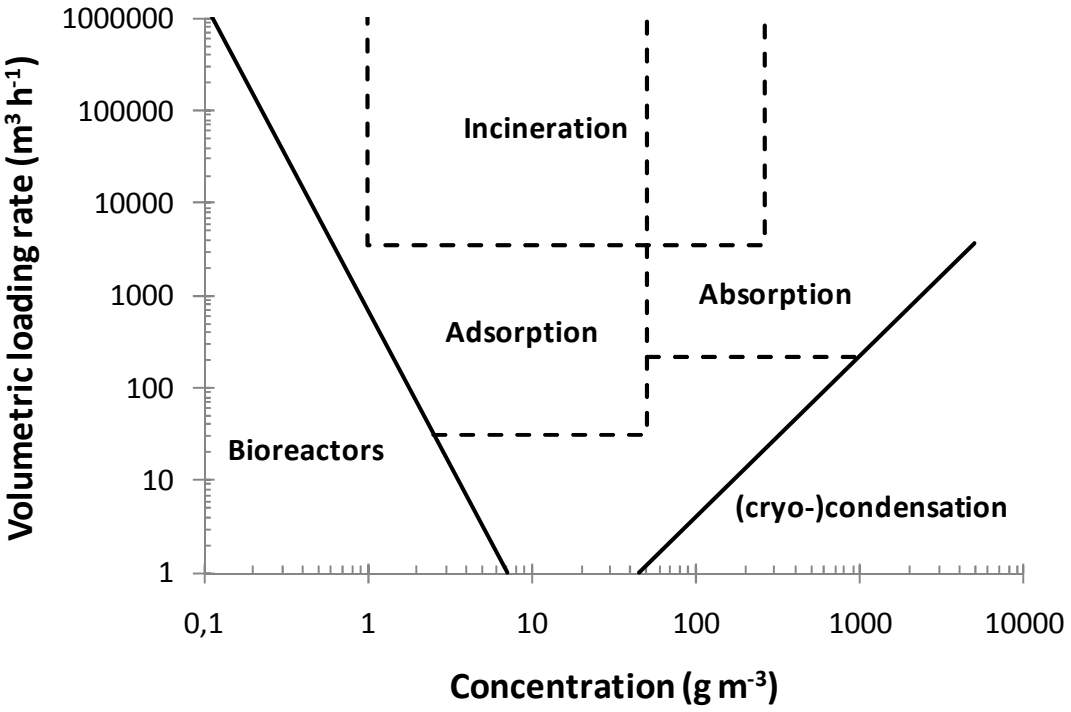


Figure 1.3: Application limit range of major biological and non-biological air pollution control technologies (Kennes et al., 2001).

1.2.3.1 Biofiltration

Biofiltration is the oldest and most popular biotechnique and has now been used for several decades (Kennes and Thalasso, 1998). It was originally developed to treat odorous compounds in waste gases, but more recently biofilters are used for a wide range of organic and inorganic pollutants which are present in different industrial activity emissions. Nowadays biofiltration is a worthy alternative for the conventional physical-chemical air treatment techniques.

In a biofilter, see Fig. 1.4, the contaminated gas is humidified and passed through a fixed bed, which is packed with an organic carrier material. This carrier material acts as surface to immobilize the microorganisms. The biological oxidation of the VOC occurs after they diffused from the gas phase into the biofilm which is covered by a water layer. Biofiltration is an effective and inexpensive method to treat large volumes of low VOC concentrations and is environmental friendly due to the low CO_2 production. The major drawback of biofilters is the difficulty to control the moisture content and the pH. Also clogging of the medium is possible due to the growth of biomass and the presence of particulate matter in the waste air streams (Mudliar et al., 2010).

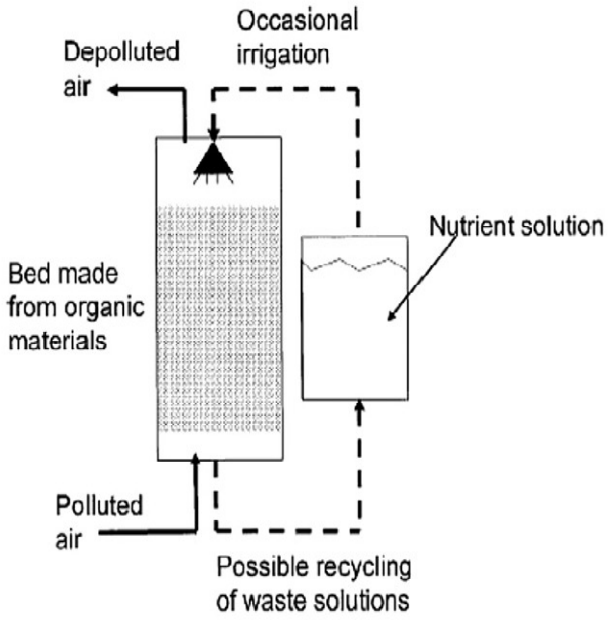


Figure 1.4: Schematic diagram of a biofilter (Delhomenie and Heitz, 2005)

The choice of the organic packing material is a fundamental parameter, as it influences the performance of the biofilter. The packing material needs to provide a high specific surface area for biomass attachment and gas-biofilm exchange. To prevent bed drying, which can cause cracking and by-pass flows in the reactor followed by a decrease in the overall performance (Gostomski et al., 1997), a good water retaining capacity of the filter bed is required. Also the moisture content of the filter bed is an important parameter which plays a key role in the biofilter performance as microorganisms need water for their microbial activities. Too low moisture content leads to a reduction in the biodegradation rate, while excessive water leads to the reduction of oxygen diffusing to the biofilm and reduces the transfer rate of hydrophobic pollutants to the biofilm (Delhomenie and Heitz, 2005). The humidity of the inlet gas, the water retaining capacity of the packing material, the gas flow rate through the bed and the compound degradation by biological oxidation (exothermic reaction) are the factors affecting the bed moisture content. The moisture content should

be about 60 % to maintain a good elimination and microbial growth in a biofilter (Sun et al., 2002). The performance of a biofilter is also influenced by the porosity of the packing material. A high porosity allows a homogenous distribution of the gases through the biofilter and avoids high pressure drops along the bed. The most frequently employed packing materials are peat, soil and compost supplemented with additives such as woodchips or barks, glass beads or polystyrene to increase the stability of the medium and to prevent compaction of the biofilter bed.

The EBRT, defined as the ratio of the volume of the bed to the volumetric air flow rate, is also considered as a critical parameter which can affect the biodegradation performance (Elmrini et al., 2004). By increasing the flow rate the contact time between the biofilter media and the gaseous emissions decreases, which can lead to a decrease in VOC mass transfer to the biofilm and a decrease in biodegradation. According to the literature, a good removal efficiency and biofilter performance can be reached at a residence time which is at least higher than the time required for the diffusion process, especially when dealing with hydrophobic VOC, as the VOC first need to transfer from the gas phase to the biofilm before biodegradation can occur (Berenjian and Malmiri, 2012; Delhomenie and Heitz, 2005).

Partitioning equilibrium of the pollutant between the gas and liquid phases is described by Henry's law, see Eq. (1.8), with C_g is the pollutant concentration in the gas phase (g m^{-3}), C_l the pollutant concentration in the liquid phase (g m^{-3}) and H the dimensionless Henry law coefficient.

$$H = \frac{C_g}{C_l} \tag{1.8}$$

The transfer from the air to the aqueous phase will therefore be harder for pollutants with a high Henry's law coefficients, e.g. hexane. The gas liquid partitioning will also be influenced by the salt concentration, the presence of other compounds in the liquid phase and the temperature (Coquelet et al., 2008; Dacey et al., 1984; Iliuta and Larachi, 2007; Peng and Wan, 1998; Suleimenov and Krupp, 1994). The mass transfer of the pollutants from the gas phase to the biofilm, provides the VOC to the microorganisms to be used as substrate. In order to have an efficient biodegradation, the biofilter needs to support different communities of microorganisms and the activities of microorganisms need to be controlled (Delhomenie and Heitz, 2005; Ralebitso-Senior et al., 2012). Critical parameters which effect the activities of microorganism are pH (Lu et al., 2002), water content (Ranasinghe and Gostomski, 2003; Swanson and Loehr, 1997; van Lith et al.,

1997), nutrients such as N, P and K (Morgenroth et al., 1996) and temperature (Swanson and Loehr, 1997). Most microorganisms in a biofilter prefer a neutral pH, so the ideal pH in a biofilter commonly is around 7. Bacteria are usually more sensitive to pH fluctuations than fungi. Microorganisms which degrade pollutants containing S, Cl and N convert them into acid by-products; which reduce the pH of the biofilter medium and can reduce the biofilter performance. Among the packing materials used in the biofilter, the best pH buffering capacity is reached by soil, followed by compost and peat (Kennes and Thalasso, 1998; Smet et al., 1996).

The main advantages of a biofilter setup are the low initial investment and operating costs, the easy way to operate and maintain the system, the ability to degrade a wide range of compounds with efficiencies higher than 90 % for low contaminant concentrations and the lack of additional waste products. The major disadvantages are the large footprint of the bioreactor, the lower efficiency at higher concentration levels of the pollutant, the limited life time and possible clogging of the packing material and the need to follow up the operating conditions (pH, temperature, humidity...).

1.2.3.2 Biotrickling filtration

Biotrickling filtration gained more and more attention during the last decades, leading to an increase of industrial applications (Kennes et al., 2009). In biotrickling filters, the gas flows through a packed bed, while a liquid solution containing the nutrients is continuously irrigated and recirculated over the packed bed, see Fig. 1.5.

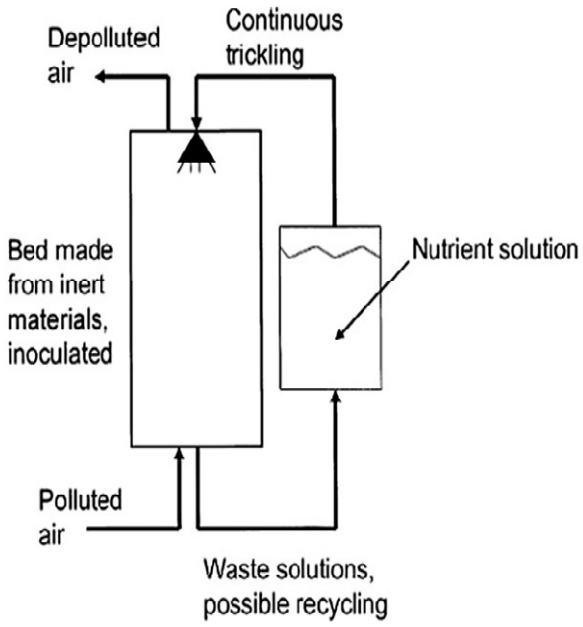


Figure 1.5: Schematic diagram of a biotrickling filter (Delhomenie and Heitz, 2005)

The packed bed is usually filled with a chemically inert carrier material such as plastic rings, synthetic resins, polyurethane foam… This inert packing material usually has a high porosity in order to avoid high pressure drops and clogging of the filter. The pollutants are initially absorbed in the liquid solution and further degraded by the microorganisms in the biofilm which is immobilized on the packing material. This concept allows a better control of the operating parameters (nutrients, pH, temperature) than for a biofilter by the continuous distribution of the nutrient solution. The major drawbacks of biotrickling filters are firstly, the limited applicability of biotrickling filters to good water soluble pollutants (H < 1) and low concentrations of VOC. Secondly, the accumulation of excess biomass in the filter bed, resulting in an increase of biofilm thickness which can cause problems such as clogging and increasing pressure drops.

1.2.3.3 Bioscrubbing

A bioscrubber, see Fig. 1.6, consists of two separate, but interconnected units: a scrubber unit and an activated sludge system or a bioreactor. In the scrubber unit, the contaminated gas is put in contact with an aqueous solution which is sprayed over the synthetic packing material. This results in the transfer of the pollutants from the gas phase into the liquid phase. The washed gaseous phase is discharged at the top of the column while the contaminated liquid phase is pumped towards a bioreactor where the absorbed pollutants are degraded by microorganisms. These microorganisms grow in suspended flocs in the aqueous phase. Before recycling the nutrient solution back over the absorption column, the biomass is first separated from the aqueous solution and purged or recycled to the bioreactor.

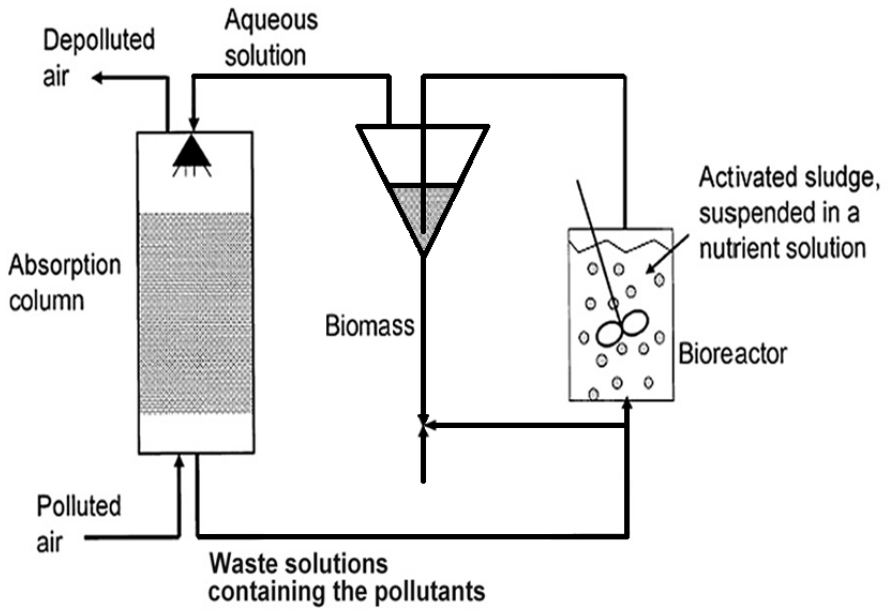


Figure 1.6: Schematic diagram of a bioscrubber (based on Delhomenie and Heitz, 2005)

Bioscrubbers are very suitable for highly water soluble pollutants since absorption of the pollutant in the liquid phase based on air-aqueous mass transport is necessary. The main advantage of the bioscrubber is the possibility to control the operating parameters such as pH, temperature and nutrients better than for a biofilter. A limitation of bioscrubbers is the quite low specific surface area for liquid/gas transfer (Delhomenie and Heitz, 2005; Kennes et al., 2009). The synthetic packing material used in bioscrubbers needs to maximize the mass transfer from the air to the liquid phase, but also maintains a low pressure drop. (Shareefdeen and Singh, 2005).

1.2.3.4 Membrane bioreactor

The last two decades there has been *a significant growth* in the industrial *applications* of membrane technology. Membrane systems are now available in several different forms and sizes and can be used for a number of different, very characteristic separation processes. Some of the advantages of this separation system over the traditional techniques are the small footprint, the selectivity towards the process and the use of one universal design for all different situations. In wastewater treatment plants, membrane bioreactors are already commonly applied in order to separate the clean water from the actual bioreactor using a selectively permeable membrane with pores sized to permit the passage of water molecules, but small enough to retain a wide range of particulates, sludge and dissolved compounds. The application of membrane bioreactors for air treatment is gaining more interest and different membrane bioreactor configurations have already been used at lab-scale. (Álvarez-Hornos et al., 2011, 2012; De Bo et al., 2003; Kim and Kim, 2005; Kumar et al., 2009; Lebrero et al., 2013b). The choice of the applied module configuration depends generally on economics, compactness of the system and ease of operation, cleaning and maintenance. A flat sheet membrane has a low packing density (< 100 - 400 m^2 m^{-3}), but has a low fouling tendency and is easy to clean, while a hollow fibre membrane has a very high packing density (< 30000 m^2 m^{-3}), but has a very high fouling tendency and is very hard to clean.

In a MBR used for air treatment, the liquid side of the reactor will be separated from the gas side by using a dense or composite membrane. At the liquid side of the MBR an aqueous phase containing nutrients and inoculated with microorganisms is recirculated continuously. At the gas side a polluted air stream is fed to the reactor and the gaseous pollutants will diffuse through the membrane, where they will be degraded by the biofilm attached on the membrane surface or by the microorganisms in suspension. The flux of the different pollutants over the membrane can be described by Eq. (1.9), with F the mass flux of the compound through the membrane (g s^{-1}), K_{ov} the overall mass transfer

coefficient (m s^{-1}), A the membrane surface area (m^2), H the dimensionless air-water partition coefficient or Henry law coefficient (g m^{-3}/g m^{-3}) and C_g and C_l respectively the concentration in the gas and liquid phase (Reij et al., 1998).

$$F = K_{ov} \cdot A \cdot \left(\frac{C_g}{H} - C_l \right) \tag{1.9}$$

In this case, the driving force for the compounds to diffuse through the membrane is based on a concentration gradient between the liquid phase and the gas phase. This driving force highly depends on the air-liquid partitioning coefficient of the pollutant. The driving force for a pollutant with a low H value will be higher than the driving force for a compound with a high H value. Also the microbial activity will influence the driving force, as C_l decreases with increasing bioactivity. The overall mass transfer resistance, $1/K_{ov}$, is a combination of the resistance in the gas phase $1/k_g$, membrane $1/k_m$, biofilm $1/k_b$ and liquid phase $1/k_l$, see Fig. 1.7 (Kumar, 2010).

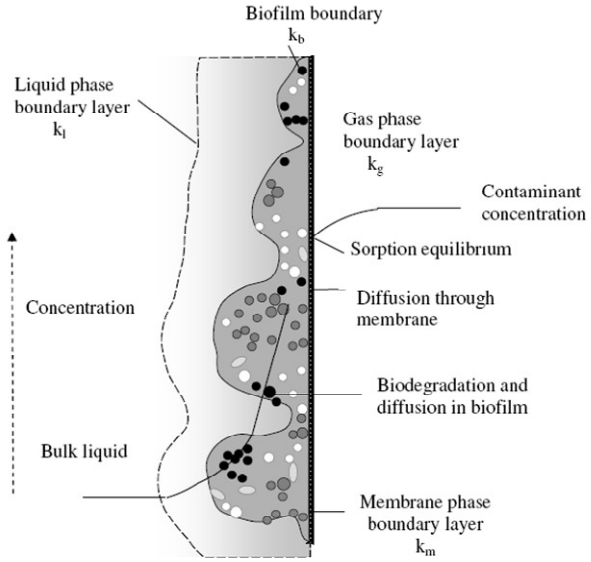


Figure 1.7: Mechanism of a membrane based biological waste gas treatment (Kumar, 2010).

The main advantage of a MBR is the easy way to control the microbial degradation process (pH, nutrients, temperature), due to the continuous recirculation of the aqueous phase and the independent control of gas and liquid phase. Other advantages are the high specific surface area, the low pressure drop and the absence of preferential flowing. The high selectivity of the membrane material can enhance the potential to eliminate VOC characterized by poor water solubility, by lack of biodegradability and by toxicity (Reij et

al., 1998). Some hydrophobic membrane materials such as PDMS or polyolefin can increase the mass transfer of poorly water soluble compounds. Possible disadvantages of a MBR are the high investment costs, the additional mass transfer resistance caused by the membrane, a decreased biofilm activity as the biofilm ages and clumping and clogging of hollow fibre membranes at high biofilm growth.

Different lab-scale studies have already indicated the good performance of a MBR for the biodegradation of a wide range of VOC with different hydrophobicity (Kumar et al., 2008), but studies on the performance of a MBR for the removal of mixtures is scarce. Therefore this thesis will focus on the removal of a VOC mixture out of a waste air stream using a MBR.

1.2.3.5 Two-phase partitioning bioreactor

Another emerging technique for the removal of both hydrophilic and hydrophobic compounds is the TPPB (Dumont et al., 2013). This biotechnique is based on the addition of a NAP to the bioreactor in order to increase the low transfer rates of hydrophobic gaseous pollutants from the gaseous phase to the microorganisms, which is one of the main limitation of the current biological air treatment techniques (Hernández et al., 2012). The use of a with water immiscible and biocompatible organic solvent, e.g. silicone oil, helps to increase the driving force for especially hydrophobic compounds to transfer from the gas phase to the microorganisms and can reduce the exposure of the microorganisms to inhibitory substances by lowering their concentrations in the aqueous phase (Muñoz et al., 2007). Due to the addition of a NAP a part of the polluted emissions will absorb in the NAP, so higher amounts of toxic organic substrates can be fed to the bioreactor as the cells in the aqueous phase are only exposed to very low concentrations (Daugulis, 2001). A suitable NAP should be inexpensive, not biodegradable, not toxic for the microbial community and form a good emulsion with water.

The construction of the TPPB is done in such a way that the bioreactor is mechanically stirred to ensure a good emulsion of the aqueous phase and the NAP. In conventional systems (biofilter, biotrickling filter and bioscrubber), the VOC removal of hydrophobic compounds is limited by the slow substrate transfer to the aqueous phase, see Fig. 1.8(a). In a TPPB, see Fig. 1.8(b), hydrophobic compounds can easily transfer from the gaseous phase to the NAP, while the substrate concentration in the aqueous phase is maintained at a very low level due to microbial cultures. This increases the overall transfer from the pollutants to the aqueous phase. Some microorganisms can even adhere to the non-aqueous phase and directly take up the contaminants without transferring first to the aqueous phase (Muñoz et al., 2007).

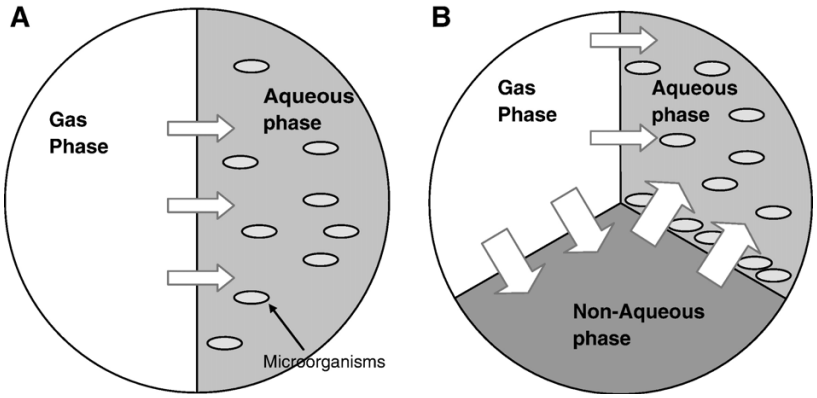


Figure 1.8: Hydrophobic VOCs and O_2 in bioreactors. A is conventional bioreactor without organic phase and B is the two-phase partitioning bioreactor (TPPB) (Muñoz et al., 2007).

Some advantages of the TPPB in contrast to conventional bioreactors are that the TPPB configuration makes use of the entire bioreactor volume, as there is no packing material which occupies a big part of the reactor volume (McNevin and Barford, 2000), the magnetic stirrer helps in efficient control of the environmental conditions (pH, temperature, nutrients) and prevents the overgrowth of biomass, the bioreactor can be loaded with very large quantities of pollutants without risks of microbial inhibition and the reactor is suitable to treat hydrophobic compounds (Muñoz et al., 2007). Next to this, the addition of a NAP will also decrease the competitive inhibition. Micro-organism which are able to degrade several compounds, will always first degrade the most available compound, but by adding a NAP to the reactor the availability of hydrophobic compounds will increase, followed by an increase in the removal efficiency for these compounds.

1.3 MICROBIOLOGICAL ASPECTS OF BIOLOGICAL AIR TREATMENT

In a bioreactor for waste air treatment, biomass is acting as a catalyst in the different oxidation processes. Therefore it is important to have more insight on its behaviour, metabolism and growth in the different bioreactors. In a bioreactor, the biomass can be provided by inoculation or by an organic carrier. In a biofilter, the organic packing material normally contains a high number of different microorganisms that can adapt to the applied conditions, so no inoculation is necessary to reach a sufficient removal of the

different pollutants, but sometimes inoculation with a specific culture can be recommended to decrease the adaptation period and even increase the reactor performance. Next to this, the packing material can provide the nutrients needed for the microorganisms to reach a good performance (Kennes and Thalasso, 1998). In a biotrickling filter inoculation is always necessary to provide a high density of non-specific or specially selected microorganisms on the synthetic packing material. Inoculation with a single culture can be beneficial for the reduction of some specific VOC, but is very hard to use on industrial scale, due to the lower stability and flexibility towards pH, temperature and load changes. Mixed cultures confer a much higher robustness to biological gas treatment systems (Cabrol and Malhautier, 2011).

The last decades an increasing number of studies are performed, investigating the microbiology in bioreactors. A lot of these studies deal with the isolation and identification of microbial groups and species, but knowledge about the interaction between these different groups and the influence of the microbiology on the reactor performance is limited. Fungi and bacteria are the most common microorganisms inside a bioreactor. Bacteria have a higher substrate consumption and growth rate, while fungi are more resistant to low water activity and acid conditions, develop aerial structures, hyphae, which provide a large surface area allowing a direct mass transfer of the pollutant from the gas phase into the biological phase (Spigno and De Faveri, 2005; van Groenestijn et al., 2001) and contain many species capable of hydrocarbon degradation, e.g. the fungi *Fusarium solani* (Arriaga and Revah, 2005b) and *Aspergillus niger* (Spigno et al., 2003) are able to degrade hexane. Although hexane is very poorly water soluble and hardly metabolized because of its short hydrocarbon chain, bacteria belonging to the class of Actinomycetes like *Rhodococcus ruber* can use hexane as a carbon source (Amouric et al., 2006). Another species which can often be found in bioreactors is *Rhodococcus phenolicus* which is capable of degrading aromatic compounds like toluene and ethylbenzene (Rehfuss and Urban, 2005). Similarly, microorganisms belonging to the *Mycobacterium* genus, which are known as slow-growing bacteria and are able to degrade toluene at low concentrations (Juteau et al., 1999). Member of the *Chlamydiae phylum* were also found in a bioreactor treating gaseous toluene (Estrada et al., 2012). Previous literature studies have detected members of the *Dokdonella* genus in bioreactors treating sulfurous compounds like DMS, ammonia and VOCs (Maestre et al., 2010; Lebrero et al., 2012).

The biomass attached on the packing material constitutes the biofilm and generally has a rugged, mushroom-like shape under relatively low shearing forces (Engesser and Plaggemeier, 2000). The development of a biofilm occurs in 5 steps: (i) the initial attachment of the microbial cells to the surface of the packing material; (ii) the production

of exopolymeric substances which results in a firm irreversible adhesion; (iii) early development of the biofilm structure; (iv) maturation of the biofilm structure and (v) dispersion of cells out of the biofilm. A mature biofilm is indicated by the complex biofilm architecture which consists out of a various number of bacterial microcolonies. These microbial communities are dynamic in space and time in terms of density, diversity and structure (Cabrol and Malhautier, 2011). Some regions of the biofilm can be less dense allowing water and gas channels to penetrate deep inside the complex community, which enables nutrient, oxygen and substrate transport to these regions (Stoodley et al., 2002). The spatial and temporal dynamics of the microcolonies are both correlated and uncoupled to the ecosystem functions in literature, depending on the analytical tool used to explore the microbial diversity, the way of calculating the diversity, similarity and stability, the time scale and the specific function and population which are targeted (Cabrol and Malhautier, 2011; Cabrol et al., 2012a). The diversity and relative abundance of the different microbial communities may also be influenced by the composition of the emission and the environmental operating conditions such as pH, temperature, moisture content and packing material (Ding et al., 2008). Microbial diversity is often analysed before and after an experiment, due to sampling, budgetary or time-limit constrains, but the community which colonized the bioreactor can be completely different from the initial communities (Cabrol et al., 2012b), so conclusions found in literature must be considered with caution. Significant temporal microbial community dynamics can already occur at relatively stable operating conditions, but the initial diversity will be determined for the selection of the most fitted community (Cabrol et al., 2012b; Li and Moe, 2004).

The main group of microorganisms in a bioreactor are aerobic which means that they use O_2 as electron acceptor for their own metabolism. The VOC which are fed to the reactor are used as carbon source and will mainly be transformed to CO_2, H_2O, biomass and energy through mineralization, partial oxidation or co-metabolic degradation (especially for chlorinated organics). Microbial growth in a bioreactor is very important as an excessive increase in biomass can reduce the reactor performance, due to clogging, by-pass flows and increasing pressure drop. This growth rate depends of the inlet load, temperature, pH and the presence of toxic or inhibitory substances. The rate of VOC utilization at any point within the biofilm, r, is assumed to follow the Monod kinetic, see Eq. (1.10), which is analogous to the Michaelis–Menten theory for enzyme activity with Km, the half-saturation constant (g m^{-3}), μ_m the maximal growth rate (g new cells g $cells^{-1}$ d^{-1}) and C the VOC concentration (g m^{-3}).

$$\mu = \mu_m \cdot \frac{C}{Km + C} \tag{1.10}$$

As the bacteria are growing at the maximal rate, the substrate will also be consumed at the maximal rate, so the maximal growth rate of the bacteria, μ_m, is related to the maximal volumetric elimination rate, r_m (g m^{-3} h^{-1}), and this by Eq. (1.11) with X the biomass concentration (g m^{-3}) and Y the biomass yield coefficient (g g^{-1}).

$$r_m = \frac{\mu_m \cdot X}{Y} \tag{1.11}$$

At steady-state conditions, the kinetic parameters X, Y will be constant, so when C >> Km, the kinetic order approximates zero, resulting in a constant growth rate equal to μ_m and elimination rate equal to r_m. In these conditions the growth-rate is independent of the VOC concentration. If C << Km, the growth-rate follows a first-order kinetic.

1.4 CONCLUSIONS AND OUTLOOK

The use of biotechnologies for waste air treatment has increased during the last decades, which resulted in a large amount of data and additional knowledge. A lot of research has been done to determine the influence of variable operating parameters on the reactor performance and to get more insight in the microbial ecology, but these studies also encountered some limitations, which gives room for further research.

In order to find practical applications for the biodiversity-ecosystem function relationship in bioreactors, it will be necessary to perform more research focusing on the active and functional populations which are actually involved in the compound degradation (Cabrol and Malhautier, 2011). This thesis will mainly focus on the analytical and process limitations, so the limitations in microbial knowledge and analysis techniques will not be discussed further in this research.

To reduce the analytical limitations, a new analytical technique, selected ion flow tube mass spectrometry, was used, which made it possible to measure concentrations online and to get more insight on the immediate response of a bioreactor on condition changes.

One of the major process limitations for biological air treatment technologies is the high residence time in comparison with other physical-chemical techniques like thermal and catalytic incineration, especially when treating a mixture containing hydrophobic compounds. Therefore a second focus of this study revolves around improving existing

biotechniques and searching for new, innovative treatment technologies in order to improve the removal of VOC mixtures.

Chapter 2 Ethyl benzene removal under mesophilic conditions in a biofilter with *Macadamia ternifolia* nutshells as a carrier material[a]

SUMMARY

Biofilters are suitable to treat industrial emissions polluted with VOC, responsible for photochemical smog and the depletion of the ozone layer. This study analyzes the performance of a biofilter with *Macadamia ternifolia* nutshells as a carrier material treating air streams contaminated with ethyl benzene under mesophilic conditions with continuous feeding.

The biofilter was operated continuously during 5 months applying several IL, EBRT and temperatures. At a temperature of 303 ± 1 K removal efficiencies (RE) higher than 90 % were obtained for IL lower than 85.6 g m^{-3} h^{-1} and 70.6 g m^{-3} h^{-1} at EBRT of 150 and 90 s respectively. The yield coefficient resulted in 0.73 g of dry biomass formed per g of ethyl benzene degraded. The half-saturation constant Km and maximal volumetric elimination rate r_m were calculated for EBRT of 90 s, Km = 0.28 ± 0.09 g m^{-3} and r_m = 89 ± 11 g m^{-3} h^{-1}, and 150 s, Km = 0.72 ± 0.18 g m^{-3} and r_m = 117 ± 15 g m^{-3} h^{-1}.

[a]Redrafted after Volckaert, D., Álvarez-Hornos, F.J., Heynderickx, P.M., Kittikoon, C., Van Langenhove, H. 2013. Ethylbenzene removal under mesophilic conditions in a biofilter with *Macadamia ternifolia* nutshells as a carrier material. J. Chem. Technol. Biotechnol., 88(1), 81-87.

From the presented experimental data, a biofilter with *Macadamia ternifolia* nutshells (waste material in Thailand) as a carrier material is considered to be a good option for air treatment in tropical areas with typical temperatures varying from 292 to 313 K, using ethyl benzene as a test substrate.

2.1 INTRODUCTION

Gaseous emissions of industrial plants, such as wastewater treatment plants (Lebrero et al., 2011) and paint industry (Paca et al., 2010), contain VOC, which are characterized by a vapour pressure of 10 Pa or higher (at 293 K). These emissions can affect the environment as well as the human health. For this reason, environmental regulations became stricter over the past decades to lower the emissions of VOC from industrial sources. In tropical areas such as Thailand, the air pollution by VOC is a real problem, so it would be a benefit if biofiltration could be implemented in such a climate conditions.

Biofiltration is a very attractive technique for VOC removal of waste air streams with low VOC concentrations and high flow rates, because of its simplicity, the low cost and the harmless residues (Álvarez-Hornos et al., 2007; Kennes et al., 2009). Several studies have proven the possibility of VOC removal in biofilters, biotrickling filters and membrane bioreactors at mesophilic temperatures, usually with the application of inoculation (Álvarez-Hornos et al., 2011; Leson and Winer, 1991; Sercu et al., 2006; Sercu et al., 2005a). In these techniques microorganisms are used to degrade the pollutants present in the waste air. In addition these techniques have been classified as Best Available Techniques (BAT) for the abatement of low VOC concentration waste gas streams in the chemical sector by the European IPPC Bureau (EU, 1999).

Previous studies of ethyl benzene (EB) removal in biofilters were focused on evaluating the performance of the system at ambient temperature and with conventional packing materials such as peat, compost and soil (Álvarez-Hornos et al., 2008a; Kennes and Thalasso, 1998; Son and Striebig, 2001). The present laboratory study was set up to explore the potential use of a biofilter at tropical conditions, typical for Thailand, with EB as pollutant, one of the VOC largely emitted by the Thai industry (Sarawut, 2006). Macadamia (*Macadamia ternifolia*) nutshells, a local waste product, were used as a carrier material at a working temperature of 303 K, the average overall temperature in Thailand (Sootsukon et al., 2000). An advantage of the nutshells is the ability to release co-substrates which are able to support microbial growth on the packing material. In addition

the macadamia nutshells have a high resistance to VOC attack and can therefore be used longer in a bioreactor than the more conventional support materials like peat, compost, woodchips… (Lebrero et al., 2014). To illustrate the effect of temperature variation in the mesophilic range on the reactor performance, the biofilter was also operated at temperatures ranging from 292 to 313 K. To measure the biofilter activity over the reactor depth, the biofilter was designed with several axial sampling ports, so an axial concentration profile through the reactor could be recorded. An important trend in biofiltration is to determine the biokinetic parameters by using existing models (Chiu et al., 2006; Delhomenie et al., 2002; Mohseni and Allen, 2000; Prenafeta-Boldú et al., 2008), as these parameters may differ considerably with those found in literature depending on the experimental conditions in which the parameters were obtained.

The goal of this work was threefold. First, to research the potential of the macadamia nutshells to be used as a carrier material in a biofilter. Second, to check the influence of the temperature, corresponding to typical temperatures in Thailand on the reactor performance. Third, to study the degradation performance of the biofilter with EB as a test substrate by acquisition of axial concentration profiles along the bioreactor depth as well as the CO_2 production. These experimental data were fitted to a mathematical model based on the Michaelis-Menten theory for enzyme activity in order to determine typical biokinetic parameters. Further, a significant analysis of the biofilter degradation data against data from other similar studies was performed.

2.2 MATERIALS AND METHODS

2.2.1 Characterization of packing material

The macadamia nutshells used in the experiments were waste from the macadamia nut production of 2010 at the Royal Agricultural Station Doi Tung, Chiangrai, Thailand. The nutshells were crushed and screened for sizes between 7 to 13 mm, which was at least 8 times smaller than the diameter of the reactor, 104 mm, in order to avoid preferential flow along the reactor walls (Heynderickx et al., 2009). The shells were still big enough to prevent a high increase of pressure drop through the reactor. During the experiment the maximal pressure drop along the complete reactor depth remained under the 1 kPa m^{-1} which is relatively low to the pressure drops of 1.4 to 20 kPa m^{-1} observed in other biofilters with typical organic packing materials at long operation periods (Estrada et al., 2013).

Several physical-chemical properties of the macadamia nutshells were measured. The moisture content of the packing material was determined by Eq. (2.1), with m_N and m_{DN} the mass of the nutshells at ambient conditions and the mass of the dry nutshells after 24 hours drying in an oven at 383 K, respectively:

$$\text{Moisture content} = \frac{m_N - m_{DN}}{m_N} \cdot 100 \tag{2.1}$$

In order to obtain the density of the macadamia nutshell material, Eq. (2.2) was used in ambient conditions with m_{BN} and m_{BNW} the mass of the bottle only containing nutshells and the mass of the bottle filled with nutshells and water. V_B represents the volume of the bottle.

$$\rho_{nutshells} = \frac{m_N}{V_B - \frac{(m_{BNW} - m_{BN})}{\rho_{H_2O}}} \tag{2.2}$$

The apparent (bulk) density was determined by putting a given mass of nutshells into a volume of known dimensions.

By applying Eq. (2.3) the water retaining capacity of the nutshells was measured with m_W the mass of the water poured over the dried nutshells and m_{NW} the mass of the nutshells 10 min after pouring the water, to measure the retained water:

$$\text{Water retaining capacity} = \frac{m_{NW} - m_{DN}}{m_W} \cdot 100 \tag{2.3}$$

The ash content was determined by Eq. (2.4) with m_N the mass of the nutshells at ambient conditions which were put in a crucible, that was preheated during 6 hours at 393 K, and m_{ash} the mass of the ash that remained after placing the nutshells in a furnace at 973 K for 12 hours:

$$\text{Ash content} = \frac{m_{ash}}{m_N} \cdot 100 \tag{2.4}$$

2.2.2 Biofilter reactor

The bioreactor was constructed with 6 identical, cylindrical modules of Plexiglas and had a total length of 1.0 m and an internal diameter of 0.1 m, which resulted in a total bed volume of 7.85 l. Over the complete length of the reactor there were 7 different sampling ports to measure the VOC and the CO_2 gas concentrations, i.e., inlet, outlet and 5 intermediate ports as shown in Fig. 2.1.

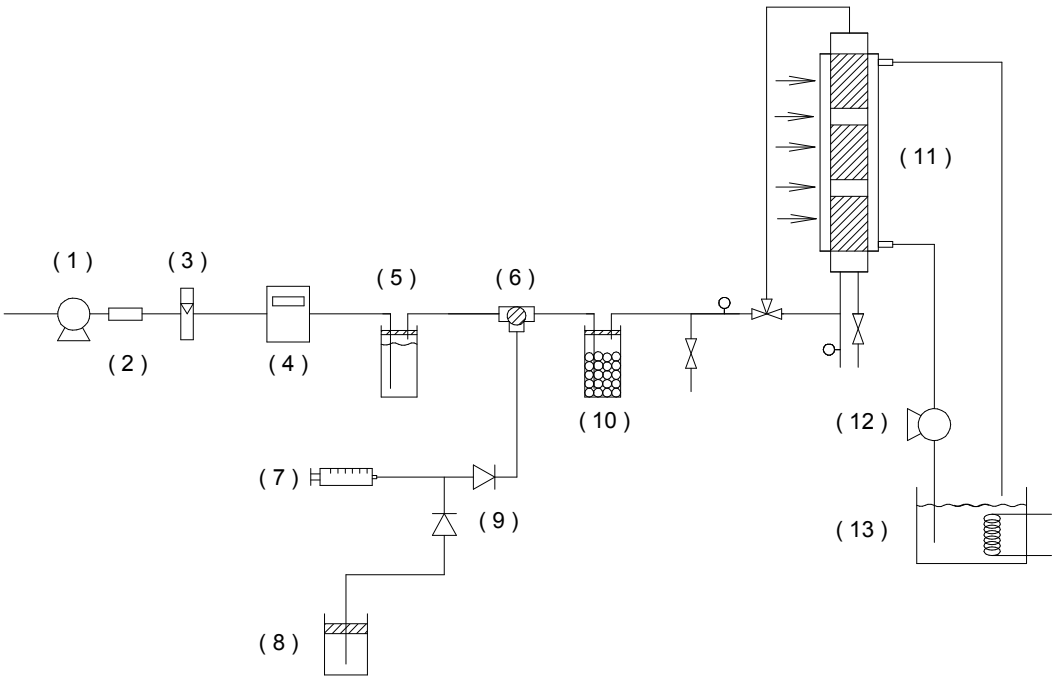


Figure 2.1: Schematic diagram of biofilter. Arrows indicate the position of sampling points. (1) Air pump, (2) mass flow controller, (3) read-out unit, (4) flow meter, (5) humidifier, (6) T-piece, (7) syringe pump, (8) ethylbenzene, (9) one way valves, (10) gas mix bottle, (11) biofilter with water jacket, (12) liquid pump, (13) heated water bath.

Crushed macadamia nutshells (7 < size < 13 mm) were used as biofilter media on which the microorganisms could grow. The temperature in the biofilter was controlled by a water jacket. Humidified air, polluted with the VOC by using a syringe pump (New Era, infusion/withdraw NE 1000 Model), was pumped through the biofilter from top to bottom with flow rates ranging between 0.19 and 0.31 $Nm^3\ h^{-1}$. Due to the higher working temperature (303 K) and the low water retaining capacity of the macadamia nutshells, it was necessary to humidify the column twice a day. The nutrients were added once a day. Both nutrients and water, were added at the top of the reactor. 80 % of the leachate (160 ml a day) was recycled to humidify the reactor, while 20 % (40 ml a day) was purged. The necessary macro and micronutrients were incorporated using a pH buffered nutrient solution (pH 7) containing KNO_3, 10.7 g L^{-1}, KH_2PO_4, 3.0 g L^{-1}, K_2HPO_4, 3.0 g L^{-1},

$MgSO_4 \cdot 7H_2O$, 0.5 g L^{-1}, P, Ca, Fe, Zn, Co, Mn, Mo, Ni, B and vitamins at trace doses. The volume of nutrients added was kept at a C:N:P ratio of 100:5:1(Shareefdeen and Singh, 2005). This ratio was weekly checked by measuring the nutrients in the leachate, i.e., total phosphate, total nitrogen and nitrate concentrations. The activated sludge used to inoculate the reactor came from a wastewater treatment plant (Ossemeersen, Ghent) and was first preadapted during 2 weeks by adding only EB as carbon source for the sludge in order to acclimate the mix of microbes in the sludge.

2.2.3 Process conditions

The biofilter was operated continuously during 5 months in which VOC gas concentrations were applied ranging from 0.5 to 3.0 g_{EB} Nm^{-3}. The applied operational conditions are summarized in Table 2.1. Two experiments (Exp1 and Exp2) were conducted to analyze the effect of the EBRT on the performance of the biofilter at 303 K. From Exp1(A to D) the biofilter was operated under continuous (without interruption of the inlet load) and stationary (constant inlet load for long periods) loading during 2 months with a gas EBRT of 150 s and EB inlet concentrations varying from 0.5 g Nm^{-3} to 3.0 g Nm^{-3} at 303 K. In the next 2 months, Exp2(A to C), a variation of EB inlet concentrations from 0.5 g Nm^{-3} to 2.0 g Nm^{-3} was used at an EBRT of 90 s and 303 K. In Exp3 the temperature of the biofilter was varied from 303 ± 1 K to 292 ± 1, 299 ± 1 and 313 ± 1 K using an external, heated water jacket and with a constant EB inlet concentration of 2.0 g Nm^{-3} and an EBRT of 90 s.

Table 2.1: Operational parameters for biofilter experiments.

	Exp1				**Exp2**			**Exp3**		
	A	**B**	**C**	**D**	**A**	**B**	**C**	**A**	**B**	**C**
C_{EB} (g Nm^{-3})	0.5	1.0	2.0	3.0	0.5	1.0	2.0	2.0	2.0	2.0
IL (g m^{-3} h^{-1})	12	24	48	72	20	40	80	80	80	80
EBRT (s)	150	150	150	150	90	90	90	90	90	90
T (K)	303 ± 1	303 ± 1	303 ± 1	303 ± 1	303 ± 1	303 ± 1	303 ± 1	292 ± 1	299 ± 1	313 ± 1

The empty bed residence time, EBRT (s), the removal efficiency, RE (%), the inlet load, IL (g m^{-3} h^{-1}), the elimination capacity, EC (g m^{-3} h^{-1}), and the produced CO_2 (g m^{-3} h^{-1}), were determined using the relationships between the inlet and outlet VOC concentration, C_{in} and C_{out} (g Nm^{-3}), the inlet and outlet CO_2 concentration, $C_{CO_2,in}$ and $C_{CO_2,out}$ (g CO_2 Nm^{-3}), the gas flow rate, Q (Nm^3 h^{-1}) and the total reactor volume V (m^3), respectively described by Eqs. (2.5) to (2.9):

$$RE = 100 \cdot \left(1 - \frac{C_{out}}{C_{in}}\right) \tag{2.5}$$

$$EBRT = \frac{V}{Q} \tag{2.6}$$

$$IL = \frac{C_{in}}{EBRT} \tag{2.7}$$

$$EC = \frac{C_{in} - C_{out}}{EBRT} \tag{2.8}$$

$$Produced\,CO_2 = \frac{C_{CO_2,out} - C_{CO_2,in}}{EBRT} \tag{2.9}$$

2.2.4 Analytical techniques

The EB concentration in the gas flow at the inlet, outlet and 5 intermediate sampling ports of the biofilter were monitored daily by taking gas samples of 500 µl using a 1.0 ml GASTIGHT® syringe at each measuring point. Analysis of the samples were performed by using a FID gas chromatograph (6890 Series, Agilent Technologies, USA) equipped with an HP-5 capillary column (30 m × 0.32 mm × 0.25 µm, Agilent Technologies, USA) and He was used as carrier gas at a flow rate of 2.3 cm^3 min^{-1}. Temperatures for the injector, oven and detector were respectively 573, 308 and 523 K. The CO_2 gas concentration at the several measuring points was determined by using a CARBOCAP® carbon dioxide analyser (GM70 model, Vaisala, Finland). Also the pressure over the different sampling ports was monitored daily (Testo 511). The pH, conductivity (Hanna Instruments, HI98312), suspended solid and dissolved oxygen (WTW Oxi3210) in the leachate were monitored weekly. COD, total phosphate, total nitrogen and nitrate concentrations in the leachate were also measured weekly with Nanocolor® tube tests (Macherey–Nagel, Germany).

2.3 RESULTS AND DISCUSSION

2.3.1 Macadamia nutshell properties

According to Eqs. (2.1) and (2.3) the average of the macadamia nutshells' moisture content was measured to be 7 w/w% and the water retaining capacity 17 w/w%. These values are quite low compared with regular packing materials, see Table 2.2.

Table 2.2: Summary and comparison of packing material properties.

	Fibrous peat	**Compost**	***Macadamia ternifolia* nutshells**
Moisture content (w/w%)	68 [a]	65 [b]	7
Water retaining capacity (w/w%)	88 [c]	70 [d]	17
Density (g ml^{-1})	0.13 [c]	1.10 [b]	1.30
Ash content (w/w%)	5 [c]	22 [e]	22

[a] (Van Langenhove et al., 1986); [b] (Morgan-Sagastume and Noyola, 2006); [c] (Álvarez-Hornos et al., 2008a); [d] (Oh et al., 2009); [e] (Abumaizar et al., 1998)

To compensate for the low moisture content and water retaining capacity, the biofilter was humidified twice a day with 80 ml distillated water and 160 ml of the leachate out of the reactor. In this way, nutrients that were washed away with the leachate could be reused. The average density of the macadamia nutshells, determined by Eq. (2.2), was 1.3 g ml^{-1} and the apparent density 0.63 g ml^{-1}. The ash content was 22 w/w%, using Eq. (2.4), which is comparable with the ash content of fibrous peat, 5 w/w%, and compost, 22 w/w%, see Table 2.2.

2.3.2 Pressure drop

Fig. 2.2 indicates the pressure drop over the reactor during the experimental period. At the highest EBRT of 150 s the pressure drop remained around 0.47 ± 0.09 kPa m^{-1}. As soon as the EBRT was decreased to 90 s, the pressure drop increased to about 0.80 kPa m^{-1}. The next 20 days, the pressure drop still increased slightly till a constant pressure drop of about 0.87 ± 0.02 kPa m^{-1} was reached.

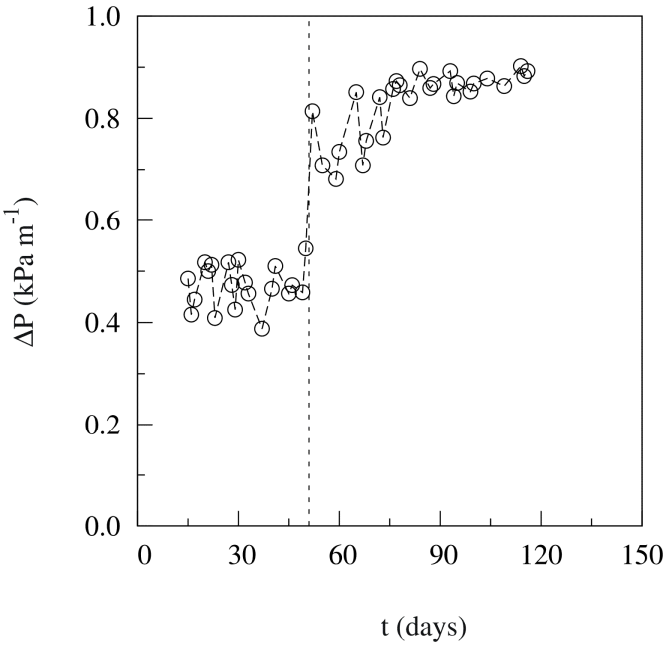


Figure 2.2: Pressure drop vs. time

2.3.3 Biofilter performance

The variation of the IL and the RE with time during the entire experimental period were plotted in Fig. 2.3. As can be observed from Fig. 2.3 there was a start-up period of 10 days to develop a suitable biofilm and a high quality inoculum. After this start-up period RE higher than 95 % were reached at an IL of 12 (Exp1-A), 24 (Exp1-B) and 48 g m^{-3} h^{-1} (Exp1-C). When increasing the IL from 48 to 72 g m^{-3} h^{-1} (Exp1-D) the RE fell back to 60 % and the biofilm needed 1 week of adaptation to reach a higher performance again (RE > 87 %). For an EBRT of 90 s (Exp2), a high RE (> 95 %) was reached for an IL of 20 (Exp2-A) and 40 g m^{-3} h^{-1} (Exp2-B). At the highest applied IL of 80 g m^{-3} h^{-1} (Exp2-C) the RE decreased to 85 %. In Exp3 an increase in RE can be noticed with increasing temperature in the mesophilic range between 292 K (Exp3-A) and 313 K (Exp3-C).

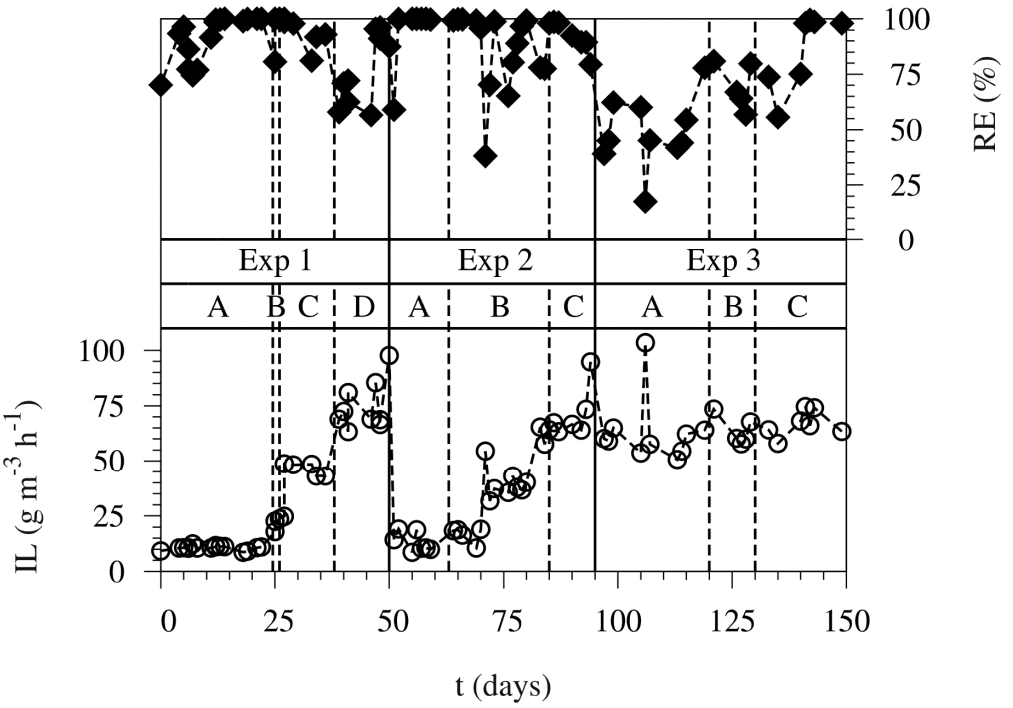


Figure 2.3: Monitoring of the biofilter performance for the entire experimental period (Exp1 to 3). (○) Inlet load (IL) of ethylbenzene; (◆) removal efficiency (RE) of ethylbenzene.

The EB concentration profile versus the reaction time in the biofilter, defined as the fraction of bed length x EBRT, is given in Fig. 2.4.

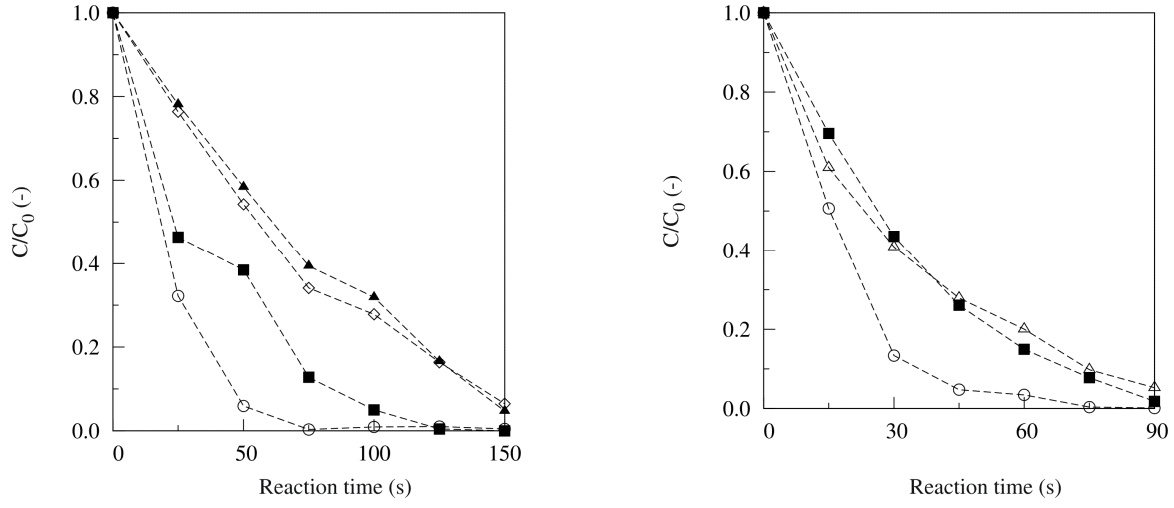


Figure 2.4: Relative ethylbenzene concentration vs. reaction time at 303 K working (a) at an empty bed residence time of 150 s. (○) Inlet load (IL) = 12 g m^{-3} h^{-1} (Exp1-A); (■) IL = 24 g m^{-3} h^{-1} (Exp1-B); (▲) IL = 48 g m^{-3} h^{-1} (Exp1-C); (◇) IL = 72 g m^{-3} h^{-1} (Exp1-D) and (b) at an EBRT of 90 s. (○) IL = 20 g m^{-3} h^{-1} (Exp2-A); (■) IL = 40 g m^{-3} h^{-1} (Exp2-B); (Δ) IL = 80 g m^{-3} h^{-1} (Exp2-C).

After a reaction time of 25 s the RE of EB in the air stream amounted 68, 54, 22 and 24 % for an IL of 12, 24, 48 and 72 g m^{-3} h^{-1} respectively and an EBRT of 150 s, see Fig. 2.4(a). At the lowest IL of 12 g m^{-3} h^{-1} a RE of more than 90 % was reached after only 50 s, while it took more than 125 s to reach a RE higher than 90 % at the highest IL of 48 and 72 g m^{-3} h^{-1}. At an EBRT of 90 s the RE of EB in the air stream amounted 49, 30 and 39 % for respectively an IL of 20, 40 and 80 g m^{-3} h^{-1} after 15 s reaction time (Fig. 2.4(b)).

At the lower IL, 12 and 24 g m^{-3} h^{-1} for 150 s EBRT and 20 g m^{-3} h^{-1} for 90 s EBRT, a linear degradation could be observed in the first stages of the reactor. The higher the IL, the longer the period of apparent linear degradation. Moreover, at the highest IL, 48 and 72 g m^{-3} h^{-1} for 150 s EBRT and 40 and 80 g m^{-3} h^{-1} for 90 s EBRT, an almost linear decrease of the concentration with reaction time could be observed over the entire biofilter depth. A possible explanation for this linear decrease could be found by using Eq. (2.10), which is based on Monod kinetic, with Km, the half-saturation constant, and r_m, the maximal volumetric elimination rate, as parameters which was previously mentioned in part 1.4.

$$r = r_m \cdot \frac{C}{Km + C} \tag{2.10}$$

At the top of the reactor the following assumption could be made, C >> Km, resulting in a constant elimination rate, $r = r_m$, and a linear degradation profile. Once the EB concentration decreased significantly, this assumption was not valuable anymore and no more linear degradation could be observed. The higher the IL, the longer the period in which the assumption, C >> Km, was valid as well as the longer the apparent linear degradation profile.

The variation of the CO_2 production with the EC at 303 K (Exp1-2) is presented in Fig. 2.5.

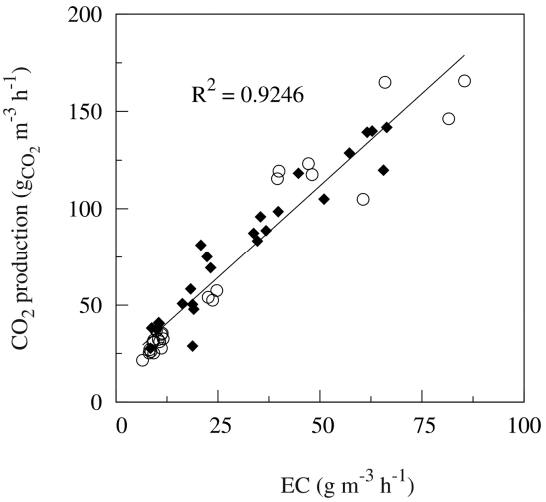


Figure 2.5: Produced CO_2 vs. elimination capacity (EC) at 303 K and inlet loads mentioned in Table 2.1 (Exp1 and 2). (○) Empty bed residence time (EBRT) = 150 s; (◆) EBRT = 90 s.

A linear relationship was found between the EC and the CO_2 production and linear regression resulted in a value of 1.90 ± 0.08 g m^{-3} h^{-1} of CO_2 produced for each g m^{-3} h^{-1} of EB eliminated. This indicates that for each mol m^{-3} h^{-1} of EB degraded, 4.6 mol m^{-3} h^{-1} of CO_2 was formed, ignoring the organic content and the CO_2 accumulated in the leachate (< 10 % of the total C in the outlet). Assuming a general biomass composition formula of $C_5H_7O_2N$, the overall yield coefficient Y_{XS}, defined as g of dry biomass per g of EB consumed could be determined from the biodegradation reaction balance (Delhomenie and Heitz, 2003). When using only EB and taking into account the calculated ratio of 4.6 mol m^{-3} h^{-1} of CO_2 formed for each mol m^{-3} h^{-1} of EB consumed, the reaction balance could be written as Eq. (2.11), resulting in an Y_{XS} value of 0.73 g dry biomass synthesized per g EB degraded:

$$1.5\ C_8H_{10} + 10.3\ O_2 + NH_3 \rightarrow C_5H_7O_2N + 6.7\ CO_2 + 5.3\ H_2O \qquad (2.11)$$

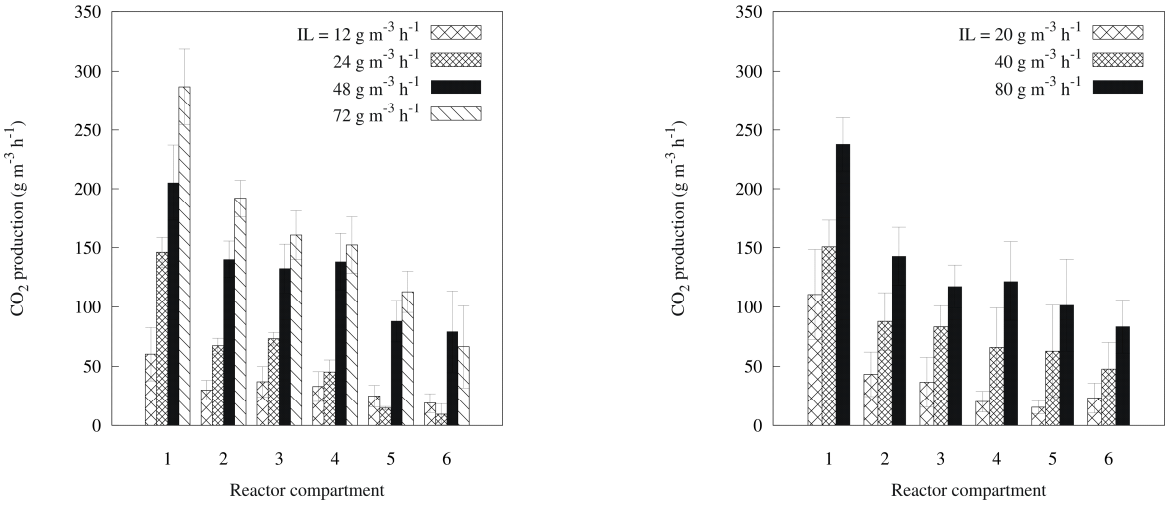
Recalculating the yield coefficient to the carbon level, resulted in a biomass yield coefficient value of 0.43 gC dry mass synthesized per gC EB degraded which is comparable with the yield coefficient obtained from earlier studies (Table 2.3).

Table 2.3: Summary and comparison of Yield coefficients (Y_{XS}), with EBRT the empty bed residence time and T the temperature.

Compound	Packing material	EBRT (s)	T (K)	Y_{XS} (g $C_{biomass}$ g^{-1} $C_{compound}$)
EB	*Macadamia ternifolia* nutshells	90	303	0.43
Ethyl Acetate	Peat	90	296 - 302	0.13 [a]
Toluene	Peat	90	296 - 302	0.16 [a]
Butyl Acetate	Coal particles	90	298 - 308	0.27 [b]
Styrene	-	-	298	0.40 [c]

[a] (Álvarez-Hornos et al., 2007); [b] (Lu et al., 2004); [c] (Jorio et al., 2005)

This indicates a high biomass growth in the biofilter, 43 % of the carbon degraded by the microorganisms was transformed in additional biomass, while 57 % of the carbon degraded was used for CO_2 production. This production of CO_2 by the microorganisms shows that not absorption in the liquid phase, but the microbial metabolism was the main factor responsible for the removal of EB in the biomass.



(a) (b)

Figure 2.6: Produced CO_2 for each compartment separately at 303 K. (a) for an empty bed residence time (EBRT) of 150 s. (▨) Inlet load (IL) = 12 g m^{-3} h^{-1} (Exp1-A); (▩) IL = 24 g m^{-3} h^{-1} (Exp1-B); (■) IL = 48 g m^{-3} h^{-1} (Exp1-C); (▧) IL = 72 g m^{-3} h^{-1} (Exp1-D) and (b) for an EBRT of 90 s. (▨) IL = 20 g m^{-3} h^{-1} (Exp2-A); (▩) IL = 40 g m^{-3} h^{-1} (Exp2-B); (■) IL = 80 g m^{-3} h^{-1} (Exp2-C).

Figure 2.6 represents the CO_2 production for each reactor stage. For every IL the CO_2 production was significantly higher in the first stage compared with the production in the

other stages. From Eq. (2.11) can be derived that the more EB is degraded, the more CO_2 is produced, in accordance with the observation that the first part of the biofilter degraded the most EB, as mentioned in Fig. 2.4. At the highest IL, where linear degradation occurs about the same amount of CO_2 is produced for each g of EB consumed, e.g., at an IL of 72 g m^{-3} h^{-1} and an EBRT of 150 s the EB was degraded almost evenly along the reactor depth, see Fig. 2.4(a). In the first stage of the reactor the EC valued 105 g_{EB} m^{-3} h^{-1}, with a CO_2 production of 60 g_{CO_2} m^{-3} h^{-1} resulting in a yield coefficient of Y_{XS} = 1.4 g of dry mass produced per g of EB degraded. In the second stage of the reactor about the same amount of EB was degraded, EC = 100 g_{EB} m^{-3} h^{-1}, with a CO_2 production of 37 g_{CO_2} m^{-3} h^{-1}, resulting in a yield coefficient Y_{XS} = 1.5 g of dry mass produced per g of EB degraded. The yield coefficients of the first (1.4 g dry mass produced per g EB degraded) and second (1.5 g of dry mass produced per g EB degraded) reactor part are much higher than the overall yield coefficient of the reactor (0.73 g dry mass produced per g EB degraded), which indicates that the highest growth of biomass occurred in these parts.

2.3.4 Influence of temperature

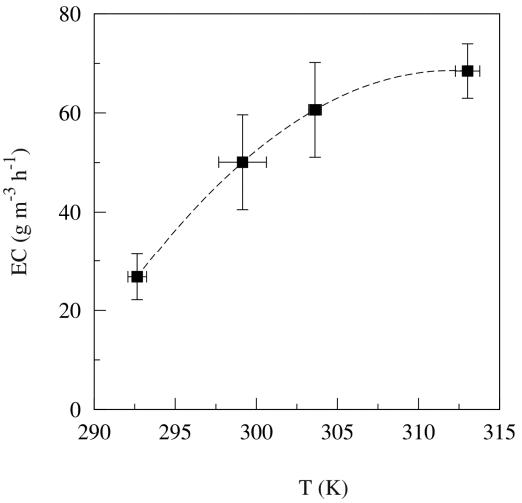


Figure 2.7: Elimination capacity (EC) vs. Temperature (T) at an empty bed residence time = 90 s. Table 2.1, Exp2-C and Exp3.

The effect of the temperature on the performance of the biofilter, represented as EC, at an EBRT of 90 s and an IL of 80 g m^{-3} h^{-1} (Exp3) is shown in Fig. 2.7. With an increasing temperature the microbial activity of the mesophilic bacteria will increase, but the solubility of the EB will decrease, resulting in a local maximal value for the EC (Darlington et al., 2001; Jin et al., 2007), i.e., at ± 312 K, EC = 68.5 g m^{-3} h^{-1}. At lower temperatures bacterial growth is known to decrease (Zwietering et al., 1991) and also foam formation was visible on the leachate. The decrease in EC at lower temperature

could therefore also be influenced by the decrease in bacterial growth and by the foam formation causing clogging in the reactor and limiting the mass transfer of the pollutant through the biofilm, which corresponds to the findings of Luvsanjamba et al. (2007). At higher temperatures protein denaturation thermal decomposition and collapsing of the cytoplasmic membrane of mesophilic bacteria can occur.

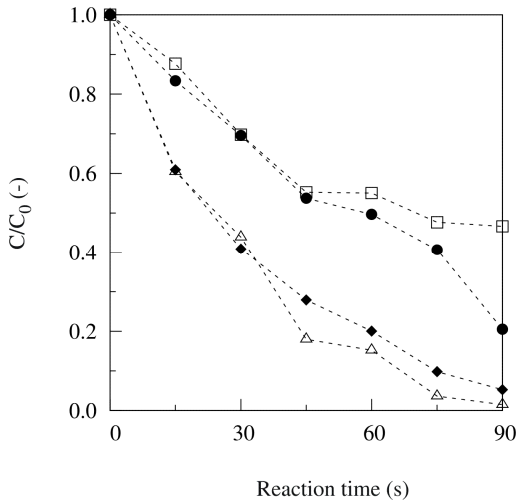


Figure 2.8: Relative ethylbenzene concentration vs. reaction time for an inlet load = 80 g m^{-3} h^{-1} working at an empty bed residence time of 90 s. (□) T = 292 ± 1 K (Exp2-C); (●) T = 299 ± 1 K (Exp3-A); (◆) T = 303 ± 1 K (Exp3-B); (Δ) T = 313 ± 1 K (Exp3-C).

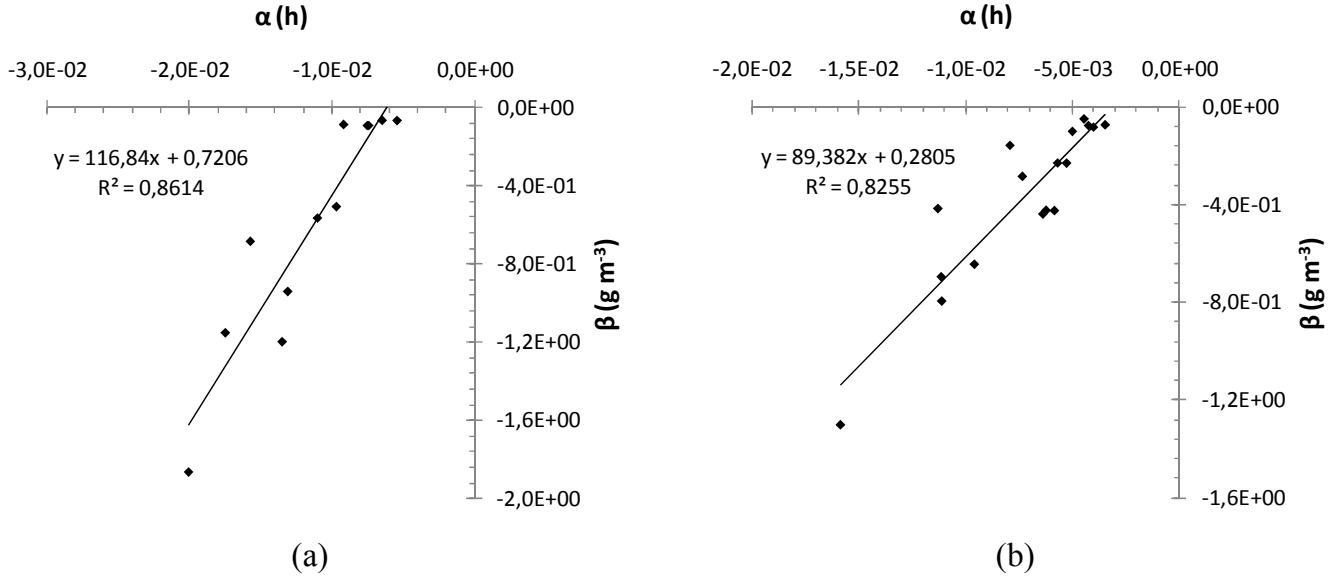
Plotting the concentration profiles as function of the reaction time along the depth of the reactor at an IL of 80 g m^{-3} h^{-1} and an EBRT of 90 s for different temperatures, see Fig. 2.8, resulted in a linear decrease of the EB concentration at lower temperatures (292 and 299 K). At 303 K and 313 K most of the EB was already removed in the first 3 stages of the reactor, RE > 80 %, which can be explained by the higher biological activity at these temperatures.

2.3.5 Biodegradation kinetics

From Eq. (2.10), Eq. (2.12) could be derived (Prenafeta-Boldú et al., 2008), which was applied to determine the biodegradation kinetics, Km and r_m, using the acquired experimental data:

$$C_{in} - C_{out} - Km \cdot \ln\left(\frac{C_{out}}{C_{in}}\right) - r_m \cdot \frac{V}{Q} = 0 \qquad (2.12)$$

This model is used assuming the following assumptions: (1) steady-state conditions were reached for each applied inlet load, (2) the biomass activity was evenly distributed throughout the biofilter bed and (3) the EB removal rate followed the Michaelis-Menten kinetics. Plotting $\beta = \frac{C_{in} - C_{out}}{\ln\left(\frac{C_{out}}{C_{in}}\right)}$ versus $\alpha = \frac{EBRT}{\ln\left(\frac{C_{out}}{C_{in}}\right)}$, as shown in Fig. 2.9, resulted in a linear regression with r_m and Km the corresponding slope and intercept.



(a) (b)

Figure 2.9: $\beta = \frac{C_{in} - C_{out}}{\ln\left(\frac{C_{out}}{C_{in}}\right)}$ vs. $\alpha = \frac{EBRT}{\ln\left(\frac{C_{out}}{C_{in}}\right)}$ at 303 K for an empty bed residence time (EBRT) of (a) 150 s and (b) 90 s.

This regression resulted in a Km = 0.72 ± 0.18 g m^{-3} and r_m = 117 ± 15 g m^{-3} h^{-1} for an EBRT of 150 s, see Fig. 2.9(a). Analysis of the experimental data corresponding to an EBRT of 90 s gave a Km = 0.28 ± 0.09 g m^{-3} and r_m = 89 ± 11 g m^{-3} h^{-1}, see Fig. 2.9(b). Indeed, an increase in EBRT, giving rise to a higher contact time between the contaminated air and the biofilm on the packing material, is known to give a higher value for r_m (Andres et al., 2006; Chiu et al., 2006; Liu et al., 2009). If these r_m values are compared with values out of previous studies, see Table 2.4, it appears that the macadamia nutshells as packing material perform similar to the best carriers used in comparable studies.

Table 2.4: Summary and comparison of the kinetic parameter r_m (maximal volumetric elimination rate) for ethylbenzene with EBRT the empty bed residence time and T the temperature.

Packing material	EBRT (s)	T (K)	r_m (g m^{-3} h^{-1})
Macadamia ternifolia nutshells	90	303 ± 1	89 ± 11
Macadamia ternifolia nutshells	150	303 ± 1	117 ± 15
Peat	125	297 - 301	117 [a]
Fibrous peat	127	300	120 [b]
Soil	127	296	45 [b]
Composite rock wool-compost	48	293 - 305	34.3 [c]

[a] (Gabaldón et al., 2004); [b] (Álvarez-Hornos et al., 2008a); [c] (Cho et al., 2009)

The experimental values of the EC with respect to the IL at two values for EBRT are presented in Fig. 2.10. The dashed lines were calculated by Eq. (2.13), which was obtained from Eq. (2.12) after substitution of Eqs. (2.5) to (2.7).

$$IL = \frac{EC}{1 - \exp\left[\frac{(EC - r_m)\cdot EBRT}{Km}\right]} \tag{2.13}$$

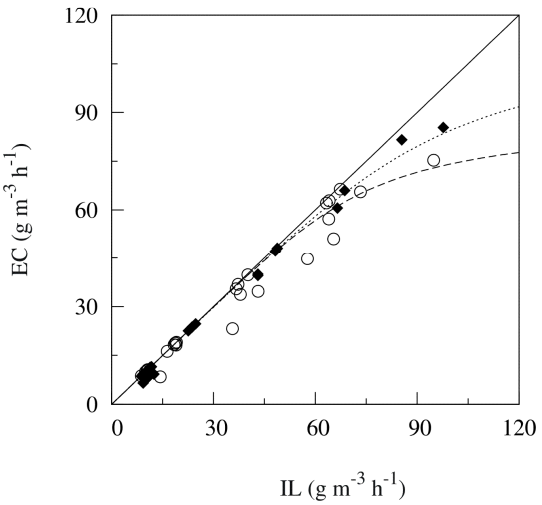


Figure 2.10: Elimination capacity (EC) vs. Inlet load (IL) at an (◆) empty bed residence time (EBRT) = 150 s; (○) EBRT = 90 s for EB at 303 K.

By applying the obtained r_m and Km values in Eq. (2.13) the data at an EBRT of 90 s and 150 s could be modeled sufficiently. A sample standard deviation, see Eq. (2.14), of only 4.49 g m^{-3} h^{-1} and 1.77 g m^{-3} h^{-1} was obtained at an EBRT of 90 s and 150 s respectively between the experimental data and the data obtained by the model.

$$s = \sqrt{\frac{\sum_{i=1}^{N} \left(EC_{i;exp} - EC_{i;calc}\right)^2}{N-1}} \qquad (2.14)$$

Using Eq. (2.12) it could be calculated that a RE of 90 % or more will be obtained for IL lower than 70.6 g m^{-3} h^{-1} (EC = 63.5 g m^{-3} h^{-1}) at an EBRT of 90 s and for IL lower than 85.6 g m^{-3} h^{-1} (EC = 77.0 g m^{-3} h^{-1}) at an EBRT of 150 s.

2.4 CONCLUSIONS

The results obtained by the lab-scale biofilter in this study illustrate the possibility to a successful use of the macadamia nutshells, a waste material in Thailand, as a carrier material in a bioreactor for waste gas polluted with EB. Following properties were obtained from the nutshells: moisture content (7 w/w%), water retaining capacity (17 w/w%), nutshell density (1.3 g ml^{-1}), apparent density (0.64 g ml^{-1}) and ash content (22 w/w%). A mathematical model based on the Michaelis-Menten theory was fitted to the experimental data in such a way that the half-saturation constant Km and the maximal volumetric elimination rate r_m could be calculated for an EBRT of 90 s, Km = 0.28 ± 0.09 g m^{-3} and r_m = 89 ± 11 g m^{-3} h^{-1}, and 150 s, Km = 0.72 ± 0.18 g m^{-3} and r_m = 117 ± 15 g m^{-3} h^{-1}. These r_m values are similar with the parameters of the best carrier materials used in comparable studies. Since the emission limit for ethylbenzene amounts 100 mg Nm^{-3} in Belgium, this biofilter can perfectly be used for emissions up to ± 1.5 g m^{-3} and 2.5 g m^{-3} at an EBRT of respectively 90 and 150 s.

The results also show that macadamia nutshells can be successfully used as a packing material at higher temperatures from 292 to 313 K in the mesophilic range, if the bed is humidified twice a day. At the lowest temperatures in this range, more attention has to be paid concerning clogging of the reactor by foaming, resulting in a lower performance. The best performance of the reactor could be found at 312 K with an EC of 68.5 g m^{-3} h^{-1}.

EC and CO_2 production were well correlated and a yield coefficient of 0.73 g dry biomass produced per g of EB degraded was calculated.

Chapter 3 SIFT-MS a novel tool for monitoring and evaluating a biofilter performance

SUMMARY

Biofilters are suitable to treat industrial emissions polluted with volatile organic compounds. This study investigates the SIFT-MS as a new and fast analysis apparatus to determine the performance, the biokinetic parameters and the porosity of a biofilter in a short period of time, ± 60 hours. SIFT-MS is also used to obtain more information about mass transfer resistance and reaction limitation which can occur in bioreactors. Online analyses were performed on a biofilter packed with a mixture of compost and wooden dowels, treating an air stream contaminated with dimethyl sulphide (DMS), hexane and toluene. Measurements to determine the biokinetic parameters were performed in less than three days to keep the biomass about constant. The half-saturation constant, Km, and the maximal volumetric elimination rate, r_m, for DMS were calculated based on measurements at 35, 60 and 90 s EBRT. Using pulse injections, the porosity of the biofilter, 40.2 ± 0.3 % could be determined online and information about mass transfer resistance and reaction limitation could be collected. For compounds with a high Henry law coefficient, mass transfer resistance becomes significant at lower gas velocities.

3.1 INTRODUCTION

VOC are responsible for several environmental problems, such as photochemical smog and the depletion of the ozone layer. DMS, hexane and toluene are VOC which are often found in waste gases of industrial sources and the harmful nature of these molecules makes that an efficient method is needed to purify waste gases containing DMS, hexane

or toluene. Some physical properties of the different compounds can be found in Table 3.1. DMS is often found in waste gases of wastewater treatment plants and paper industry (Lebrero et al., 2013a) and is known to have a very low olfactory threshold, with an unpleasant smell and a relative high solubility in water (low Henry law coefficient, 0.048). Bacterial cultures responsible for the degradation of DMS are known to be slow growers (Hayes et al., 2010). Hexane has the highest Henry law coefficient and is the least soluble in water. It is emitted by various industries, e.g., the petrochemical industry and the edible oil producing industry (Arriaga and Revah, 2005b). Toluene is a VOC largely used in many industrial activities such as petroleum production or paint and varnish manufacturing operations (Álvarez-Hornos et al., 2008b), with a Henry law coefficient which is about 10 times higher than the one of DMS and about 100 times lower than the one of hexane, see Table 3.1. The Henry law coefficient which is related to both the volatility and the solubility of the compound in water is a very important characteristic that affects the performance of biofilters, since the transport of the VOC from the gas phase to the biofilm, which is composed of more than 90 % water, could be rate limiting (Zhu et al., 2004). Hydrophilic compounds (low Henry law coefficients) are removed more easily, than hydrophobic compounds (high Henry law coefficients) and deposit additional cell mass in a conventional biofilter (Kim et al., 2005). Biofiltration is a reliable technology to treat waste gases containing VOC and is interesting because of its low cost, its non-generating of hazardous residues and its ability to remove odorous compounds (McNevin and Barford, 2000; Mohseni and Allen, 2000; Rappert and Muller, 2005). In spite of these advantages, biofiltration effectiveness is affected by the relative slow reaction and growth of the biomass compared to concentration changes which can occur in industrial processes. Microorganisms are indeed sensible to high concentration peaks that can abruptly reduce the performance of the process (Vedova, 2008). The laboratory study presented here was therefore set up to study online the transient behaviour of a biofilter, this by measuring the immediate response of a typical biofilter on several applied concentration steps and pulses by using SIFT-MS. Advantages of the SIFT-MS approach include the ability to measure VOC concentrations online, less than 250 ms for one analysis, and the sensitivity to low ppbv levels. At present, most studies on biofiltration utilize GC-MS technology (Zehraoui et al., 2012), which usually needs a preconcentration step and typical analytical run times of at least 30 min to 1 hour for VOC mixtures.

When studying a biofilter it is valuable to determine the half-saturation constant, Km, and maximal volumetric elimination rate, r_m, by using existing models (Chiu et al., 2006; Delhomenie et al., 2002; Mohseni and Allen, 2000; Prenafeta-Boldú et al., 2008; chapter 2 in this thesis), as these parameters may, differ considerably with those found in literature depending on the experimental conditions in which the parameters were obtained. The first goal of this study is to investigate if SIFT-MS can help to retrieve this information in

a fast way. Therefore a first part of this study analyzes the performance of a biofilter treating an air stream contaminated with DMS online using SIFT-MS. These measurements were performed in a short period of time (60 hours) to keep the biomass constant. A second aim of the study is to monitor the response of the biofilter on inlet step and pulse concentration changes. A third objective of this study is to use the SIFT-MS in order to obtain more information about mass transfer resistance and reaction limitation in a biofilter by pulse injections of DMS, hexane and toluene. Finally the SIFT-MS was applied to determine the porosity of the biofilter online and to measure the net residence time (NRT) of a compound in the biofilter.

Table 3.1: Compound properties.

Compound	DMS	Hexane	Toluene
Group	Sulphide	Alkane	Aromatic
Solubility in H_2O at 25 °C (g L^{-1})	45 [b]	0.016 [b]	0.32 [b]
Vapour pressure at 25 °C (mmHg)	647 [b]	151 [b]	27.7 [b]
Henry law coefficient (-) (C_g/C_l) [a]	0.048	44	0.43

[a] Calculated using the solubility and the vapour pressure

[b] (SciFinder)

3.2 MATERIALS AND METHODS

3.2.1 Bioreactor system

An overview of the experimental set-up is presented in Fig. 3.1. A mixture of wooden dowels (length = 15 mm; diameter = 6 mm; 60 V%) and compost (40 V%) was used as carrier material in a cylindrical bioreactor composed of Plexiglas, with a total length of 580 mm and an internal diameter of 54 mm. The sludge used to inoculate the reactor came from a wastewater treatment plant (Ossemeersen, Ghent, Belgium) and was first preadapted with a mixture of DMS, hexane and toluene. Afterwards the biofilter was also inoculated with a pure culture of *Hyphomicrobium* VS, known to degrade DMS and to be a slow grower with a doubling time of 24 hours (Sercu, 2006). Air was loaded with pure DMS or with a mixture of DMS, hexane and toluene by using a syringe pump (New Era, infusion/withdraw NE 1000 Model) and it was pumped through the biofilter from bottom

to top with flow rates ranging between 0.2 and 5.6 l min^{-1} (EBRT between 398 s and 14 s for the whole reactor).

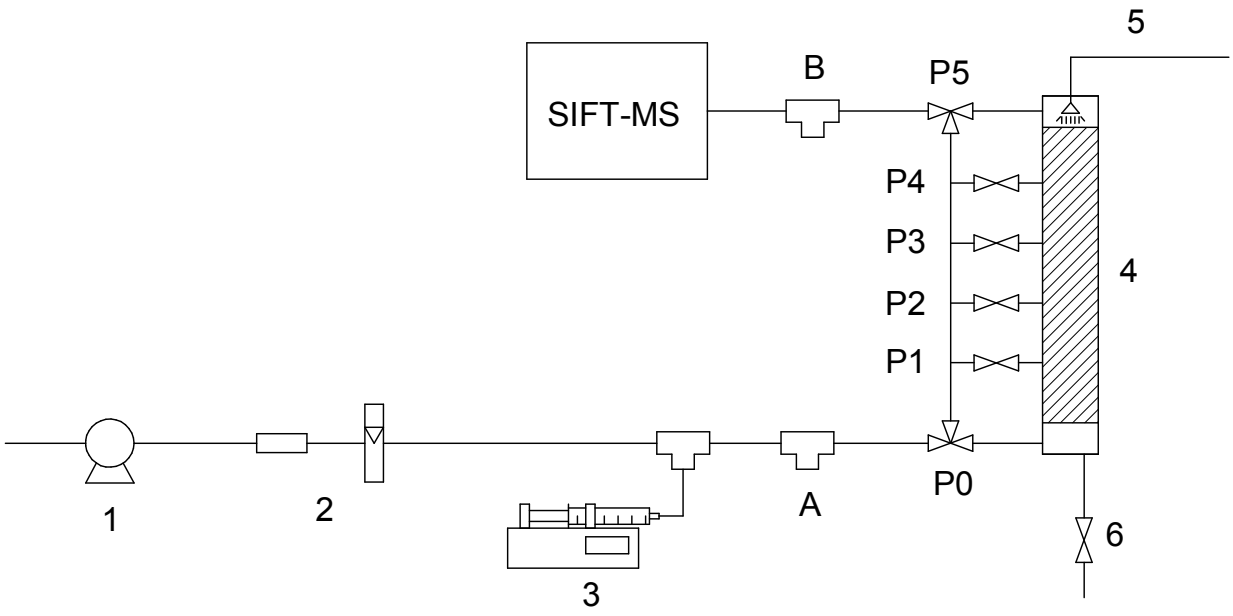


Figure 3.1: Schematic diagram of biofilter. (1) Air pump, (2) mass flow controller and read-out unit, (3) syringe pump, (4) biofilter, (5) humidifier, (6) leachate release, (A) sample port inlet, (B) sample port outlet, (P0 and P5) 3-way valves, (P1-4) intermediate ports with valves.

Nutrients were added at the top of the reactor once a day. The necessary macro and micronutrients were incorporated using a pH buffered nutrient solution (pH 7) containing KNO_3, 10.7 g L^{-1}, KH_2PO_4, 3.0 g L^{-1}, K_2HPO_4, 3.0 g L^{-1}, $MgSO_4 \cdot 7H_2O$, 0.5 g L^{-1}, P, Ca, Fe, Zn, Co, Mn, Mo, Ni, B and vitamins at trace doses. Nutrients levels added were high enough to have a C:N:P ratio of at least 100:5:1(Shareefdeen and Singh, 2005). To humidify the reactor, 150 ml of water was added at the top of the reactor each day.

3.2.2 Process conditions

In a first experiment only DMS was added to the biofilter using the syringe pump in order to determine the performance of the biofilter and the biokinetic parameters for DMS removal. During a two week start-up period a constant air flow of 2.4 l min^{-1}, EBRT = 33 s, and an IL of 5.1 g m^{-3} h^{-1}(inlet concentration 46.8 mg m^{-3}), was applied on the reactor. Once the outlet concentration remained stable for 3 days, the biofilter was operated during a short period of only 60 hours in which several inlet loads (IL), ranging from 1.8 to 15.5 g m^{-3} h^{-1} (inlet concentrations between 20 mg m^{-3} to 420 mg m^{-3}), and several EBRT, 35,

60 and 90 s, were applied. As the bacterial cultures responsible for the degradation of DMS are known to be slow growers (Hayes et al., 2010), it was possible to assume that bacterial growth was negligible during this short measuring period and that the composition of the sludge remained constant. The experiment was designed to keep the IL constant and to monitor the outlet concentrations at respectively 90, 60 and 35 s of EBRT till the outlet concentration reached a stable value. Once the outlet remained constant the biofilter was bypassed, so the corresponding inlet concentration could be determined by the SIFT-MS. Then a new inlet condition (new IL) was applied on the reactor and the outlet concentration was again monitored by the SIFT-MS.

In a second part the SIFT-MS was used to monitor the immediate response of the biofilter on changes of the DMS inlet concentration by means of step variations. The EBRT was kept constant at 90 s and the IL was decreased stepwise from 16.7 to respectively 12.6, 11.3 and 4.1 g m^{-3} h^{-1}. In order to measure the exact applied inlet concentration, the biofilter was first bypassed, to monitor the inlet concentration with the SIFT-MS. Once the inlet concentration was measured, the outlet concentration was monitored by the SIFT-MS until the outlet concentration reached a stable value. As the reactor was stabilized again, it was possible to apply a new inlet condition while measuring the outlet of the filter, in order to investigate the immediate response of the biofilter on a concentration step. Once the outlet concentration reached again a constant value, the biofilter was again bypassed in order to monitor the correct new inlet concentration.

Finally peak injections of DMS, hexane and toluene were performed in order to determine the influence of a concentration pulse on the performance of the bioreactor. These pulse injections were also used to calculate the porosity of the filter online and to obtain more information about mass transfer resistance and reaction limitation in a biofilter. Peak injections were performed by injecting manually 500 µl of headspace from the different compounds in the different sample ports A and B, see Fig. 3.1, this while operating the biofilter under a constant IL of 5.2 g m^{-3} h^{-1} for each compound and at empty bed velocities ranging from 3.6 to 147.6 m h^{-1} (flow rates from 0.2 to 5.6 l min^{-1}). When injecting a sample in port B, the original inlet peak was monitored by the SIFT-MS, see Fig. 3.2 first group of peaks. By injecting a gas sample in port A, the sample will first pass through the biofilter and a lower, broader outlet peak will be monitored by the SIFT-MS, see Fig. 3.2 second group of peaks. The form of this outlet peak depends of the compound type, the interaction with the column and packing material, the reactor volume and the air flow rate. By changing the three way valves and valves P1-4, see Fig. 3.1, the volume of the biofilter can be adjusted, so air only flows through 1, 2, 3, 4 or 5 part(s) of the filter corresponding to reactor volumes of 0.27, 0.53, 0.80, 1.06 and 1.33 L.

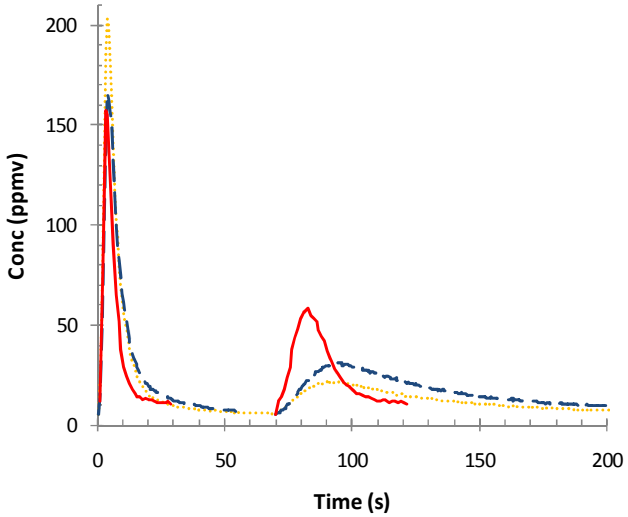


Figure 3.2: Inlet and outlet peaks for (···) DMS, (—) hexane and (---) toluene at an empty bed residence time of 35 s for the whole reactor (5 parts).

The porosity was also determined using a static method, where a bottle with a fixed volume of 1130 ml, V_B, was filled with packing material in the same way as the actual biofilter. Afterwards water was added to the bottle in order to fill up the empty spaces in the packing material, V_W. By applying Eq. (3.1), the static porosity was determined.

$$\text{porosity} = \frac{V_W}{V_B} \tag{3.1}$$

This experiment was repeated 3 times, once with packing material, which was first dried for 24 h in an oven at 383 K, a second time with packing material which was first completely saturated with water and a third time with packing material at ambient conditions.

3.2.3 Analytical techniques

The concentrations of the different compounds in the gas flow were monitored by a Voice 200® (SYFT Technologies Ltd.) SIFT-MS. In a Voice 200® precursor ions H_3O^+, NO^+ and O_2^+ are generated in a discharge ion source, a specific mass is selected by a quadrupole mass filter and then injected as selected ionic species into fast-flowing He carrier gas in a flow tube. Determination of the counts per second (CPS) of the precursor ions and the resulting product ions, as a consequence of the reaction of the former with gas phase molecules, is performed by a downstream quadrupole mass spectrometer. To determine the compound concentrations the following product ions were measured for DMS

$(CH_3)_2S^+$ [NO^+], m/z = 62; $(CH_3)_2S^+$ [O_2^+], m/z = 62; $(CH_3)_2S.H^+$ [H_3O^+], m/z = 63; CH_2S^+ [O_2^+], m/z = 46; CH_3S^+ [O_2^+] m/z = 47; for toluene $C_7H_8.H^+$ [H_3O^+], m/z = 93; $C_7H_8^+$ [NO^+], m/z = 92; $C_7H_8^+$ [O_2^+], m/z = 92 and for hexane $H_3O^+.C_6H_{14}$ [H_3O^+], m/z = 105; $C_6H_{13}^+$ [NO^+], m/z = 85; $C_6H_{14}^+$ [O_2^+], m/z = 86 . In order to prevent condensation of water vapour, the sample inlet lines are heated to ~ 373 K. He carrier gas pressure is 20 Pa at room temperature (296 – 300 K).

To confirm the absolute concentration of the three compounds in the gas flow, gas samples of 500 µl were taken at a regular basis, using a 1.0 ml GASTIGHT® syringe at the inlet and outlet of the bioreactor. Analysis of the samples were performed by using a FID gas chromatograph (6890 Series, Agilent Technologies, USA) equipped with an HP-5 capillary column (30 m × 0.32 mm × 0.25 µm, Agilent Technologies, USA) and He was used as carrier gas at a flow-rate of 2.3 $cm^3\ min^{-1}$.

3.3 RESULTS AND DISCUSSION

3.3.1 Biofilter performance

As mentioned in section 2.3.5 the biodegradation kinetics Km, half-saturation constant, and r_m, maximal volumetric elimination rate, could be determined by Eq. (3.3) which was derived from Eq. (3.2) (Prenafeta-Boldú et al., 2008; see chapter 1 and 2), by using the acquired experimental data for the DMS removal in the biofilter. This equation can be used when taking into account the following assumptions: (1) steady-state conditions were reached for each applied IL, (2) the biomass activity was evenly distributed throughout the biofilter bed and (3) the DMS removal rate followed the Michaelis-Menten kinetics.

$$r = r_m \cdot \frac{C}{Km + C} \tag{3.2}$$

$$C_{in} - C_{out} - Km \cdot \ln\left(\frac{C_{out}}{C_{in}}\right) - r_m \cdot \frac{V}{Q} = 0 \tag{3.3}$$

Plotting $\beta = \dfrac{C_{in} - C_{out}}{\ln\left(\dfrac{C_{out}}{C_{in}}\right)}$ versus $\alpha = \dfrac{EBRT}{\ln\left(\dfrac{C_{out}}{C_{in}}\right)}$, as shown in Fig. 3.3(a), results in a linear regression with r_m and Km the corresponding slope and intercept. The obtained r_m and Km values at the different EBRT are summarized in Table 3.2.

Table 3.2: Values of the kinetic parameters r_m (maximal volumetric elimination rate) and Km (half-saturation constant) at the different empty bed residence times (EBRT) for DMS.

	r_m (g m^{-3} h^{-1})		Km (g m^{-3})	
EBRT (s)	**AVG**	**STDEV**	**AVG**	**STDEV**
35	7.4	0.3	0.030	0.004
60	7.0	0.2	0.028	0.004
90	7.2	0.2	0.027	0.004

A one-way analysis of variance (ANOVA) (Powell and Jordan, 1997) shows, that there is no significant difference between the intercepts and the slopes obtained at the different EBRT, at the 95 % significance level. Linear regression of Eq. (3.3) using all the data resulted in a value for Km of 0.028 ± 0.002 g m^{-3} and a value for r_m of 7.23 ± 0.11 g m^{-3} h^{-1} independent of the EBRT.

A sample standard deviation, see Eq. (2.14), of only 0.24 g m^{-3} h^{-1}, 0.24 g m^{-3} h^{-1} and 0.19 g m^{-3} h^{-1} was obtained at an EBRT of 35, 60 s and 90 s respectively between the experimental data and the data obtained by the model.

Comparing this r_m value with literature data (see Table 3.3), it appears that the maximal volumetric elimination capacity of the biofilter is slightly higher than the one of a biofilter with sugarcane bagasse as packing material, r_m = 4.97 g m^{-3} h^{-1} , under comparable conditions; EBRT = 90 s and inoculated with *Hyphomicrobium* VS. Compared with other techniques, biotrickling and membrane filtration, the performance of the biofilter is lower. The half-saturation constant Km represents the concentration, indicated by |β|, at which half of the maximum intake rate (r_m/2) is reached (Christian and Hendriks, 2013). If resources are scarce, i.e. |β| < Km, than EC increases linearly with |β|. If resources are (more) abundant, i.e. |β| > Km, the EC levels off to the maximum value r_m. The half-saturation constant Km is reached, |β| = Km, at an IL of 5.33, 3.98 and 3.75 g m^{-3} h^{-1} for an EBRT of 35, 60 and 90 s respectively.

Table 3.3: Summary and comparison of the kinetic parameter r_m (maximal volumetric elimination rate) for DMS with EBRT the empty bed residence time and PDMS polydimethylsiloxane.

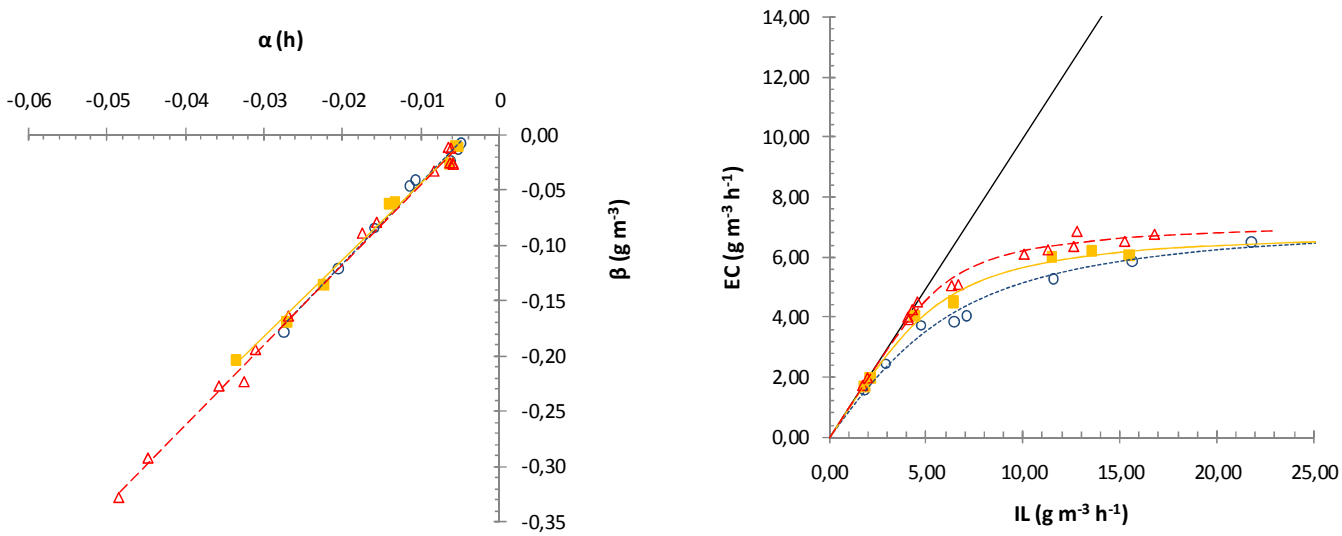
Technique	Packing material	EBRT (s)	r_m (g m^{-3} h^{-1})
Biofilter (*Hyphomicrobium* VS)	compost + woodchips	35 - 90	7.23
Biofilter (*Thiobacillus thioparus* TK-m)	sugarcane bagasse	90	3.9 [a]
Biofilter (*Hyphomicrobium* VS)	sugarcane bagasse	90	4.97 [a]
PDMS composite membrane (*Hyphomicrobium* VS)	-	24	200 [b]
PDMS composite membrane (*Hyphomicrobium* VS)	-	24	258.3 [c]
Biotrickling filter (*Hyphomicrobium* VS)	PE rings	120	57 [d]
Biotrickling filter (enriched sludge)	HDPE rings	200	45 - 75 [e]

[a] (Fernández et al., 2013); [b] (De Bo et al., 2003); [c] (Kumar et al., 2010); [d] (Sercu et al., 2005b); [e] (Luvsanjamba et al., 2008)

The experimental values of the EC with respect to the IL at the three values of EBRT are presented in Fig. 3.3(b). The drawn lines were calculated using the obtained r_m and Km values at the different EBRT in Eq. (3.4), which was derived from Eq. (3.3).

$$IL = \frac{EC}{1 - \exp\left[\frac{(EC - r_m)\cdot EBRT}{Km}\right]} \tag{3.4}$$

For IL lower than 25 g m^{-3} h^{-1}, it is clear that the EC increases with increasing EBRT. E.g. at an IL of 10 g m^{-3} h^{-1}, the EC amounts 5.1, 5.6 and 6.2 g m^{-3} h^{-1} for an EBRT of respectively 35, 60 and 90 s. A higher EBRT also results in a higher range of IL were the removal remains high. E.g. the removal efficiency (RE) remains above 90 % for IL ranging up to 0.2, 3.6 and 5.3 g m^{-3} h^{-1} for an EBRT of respectively 35, 60 and 90 s.



(a) (b)

Figure 3.3: (a) $\beta = \frac{C_{in} - C_{out}}{\ln\left(\frac{C_{out}}{C_{in}}\right)}$ vs. $\alpha = \frac{EBRT}{\ln\left(\frac{C_{out}}{C_{in}}\right)}$ and (b) Elimination capacity (EC) vs. Inlet load (IL) for an empty bed residence time (EBRT) of (○) 35 s, (■) 60 s and (Δ) 90 s. Drawn lines are based on Eq. (3.4), (···) EBRT = 35 s; (—) EBRT = 60 s and (---) EBRT = 90 s.

As the aforementioned biokinetic parameters are independent of the EBRT, it is possible to calculate the EBRT which has to be applied to reach a desired RE by Eq. (3.5).

$$EBRT = \frac{C_{in} \cdot \left(\frac{RE}{100}\right) - Km \cdot \ln\left(1 - \frac{RE}{100}\right)}{r_m} \qquad (3.5)$$

If a waste stream contains 0.5 g m^{-3} of DMS, an EBRT of 2.23 min will be needed to obtain a RE of at least 50 % and 4.3 min to reach a RE of at least 90 %, see Fig. 3.4. This is a useful tool for industrial applications, because it is possible to calculate the flow or the volume of the reactor which is needed to reach a sufficient degradation. As these measurements were performed at a constant biomass, it is clear that the RE can still increase, once the bacteria growth becomes higher and more adapted.

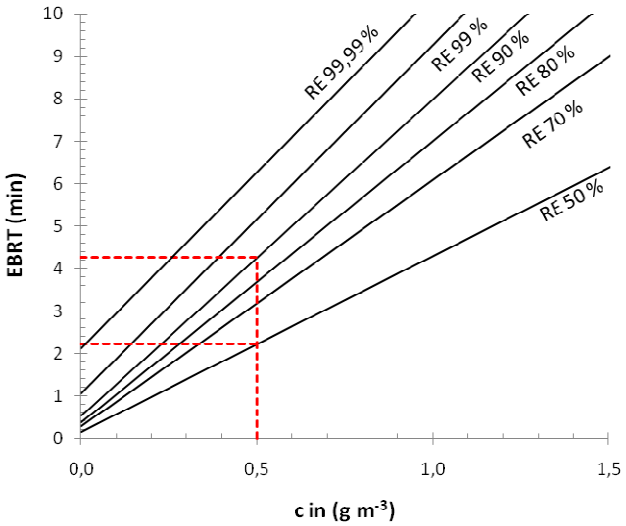
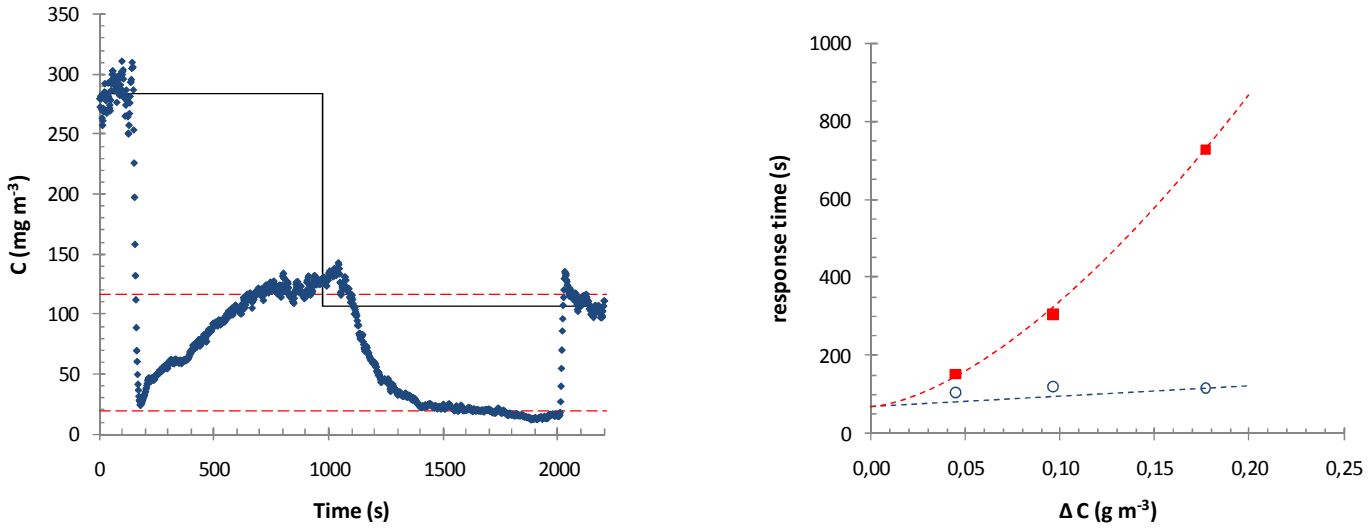


Figure 3.4: Empty bed residence time (EBRT) vs. inlet concentration (c in) of DMS for different removal efficiencies (RE).

3.3.2 Step and pulse response

3.3.2.1 Step response experiment

SIFT-MS is used to investigate the response of the biofilter on an applied DMS concentration step, see Fig. 3.5(a). From 0 to 150 s the biofilter was bypassed, to check if the inlet concentration was stable, 284 ± 14 mg m^{-3}. At 150 s, the flow was passed through the whole biofilter by switching valves P0 and P5, see Fig. 3.1, and the SIFT-MS measured the DMS biofilter outlet concentration. Once the outlet signal was stable, 122 ± 6 mg m^{-3}, the inlet concentration, measured via the bypass, was lowered to 107 ± 6 mg m^{-3} at 973 s. At this inlet concentration, the outlet concentration after the biofilter lowered to 14 ± 1 mg m^{-3}. The following response times (RT) could be calculated: RT_5 = 117 s and RT_{95} = 727 s. With RT_5 and RT_{95} respectively the time where 5 % and 95 % of the total concentration change between the two stable outlet concentrations was reached corrected for the time where the new inlet concentration was applied. RT_5 indicates how fast the biofilter will respond on a concentration change, while RT_{95} can be considered as an indication of how fast the biofilter will reach a stable concentration again.



(a) (b)

Figure 3.5: (a) Step experiment at 90 s empty bed residence time (EBRT) with (—) the applied DMS concentration step at inlet, (---) respectively 5 and 95 % of the concentration change at the outlet and (◆) measured points with SIFT-MS. (b) Response vs. applied concentration step for (○) RT_5 and (■) RT_{95} at 90 s EBRT.

At a fixed EBRT, the time to react on a concentration step, will increase slightly, increasing RT_5, with an increasing concentration step. The time it takes to reach a stable value, RT_{95}, increases much more with an increasing concentration step, see Fig. 3.5(b). E.g. RT_{95} increases from 152 s to 727 s when applying a concentration step of respectively 0.045 g m^{-3} and 0.177 g m^{-3}, while RT_5 only increases from 105 s to 117 s.

3.3.2.2 Pulse response experiment

When injecting a pulse of 500 µl headspace gas of a compound at the inlet of the biofilter a sharp defined peak was visible at the inlet stream of the reactor with a high pulse concentration, see Fig. 3.6.

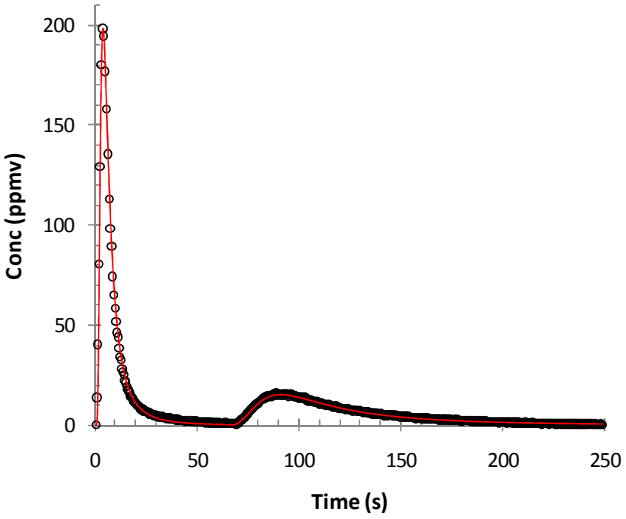


Figure 3.6: Pulse experiment with a DMS pulse at the inlet (first peak) and outlet (second paek) of the complete biofilter for 60 s empty bed residence time. With (○) the experimental data points measured with the SIFT-MS and the red line a fitting of the data.

Passing through the column, the peak maximum became much lower and the peak shape broader. In general the peak shape can be influenced by removal, interaction with the humidified packing material and longitudinal diffusion. In order to calculate parameters such as the area underneath the peak, the time to the peak top (t_{top}) and the concentration at the peak top (C_{top}), a model, expressed by Eq. (3.6), which is based on the Burr probability distribution model (Love et al., 2013), was applied on the experimental data.

$$conc(t) = E \cdot \left(\frac{C \cdot D}{B} \cdot \frac{\frac{8 \cdot t}{t_{end} - t_{start}} - A}{B} \right)^{-C-1} \cdot \left[1 + \left(\frac{\frac{8 \cdot t}{t_{end} - t_{start}} - A}{B} \right)^{-C} \right]^{-D-1} \quad (3.6)$$

With A, B, C, D and E the model parameters, t the time and t_{start} and t_{end} respectively the time at which the first and the last point of the peak appears. For example if a pulse of 500 µl hexane headspace vapour passes through the column, the total area underneath the outlet peak stays the same as the one underneath the inlet peak, indicating that the biofilter is not able to degrade any additional hexane caused by the pulse injection. Although no removal of hexane occurs, the peak maximum reduces 2.8 ± 0.6 times, while the width at half height increases 2.4 ± 0.7.times. In case of an injection of 500 µl toluene or DMS, the outlet peak top concentration decreases linearly with the decrease in peak area. The peak width at half height increases 6.1 ± 0.9 and 21 ± 5 times for respectively toluene and DMS

injections. Only for DMS, which has the lowest Henry's coefficient, the outlet peaks show more tailing than the inlet peaks.

3.3.3 Reaction limitation and mass transfer resistance

In most conditions in a reactor the rate limiting step of pollutant removal is a complex combination of mass transfer resistance and kinetic limitation. To get more insight in this process the SIFT-MS was used to collect more information about mass transfer resistance and reaction limitation which occurs in a biofilter by injecting pulses of the different compounds at different empty bed velocities and for different reactor volumes. As it is not possible to describe a pulse injection as a continuous load, the area underneath the peak, expressed in g s m^{-3}, was multiplied with the corresponding flow, expressed in m^3 s^{-1}, to determine the absolute mass of the compound in g. A fixed amount of headspace gas of each compound (500 µl), was injected manually in sample port B, see Fig. 3.1, in order to determine the area of an inlet peak. This fixed volume corresponded with an inlet mass injection of 628, 63 and 29 µg of DMS, hexane and toluene respectively. A second pulse of 500 µl headspace was applied just at the inlet of the filter, sample port A, to determine the area of the corresponding outlet peak and the absolute removal of the compound. In case of hexane, the absolute mass at the outlet corresponds to the absolute mass which was injected, so no hexane was removed; see Fig. 3.7(a). For DMS, see Fig. 3.7(b), the removal will increase with decreasing empty bed velocity, u_{EB}, and increasing reactor volume. If u_{EB} goes to zero, the DMS removal reaches a maximum value of 63.5 % to 82.4 % when using respectively 1 part of the reactor and the whole reactor volume. This corresponds with an absolute mass removal of 399 and 518 µg DMS, which is an indicator of the reaction limitation for DMS when applying respectively 1 part of the reactor and the whole reactor. In case of toluene, see Fig. 3.7(c), the removal will also increase with decreasing u_{EB} and increasing reactor volume until 100 % removal is reached. If u_{EB} goes to zero, the toluene removal reaches a maximum value of 66.0 % when using only 1 part of the reactor. This corresponds with an absolute mass removal of 19.1 µg for 1 part of the reactor. When using the whole reactor volume at an u_{EB} = 17.3 m h^{-1}, 100 % removal is reached, corresponding to an absolute mass removal of 28.9 µg toluene. At an u_{EB} < 17.3 m h^{-1} the removal remains 100 %, but there is potential to remove even more than 28.9 µg of toluene. To determine the maximal amount of toluene that potentially can be removed, the linear part of the graph can be extrapolated to the left and the intercept with the y-axis can be subtracted from the injected mass. Applying the whole reactor volume, the maximal amount of toluene which is possible to remove corresponds to 36.3 µg toluene, which indicates the reaction limitation of toluene when using the whole reactor volume. When increasing the u_{EB}, the removal decreases until a

critical u_{EB} at which 0 % removal is reached. This critical velocity is independent of the applied reactor volume. For toluene the critical u_{EB} values 84 ± 2 m h^{-1}. At an u_{EB} higher than the critical velocity, no more toluene is removed.
In general the critical u_{EB}, see point X in Fig. 3.7(a - c), will increase, with a decreasing Henry law coefficient. From this point the mass transfer resistance to diffuse into the water and in the biofilm is too high, so no removal can occur. In case of hexane this critical velocity is very low, due to the high Henry law coefficient, so no removal can occur for the whole applied range of gas velocities. For DMS, with a low Henry law coefficient, the critical velocity is not reached in the applied range of gas velocities. An indication of the critical u_{EB} can be done, by extrapolating the linear graphs to the right till the inlet and outlet masses reach the same value. This results in a critical u_{EB} of 648 ± 252 m h^{-1} for DMS.

A decreasing Henry law coefficient; will also lead to a higher potential to remove the compound, as the amount of compound that will be absorbed in respectively the water and the biofilm, increases with decreasing Henry law coefficient. The maximal amount of compound which is possible to remove, see point Y in Fig. 3.7(a - c), gives an indication of the reaction limitation, as it is not possible for the biomass to degrade more than this amount. Increasing the volume of the reactor, results in an increase of biomass available for degradation and in a higher amount of compound which is possible to remove (Y shifts down). Using this information Fig. 3.7(d) could be constructed, indicating the maximal removal of a given compound in function of the reactor volume. In this study a removal of 15 ± 6 µg of toluene per liter reactor can be reached for pulse injections, when using low velocities. For DMS a removal of 106 ± 28 µg l^{-1} can be reached, which is much higher than the one of toluene. Although DMS is a more difficult compound to degrade in biofilters compared with toluene, the Henry law coefficient plays a more important role when removing pulse injections. For a compound with a lower Henry law coefficient, the shape of the peak becomes broader when passing through the reactor, due to the high interaction with the humidified packing material. This results in a lower average concentration and lower IL, which can lead to higher RE. For example for DMS the peak width at tenth height increases already 2.2 ± 0.3 times after passing through the first part of the reactor, which results in a 2.2 ± 0.3 times lower average concentration and an IL which is about 1.8 ± 0.2 times lower. After passing 4 parts of the reactor this width increases even 19 ± 4 times, resulting in a 3.9 ± 0.9 times lower IL. For toluene the IL after 4 parts only decreases 1.1 ± 0.2 times.

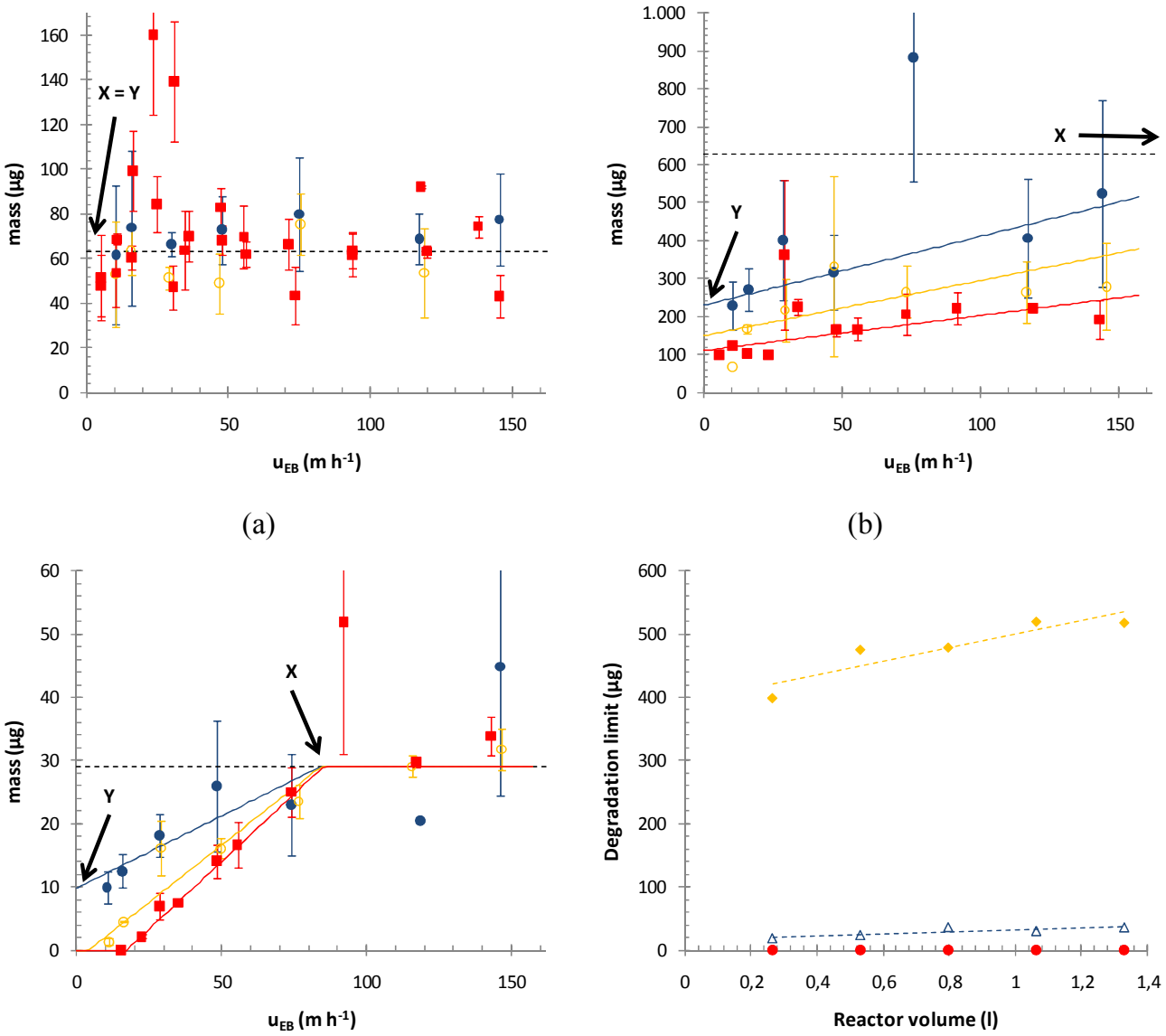


Figure 3.7: (a) Outlet mass of hexane as a function of the empty bed velocity after passing through (●) 1 part, (○) 3 parts and (■) the whole reactor.
(b) Outlet mass of DMS as a function of the empty bed velocity after passing through (●) 1 part, (○) 3 parts and (■) the whole reactor.
(c) Outlet mass of toluene as a function of the empty bed velocity after passing through (●) 1 part, (○) 4 parts and (■) the whole reactor.
Dashes lines correspond to the inlet mass.
(d) Degradation limit vs. reactor volume for (◆)DMS, (●) hexane and (Δ) toluene.

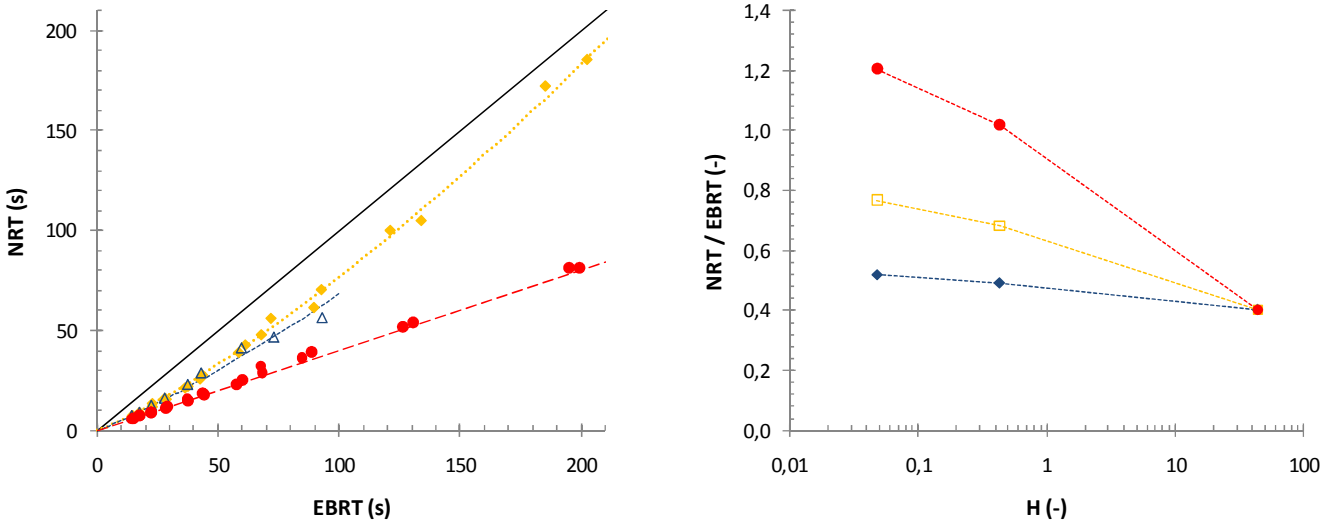
3.3.4 Net residence time and porosity

In a last part of this study, the SIFT-MS was used to determine online the NRT of the different compounds and the porosity of the biofilter, by injecting fixed pulses of the compounds (500 µl) at different EBRT. The NRT was determined by subtracting the time of injection from the time to the top of the peak. The NRT of the compound in the tubing from the reactor to the SIFT-MS, could be determined by an injection in sample port B. To determine finally the NRT in the biofilter another injection in sample port A was carried out. This NRT is a more accurate indicator for the gas residence time in the biofilter, as it indicates the exact time required for a solute to migrate through the biofilter. Furthermore, it also varies with the identity of the compound, which can be very different, and the condition of the packing material (humidity, moisture content, porosity, particle distribution...). Plotting the NRT as a function of the EBRT for the three different compounds, see Fig. 3.8(a), it is clear that for all three compounds the NRT is lower than the EBRT in the lower EBRT range. At higher EBRT, see Fig. 3.8(b), the NRT will become higher than the EBRT. For compounds with a lower Henry law coefficient, the NRT will increase faster with increasing EBRT, so the NRT becomes higher than the EBRT at lower EBRT. E.g., for DMS the NRT will be equal to the EBRT at an EBRT of 296 s. At EBRT higher than 296 s, the NRT will even be higher than the EBRT. Fig. 3.8(b) shows that the ratio NRT over EBRT will increase with increasing EBRT for compounds with a lower Henry law coefficient. Compounds with a high Henry law coefficient, like hexane, behave as inert compounds for this biofilter, so no removal occurs, see Fig. 3.7(a), and the NRT over the EBRT stays more or less constant in function of the EBRT, 0.402 ± 0.003. This ratio between the NRT and EBRT indicates the void volume in the reactor over the complete reactor volume, corresponding with the online porosity of the biofilter. Comparing the online porosity, with the porosity obtained using a more conventional static technique; see Table 3.4, shows that this online value is higher than the static porosity for the with water saturated packing material, 0.135, and lower than the static value for the porosity of dried packing material, 0.579.

Table 3.4: Porosity of a biofilter filled with a mixture of wooden dowels (60 V%) and compost (40 V%) as packing material measured by a static method.

Condition of packing material	Porosity (-)
wet	0.135
at ambient condition	0.550
dry	0.579

As the porosity depends on the humidity of the packing material, increasing porosity with decreasing humidity, and this humidity varies during operation, it is difficult to determine the exact porosity by a static method. Hence to determine the exact porosity of a biofilter at a certain moment, online measurements seem to be very useful. The online porosity not only takes into account the actual humidity and condition of the packing material, but also the presence of water in the biofilter pores and the accumulation of biomass, which all can lead to lower porosities. This online measuring of the porosity using SIFT-MS is therefore not only an easy and fast way of measuring the porosity in a biofilter, but also results in a more accurate value that is responsive to the state of the packing material.



(a) (b)

Figure 3.8: (a) Net residence time (NRT) vs. Empty bed residence time (EBRT) for (◆) DMS, (●) hexane and (Δ) toluene.
(b) NRT over EBRT vs. Henry law coefficient at an EBRT of (◆) 10, (□) 100 and (●) 500 s. Dashed lines are shown to guide the eye.

As discussed previously in this study, the NRT is a more correct indicator of the gas residence time in the biofilter and can be applied to calculate more accurate values for the IL and corresponding EC, by using Eq. (3.7) and (3.8).

$$NIL = \frac{C_{in}}{NRT} \tag{3.7}$$

$$NEC = \frac{C_{in} - C_{uit}}{NRT} \tag{3.8}$$

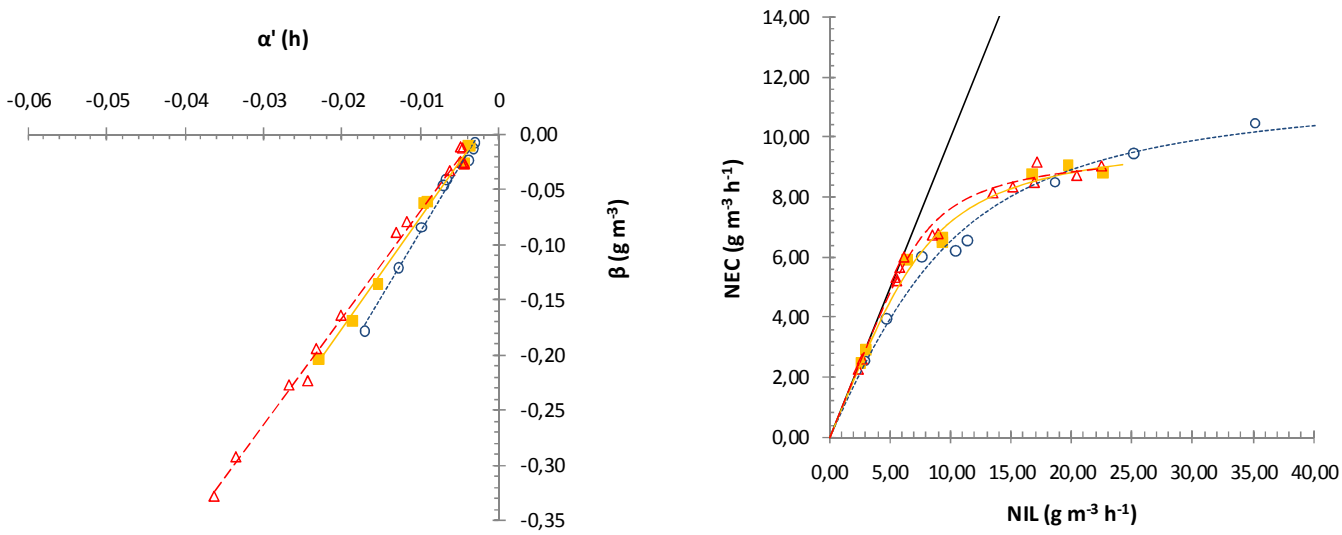
When the NRT is lower than the EBRT, the net elimination capacity (NEC) will be higher than the previously mentioned EC. The higher the Henry law coefficient, the bigger the difference between the EC and the NEC. To achieve more accurate values for the biokinetic parameters, $\beta = \frac{C_{in} - C_{out}}{\ln\left(\frac{C_{out}}{C_{in}}\right)}$ is plotted versus $\alpha' = \frac{NRT}{\ln\left(\frac{C_{out}}{C_{in}}\right)}$, with α' calculated based on the NRT, as shown in Fig. 3.9(a). Linear regression of this data results in r_m' and Km', corresponding to the slope and intercept. The on the NRT based r_m' and Km' values at the different EBRT are summarized in Table 3.5.

Table 3.5: Values of the kinetic parameters r_m' (net maximal volumetric elimination rate) and Km' (net half-saturation constant) at the different empty bed residence time (EBRT) based on the net residence time (NRT) for DMS.

		r_m' (g m^{-3} h^{-1})		**Km' (g m^{-3})**	
EBRT (s)	**NRT (s)**	**AVG**	**STDEV**	**AVG**	**STDEV**
35	21.7	11.9	0.5	0.030	0.004
60	41.2	10.2	0.3	0.028	0.004
90	67.4	9.7	0.2	0.027	0.004

As the NRT is lower than the EBRT, the r_m' values, which are based on the NRT, will be higher compared with the ones based on the EBRT. The ratio NRT over EBRT increases with increasing EBRT, resulting in a lower r_m' at a higher EBRT and a significant difference between the r_m' values.

Plotting the NEC in function of the net inlet load (NIL), for the data of DMS obtained in the first experiment, results in Fig. 3.9(b). This indicates that higher NEC are obtained for a similar NIL, e.g. at an EBRT of 35 s the NEC values 8.03 g m^{-3} h^{-1} at an NIL of 15 g m^{-3} h^{-1}, while the EC only reached 5.8 g m^{-3} h^{-1} at an IL of 15 g m^{-3} h^{-1}. The net maximal volumetric elimination rate at 35 s, also increases from 7.4 ± 0.3 g m^{-3} h^{-1} to 11.9 ± 0.5 g m^{-3} h^{-1}, while the half-saturation constant, Km, stays constant. At lower NIL the NEC will increase with increasing EBRT, but at NIL higher than 20 g m^{-3} h^{-1}, the NEC at lower EBRT will be slightly higher, due to the increasing NRT over EBRT ratio with increasing EBRT. If the ratio NRT over EBRT < 1, the EC will give an underestimation of the NEC, while if NRT over EBRT > 1, the EC will give an overestimation of the NEC.



(a) (b)

Figure 3.9: (a) $\beta = \frac{C_{in} - C_{out}}{\ln\left(\frac{C_{out}}{C_{in}}\right)}$ vs. $\alpha' = \frac{NRT}{\ln\left(\frac{C_{out}}{C_{in}}\right)}$ and (b) net elimination capacity (NEC) vs. Net inlet load (NIL) for an empty bed residence time (EBRT) of (○) and (···) 35 s, (■) and (—) 60 s and (Δ) and (---) 90 s.

3.4 CONCLUSIONS

The results obtained during this research illustrate that SIFT-MS is a suitable measuring technique to analyze online the performance of a biofilter and this in a short time period (40 hours). Due to the short analysis time it is possible to measure the biokinetic parameters for DMS removal in a biofilter with a mixture of wooden dowels (60 V%) and compost (40 V%) as packing material, while keeping the biomass cultures constant at different EBRT, resulting in an overall value of 7.23 ± 0.11 g m^{-3} h^{-1} for r_m and a value of 0.028 ± 0.002 g m^{-3} for Km. As the bacterial growth had no influence on the determination of the biokinetic parameters during this experiment, it indicates that, the biokinetic parameters Km and r_m for the removal of DMS are independent of the EBRT when the biomass remains constant. When applying a DMS concentration step at the inlet of the reactor, the outlet of the biofilter will change very fast, but the higher the applied concentration step, the more time the biofilter needs to reach a stable value again. By using pulse injections, it is possible to collect more information about mass transfer

resistance and reaction limitation in biofilters. The higher the Henry law coefficient, the lower the velocities at which mass transfer resistance becomes significant. When decreasing the volume of the reactor, mass transfer resistance will be significant at lower velocities. In this study the maximal removal of DMS, toluene and hexane amounts 106 ± 28, 15 ± 6 and 0 µg l^{-1}. The porosity of the reactor could be determined by injecting pulses of an inherent compound, in this experiment hexane, which are monitored by SIFT-MS. A value of 40.2 ± 0.3 % was obtained for the overall porosity of the whole reactor. This is a new and fast way of measuring the porosity online and results in a more accurate value for the porosity of the packing material in the biofilter compared to the value obtained with the more conventional static method, see section 3.2.2, as this online porosity depends on the actual humidity, moisture content and state of the packing material (particle size and distribution). Using the SIFT-MS, it was also possible to determine the NRT of the different compounds, which was lower than the EBRT in the lower range of EBRT. This NRT is a more accurate indicator for the gas residence time, as it indicates the exact time required for a compound to migrate through the biofilter and it varies with the identity of the compound, which can be very different. The NRT decreases with increasing Henry law coefficient of the compound, because of the lower interaction with the humidified packing material and biofilm. When the NRT is lower than the EBRT, the net maximum volumetric elimination capacity will be higher, e.g. an increase from 7.4 ± 0.3 g m^{-3} h^{-1} to 11.9 ± 0.5 for DMS at an EBRT of 35 s.

Chapter 4 Application of a non-aqueous phase in four different biotechnologies for air treatment.

Biological air treatment technologies are very suitable for hydrophilic compounds, but the performance can decrease drastically when a hydrophobic compound or a mixture of hydrophilic and hydrophobic compounds is fed to the bioreactor which leads to higher residence times and lower operational air flows to obtain a sufficiently high removal. In order to decrease these process limitations, in particular the mass transfer resistance for hydrophobic compounds to transfer from the gas phase to the liquid phase, a NAP was applied in four different air treatment biotechniques, i.e., a TPPB, a two-liquid-phase biofilter, a two-liquid-phase biotrickling filter and a two-phase partitioning membrane bioreactor (TPPMB). All four of these bioreactors were fed with a mixture of VOC with different hydrophobicity in order to get an indication of the overall performance to treat polluted air emissions containing different compounds. The NAP used for each bioreactor was silicone oil, as this is immiscible in water, non-biodegradable, non-toxic to the microbial community and exhibits a high affinity for the hydrophobic compounds, which are important properties for an adequate NAP.

4.1 SIFT-MS ANALYSIS OF THE REMOVAL OF DIMETHYL SULPHIDE, N-HEXANE AND TOLUENE FROM WASTE AIR BY A TWO-PHASE PARTITIONING BIOREACTOR

Summary

DMS, n-hexane and toluene removal from a waste air was carried out by a TPPB containing a 25/75 V% silicone oil/water emulsion inoculated with activated sludge under continuous feeding conditions. The performance of the reactor was determined using two different measuring techniques, GC-FID and SIFT-MS. While GC-measurements took several weeks, it was possible to obtain the same information with SIFT-MS in only 3 days. When feeding the TPPB only with hexane, EC of 138.9, 163.8 and 241.6 g m^{-3} h^{-1} are reached for an IL of 350 g m^{-3} h^{-1} at respectively 30, 60 and 120 s EBRT. If a mixture of DMS, hexane and toluene is fed to the bioreactor at an EBRT of 60 s EC of respectively 45, 45 and 75 g m^{-3} h^{-1} are reached for the different compounds at an IL of 100 g m^{-3} h^{-1}. This indicates that a TPPB can be applied to treat a mixture of hydrophobic and hydrophilic compounds. Excessive growth of biomass in a TPPB can lead to deteriorated aeration and a decrease in performance. By using pulse injections, the net retention time of the compounds could be determined online, which is related to the aeration and dispersion within the reactor. A low net retention time indicates bad aeration and dispersion, resulting in a low reactor performance. Therefore the net retention time can be used as a parameter indicating when biomass needs to be purged or when the aqueous medium needs to be refreshed.

4.1.1 Introduction

Air pollution is probably one of the most serious problems for the future of our planet. VOC, largely emitted in the atmosphere, are key pollutants due to their ozone depletion potential, global warming potential, potential toxicity and potential carcinogenicity. In order to reduce these VOC emissions, biological gas treatment techniques such as bio(trickling)filtration, bioscrubbing and membrane biofiltration (Delhomenie and Heitz, 2005; Kennes et al., 2001; Shareefdeen and Singh, 2005; Smet et al., 1998) have been studied and used as alternatives for the traditional physical-chemical techniques. In these biotechniques the Henry law coefficient is a very important characteristic, as it affects the performance of the reactor, since the transport of the VOC from the gas phase into the

water could be rate limiting (Zhu et al., 2004). The hydrophilic compounds (lower Henry law coefficients) enter the biofilm much more easily, than hydrophobic compounds (higher Henry law coefficients) (Kim et al., 2005), so these biotechniques are acceptable to treat hydrophilic compounds, but are often limited when dealing with more hydrophobic compounds, e.g. hexane (Arriaga and Revah, 2005a). As the hydrophobicity often limits the pollutant to transfer from the gas to the aqueous phase and industrial emissions often contain a mixture of hydrophilic and hydrophobic compounds, a solution to this problem needs to be found. TPPB which are based on the use of two immiscible liquid phases, i.e., a NAP and an aqueous phase, is therefore a good alternative (Daugulis, 2001; Muñoz et al., 2006). The NAP enhances the transfer of the more hydrophobic compounds to the micro organisms, while the aqueous phase supports the biological activity by supplying the nutrients (Bordel et al., 2010).

The laboratory study presented here was mainly set up to study the performance of a TPPB and this by using SIFT-MS as analysis apparatus. Advantages of the SIFT-MS approach include the ability to measure VOCs online, less than 250 ms for one analysis, and the sensitivity to low ppbv levels. In a first part of this study GC measurements of a TPPB fed with hexane are compared with SIFT-MS analysis in order to compare both measuring techniques. During this period, the CO_2 production was measured daily in order to check if the hexane degradation could be linked to biodegradation.

Recent studies (references) already reported promising results for the reduction of hydrophobic compounds in a TPPB, but most of these studies are based on the treatment of one single compound. As industrial emissions often contain a complex mixture of compounds, it is therefore necessary to investigate how a TPPB will perform if being fed with a mixture of compounds. In a second part of this experimental work, SIFT-MS is used to determine the performance of the TPPB when fed with a mixture of DMS, toluene and hexane. These compounds were selected because of their presence in different waste gases of industrial sources and their difference in hydrophobicity. DMS, which can often be found in the emissions of kraft pulping (Chan, 2006), is known to have a high solubility in water and a low Henry law coefficient of 0.048, while hexane has a very high Henry law coefficient of 44. Toluene has a Henry law coefficient of 0.43 which is about 10 times higher than the one of DMS and about 100 times lower than the one of hexane. Hexane and toluene are both extensively used as solvents in polymer industries, especially during the production of adhesives (Zamir et al., 2012).

Finally the SIFT-MS was used in order to determine the net residence time (NRT) of hexane in the TPPB. This NRT not only indicates the time available to reduce this

compound, but is also a good indicator to check the aeration and dispersion within the TPPB.

4.1.2 Materials and methods

4.1.2.1 Experimental set-up

An overview of the reactor set-up can be found in Fig. 4.1. A 1 L glass reactor was filled with 0.5 L of 25/75 V% silicone oil (47 V 20 Rhodorsil; VWR)/water emulsion which was inoculated with a mixed microbial culture obtained from an activated sludge (Ossemeersen WWTP, Ghent) and first pre-adapted during 1 month. Contaminated air was continuously supplied to the reactor (5) through an air disperser at flow rates ranging from 0.25 to 1.0 l min^{-1}.

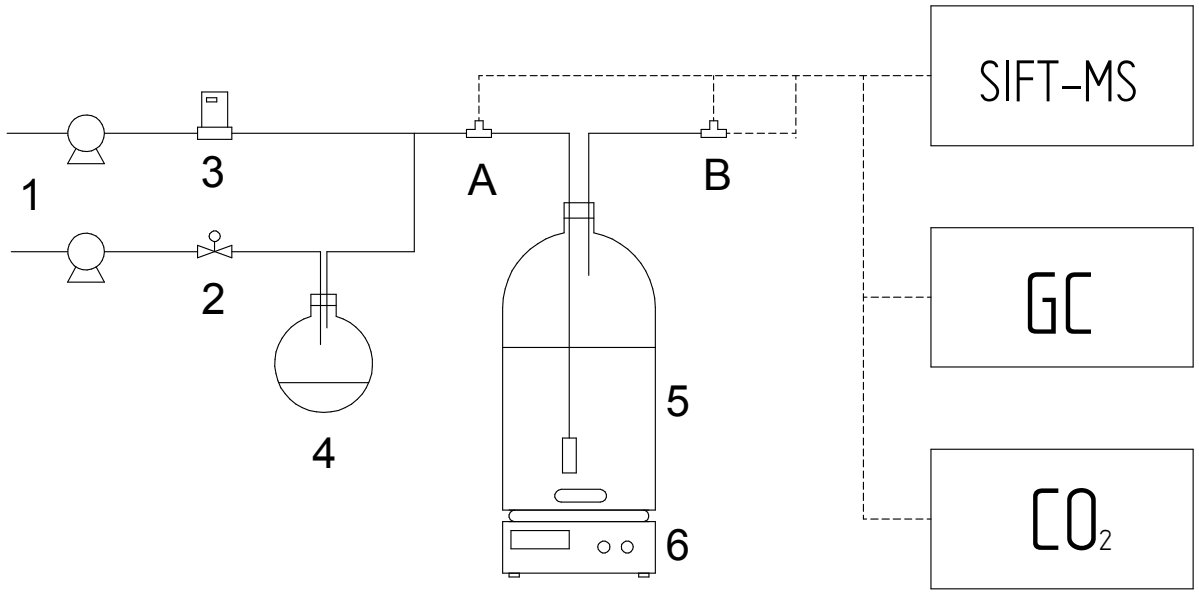


Figure 4.1: Schematic diagram of two-phase partitioning reactor. (1) Air pumps, (2) needle valve, (3) Mass flow controller, (4) flask with Liquid VOC mixture, (5) reactor, (6) magnetic stirrer, (A+B) sample ports.

Dry air was loaded with the selected VOCs by passing a small air stream through the headspace of the VOCs, which were present in the glass flask (4). By adjusting the flow of this additional air stream, using needle valve (2), the VOC concentrations could be regulated. This polluted air stream was diluted by the main air stream, which was adjusted by using a mass flow controller (Brooks Instruments, USA). The reactor was placed on a magnetic stirrer (6) (IKA RCT basic, Germany), in order to keep a good emulsion between the water and the silicone oil.

The necessary macro and micronutrients were incorporated using a pH buffered nutrient solution (pH 7) containing KNO_3, 10.7 g L^{-1}, KH_2PO_4, 3.0 g L^{-1}, K_2HPO_4, 3.0 g L^{-1}, $MgSO_4 \cdot 7H_2O$, 0.5 g L^{-1}, P, Ca, Fe, Zn, Co, Mn, Mo, Ni, B and vitamins at trace doses. These nutrients were daily added manually to the reactor in order to keep a C:N:P ratio of 100:5:1 (Shareefdeen and Singh, 2005).

4.1.2.2 Process conditions

During an adaptation period of 1 month, a mixture of DMS, hexane and toluene (50 mg m^{-3} per compound) was fed continuously to a first TPPB containing 1 L of 25/75 V% silicone oil/water emulsion which was inoculated with a mixed microbial culture obtained from a wastewater treatment activated sludge. This pre-adaptation bottle was used to stimulate the growth of bacteria which are able to use DMS, hexane or toluene as carbon source and to have a resource of fresh inoculated emulsion. After the adaptation period, 500 ml of the inoculated emulsion out of the pre-adaptation bottle was used in the actual TPPB. An emulsion of 25/75 V% silicone oil/water was added to the pre-adaptation bottle in order to keep the volume of this bottle at 1 L.

The actual TPPB was operated under continuous loading for 2 months, during which several operational conditions were tested, see Table 4.1.

Table 4.1: Operational parameters for the two-phase partitioning bioreactor experiments with EBRT the empty bed residence time.

EXP	TIME (days)	EBRT (s)	C_{in} (g m^{-3})	Compounds	Measuring technique
1	0 - 37	60	0.11 - 4.20	Hex	GC
2	38 - 40	60	0.07 - 6.34	Hex	GC/SIFT-MS
3	41 - 42	30	0.05 - 3.46	Hex	GC/SIFT-MS
4	43 - 44	120	0.33 - 12.3	Hex	GC/SIFT-MS
5	45 - 50	60	peak injection	Hex and Tol	SIFT-MS
6	51	60	0.38 - 2.47	Hex, DMS, Tol	GC

During the first 37 days of this research, only hexane was fed to the TPPB and the performance of the reactor was determined by measuring the inlet and outlet concentrations using a GC. Inlet concentrations ranged from 0.11 to 4.20 g m^{-3} at an EBRT of 60 s, which correspond to IL of 6.3 to 205.8 g m^{-3} h^{-1}. During this experiment the CO_2 production at the outlet of the bioreactor was also measured.

The next 3 days, the experiment was repeated, but measurements were conducted with the SIFT-MS. Inlet concentrations of hexane ranged in this case from 0.07 to 6.34 g m^{-3} at an EBRT of 60 s, corresponding to IL of 4.0 to 380.4 g m^{-3} h^{-1}.

In the 3th and 4th part of this research, the EBRT of the TPPB was adjusted to 30 and 120 s respectively in order to determine the influence of the EBRT on the reactor performance.

On day 45, peak injections of hexane and toluene were performed on the TPPB in order to determine the NRT of the compound in the TPPB. Peak injections were performed manually in the different sample ports A and B, see Fig. 4.1, this while operating the TPPB under a constant IL of 3.0 g m^{-3} h^{-1} for each compound and an EBRT of 60 s. When injecting a sample in port B, the original inlet peak was monitored by the SIFT-MS. By injecting a sample in port A, the sample will first pass through the TPPB and a lower, broader outlet peak will be monitored by the SIFT-MS. At the end of day 45 the emulsion in the TPPB was replaced with fresh inoculated and preadapted emulsion out of the pre-adaptation bottle and the pulse experiment was repeated on day 50.

Finally the performance of the TPPB was determined when feeding it, with a mixture of DMS, n-hexane and toluene at an EBRT of 60 s and concentrations ranging from 0.38 to 2.47 g m^{-3} for each compound. As the Henry law coefficients of these three compounds are ranging from 0.048, for DMS, to 44, for hexane, the removal of this mixture will give a good indication of the performance of a TPPB to treat hydrophilic and hydrophobic compounds.

4.1.2.3 Analytical techniques

In the first part of this study the gas concentration of hexane in the gas flow was monitored daily by taking gas samples of 500 µL using a 1.0 ml GASTIGHT® syringe at the gas inlet and outlet of the reactor. Analysis of these samples were performed by using a GC-FID (4890D Series, Agilent Technologies, USA) equipped with an HP-5 capillary column (15 m × 0.53 mm × 1.5 µm, Agilent Technologies, USA) and He as carrier gas used at a flow-rate of 2 ml min^{-1}. The CO_2 gas concentration at the outlet was determined by using a CARBOCAP® carbon dioxide analyser (GM70 model, Vaisala, Finland).

During experiments 2 - 6 (see Table 4.1), the concentrations of the different compounds in the gas flow were monitored by a Voice 200® SIFT-MS (SYFT Technologies Ltd.). In a Voice 200® precursor ions H_3O^+, NO^+ and O_2^+ are generated in a discharge ion source. A specific mass is selected by a quadrupole mass filter and then injected as selected ionic

species into fast-flowing He carrier gas in a flow tube. Determination of the counts per second (CPS) of the precursor ions and the resulting product ions, as a consequence of the reaction of the former with gas phase molecules, is performed by a downstream quadrupole mass spectrometer. To determine the compound concentrations the following product ions were measured for DMS $(CH_3)_2S^+$ [NO^+], m/z = 62; $(CH_3)_2S^+$ [O_2^+], m/z = 62; $(CH_3)_2S.H^+$ [H_3O^+], m/z = 63; CH_2S^+ [O_2^+], m/z = 46; CH_3S^+ [O_2^+] m/z = 47; for toluene $C_7H_8.H^+$ [H_3O^+], m/z = 93; $C_7H_8^+$ [NO^+], m/z = 92; $C_7H_8^+$ [O_2^+], m/z = 92 and for hexane $H_3O^+.C_6H_{14}$ [H_3O^+], m/z = 105; $C_6H_{13}^+$ [NO^+], m/z = 85; $C_6H_{14}^+$ [O_2^+], m/z = 86 . In order to prevent condensation of water vapour, the sample inlet lines are heated to ~ 373 K. He carrier gas pressure is 20 Pa at room temperature (296 – 300 K). Due to the fast analysis (less than 250 ms for one analysis), SIFT-MS makes it very easy to visualise the time at which the TPPB reaches a stable outlet concentration and a new inlet condition can be applied.

To confirm the absolute concentration of the three compounds in the gas flow which were monitored by the SIFT-MS, gas samples of 500 µL were taken at a regular basis during experiments 2 - 4 and 6, using a 1.0 ml GASTIGHT® syringe at the inlet and outlet of the TPPB and analysed with the GC.

4.1.3 Results and discussion

4.1.3.1 Hexane removal in a TPPB

Hexane biodegradation performance of the TPPB was evaluated in terms of EC in function of the IL, see Fig. 4.2. In a first experiment, the performance was determined by using a GC as analytical technique. To ensure that the biomass in the TPPB was adapted to the new inlet conditions before every analysis, the inlet conditions were only changed once a day after the previous measurement. When feeding the TPPB only with hexane, an EC of 138.2 g m^{-3} h^{-1} can be reached for an IL of 205.8 g m^{-3} h^{-1} at an EBRT of 60 s (RE = 67.1 %).

In a second part of this research SIFT-MS was used as analytical technique to measure the concentration at the in- and outlet of the TPPB. As SIFT-MS can measure the outlet concentration online (± 4 analysis per second) it is possible to indicate much faster when the reactor reaches a stable value and several different inlet conditions could be applied in only one day. Each time the outlet concentration remained about constant the TPPB was bypassed, in order to determine the corresponding inlet concentration with the SIFT-MS. Once the steady-state inlet and outlet concentrations were determined, a new IL was applied on the reactor and the outlet concentration was again monitored by the SIFT-MS.

Simultaneous GC measurements during this experiment indicated that the absolute concentrations, monitored by the SIFT-MS, did not correspond to the absolute concentrations obtained by the GC. This could easily be corrected by using a correction factor, as there is a good linearity between both techniques. The experimental data obtained with the SIFT-MS nicely follows the same trend as the data obtained with the GC, see Fig. 4.2, so SIFT-MS is a valuable alternative for GC measurements as soon as the correction factor is determined. The data obtained with the SIFT-MS also indicates that even at a very high hexane IL of 380.4 g m^{-3} h^{-1} (c_{in} = 6.34 g m^{-3}) a high EC of 169.3 g m^{-3} h^{-1} (RE = 44.5 %) will be reached using a TPPR at an EBRT of 60 s. This confirms the findings of Hernández et al. (2012), that the addition of a NAP decreases the inhibitory effects when dealing with very high inlet concentrations.

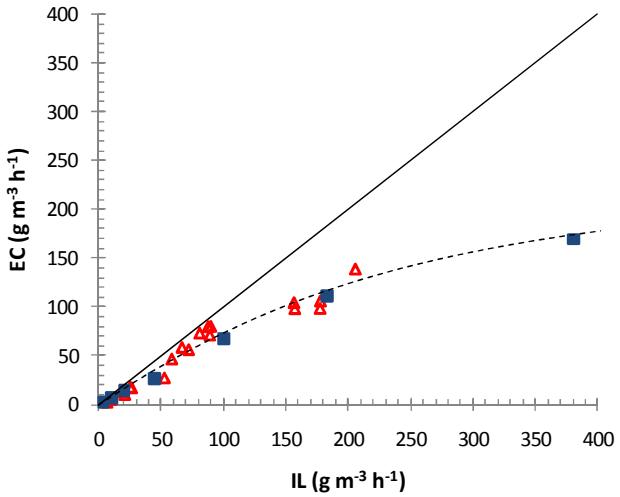


Figure 4.2: Elimination capacity (EC) vs. inlet load (IL) for hexane analyzed with (Δ) GC and (■) SIFT-MS in a two-phase partitioning bioreactor at an empty bed residence time of 60 s.

The performance of the bioreactor was also evaluated based on the production of CO_2. The variation of the CO_2 production with the EC is presented in Fig. 4.3. A linear relationship was found between the CO_2 production and the EC indicating that 0.179 gC-CO_2 m^{-3} was formed for each gC-C_6H_{14} m^{-3} reduced ignoring the dissolved CO_2. Assuming a general biomass composition formula of $C_5H_7O_2N$, the overall yield coefficient Y_{XS}, defined as g of dry biomass per g of hexane consumed could be determined from the biodegradation reaction balance (Delhomenie and Heitz, 2003). When using only hexane and taking into account the calculated ratio of 0.179 gC-CO_2 formed for each gC-C_6H_{14} consumed, the reaction balance could be written as Eq. (4.1).

$$1.01\ C_6H_{14} + 4.64\ O_2 + NH_3 \rightarrow C_5H_7O_2N + 1.09\ CO_2 + 5.10\ H_2O \qquad (4.1)$$

This resulted in a Y_{XS} value of 1.3, indicating that for each gram of hexane degraded, 1.3 g of biomass is formed. Recalculating the yield coefficient to the carbon level, resulted in a biomass yield coefficient value of 0.82 gC-dry mass synthesized per gC C_6H_{14} degraded, which indicates a very high biomass growth in the biofilter, 82 % of the carbon degraded by the microorganisms was transformed in additional biomass, while only 18 % of the carbon degraded was used for CO_2 production. The production of CO_2 by the microorganisms shows that the microbial metabolism was the main factor responsible for the removal of hexane in the biomass. When increasing the IL, partially more carbon is used for biomass production before a steady state condition is reached. Once equilibrium is reached less carbon is used for biomass growth, resulting in an increase in CO_2 production for the same EC.

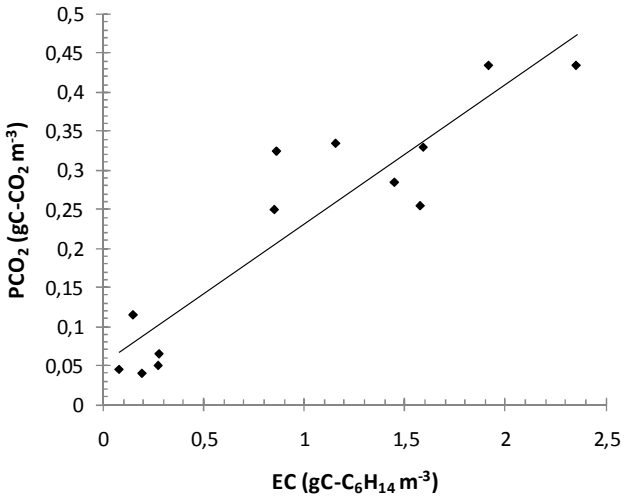


Figure 4.3: CO_2 Production vs. elimination capacity (EC) for hexane at steady state in a two-phase partitioning bioreactor at an empty bed residence time of 60 s.

The performance of the TPPB at three different EBRT expressed as EC in function of IL could be monitored, by the SIFT-MS in only 6 days, see Fig. 4.4. These results indicate a increasing trend of the EC with increasing EBRT. When decreasing the EBRT from 60 s to 30 s, the reactor performance decreases significantly. At an IL of 350 g m^{-3} h^{-1} the EC drops from 163.8 g m^{-3} h^{-1} (RE = 46.8 %) at an EBRT of 60 s to 138.9 g m^{-3} h^{-1} (RE = 39.7 %) at an EBRT of 30 s. This corresponds to a decrease in EC of 15.2 % when decreasing the EBRT by half. Increasing the EBRT from 60 s to 120 s, results in a increase in reactor performance, with an EC of 241.6 g m^{-3} h^{-1} at an IL of 350 g m^{-3} h^{-1} (RE = 69.0 %) and EBRT of 120 s. This corresponds to an increase in EC of 47.5 % when

doubling the EBRT. A higher EBRT not only increases the contact time between the contaminated air and the biomass, leading to a higher performance, but an increasing EBRT (lower air flow rate) can also increase the air transfer efficiency, which is the fraction of the supplied air that actually enters the water, although the amount of air supplied to the TPPR decreases. This can explain the higher increase in EC when doubling the EBRT from 60 to 120 s than when doubling the EBRT from 30 to 60 s.

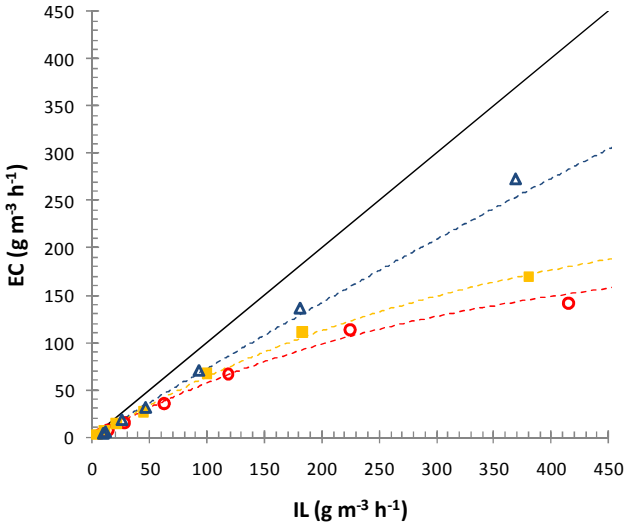


Figure 4.4: Elimination capacity (EC) vs. inlet load (IL) for hexane at an empty bed residence time of (○) 30 s, (■) 60 s and (Δ) 120 s.

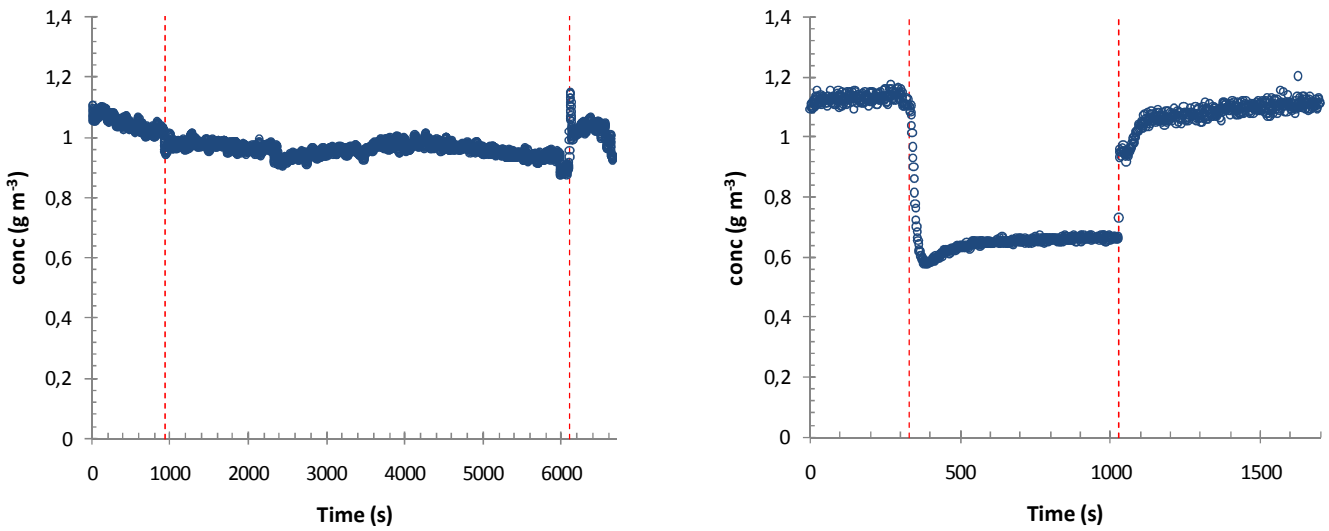
4.1.3.2 Biomass decay and re-inoculation

During experiment 1 - 4, no liquid was purged out of the reactor and a high biomass increase was visible, which confirms the high yield coefficient obtained in section 3.1. Such an active biomass growth was also observed by Muñoz et al. (2013). After experiment 4 the viscosity of the emulsion increased significantly due to the high biomass, which hindered a good aeration of the TPPB. Due to the bad aeration, the reactor performance dropped and the biomass died giving the emulsion a grey colour. Monitoring the inlet and outlet concentration of the TPPB resulted in Fig. 4.5(a). The inlet concentration was measured during 920 s. At 920 s, the outlet was monitored by the SIFT-MS, which did not significant differ with the inlet concentration. This indicates that no more degradation occurred and confirmed the decay of the biomass. At 102 min, the inlet was again monitored by the SIFT-MS in order to check if the inlet concentration remained constant during the measurement.

Before replacing the emulsion containing the death biomass, with fresh emulsion out of the pre-adaptation bottle, the NRT of hexane was measured by injecting manually a fixed amount of headspace gas of hexane (500 µL) in sample ports B and A, see Fig. 4.1. When injecting in port B, the net retention time between the reactor and the SIFT-MS (NRT_B) can be calculated by subtracting the time of injection from the time at which the top of the pulse is monitored by the SIFT-MS. By injecting 500 µL in port A, the net retention time to pass the reactor and the tubing between the reactor and SIFT-MS (NRT_A) can be determined. The difference between NRT_B and NRT_A results in the NRT of hexane, which amounts to 8.9 s in case of a TPPB with thick biomass and bad aeration.

At the end of day 45, the emulsion of the TPPB was replaced by fresh emulsion coming from the pre-adaptation bottle and was fed continuously with 50 mg m^{-3} of DMS, hexane and toluene. On day 50 the inlet concentration was increased to 1.1 g m^{-3} for each compound and the inlet and outlet concentrations for hexane were again monitored, which resulted in Fig. 4.5(b). The inlet concentrations were measured during 331 s resulting in an average inlet concentration of 1.13 ± 0.02 g m^{-3}. At 331 s, the outlet concentrations were monitored by the SIFT-MS and reached a stable average value of 0.66 ± 0.01 g m^{-3}. At 1029 s, the inlet concentrations were again monitored by the SIFT-MS in order to check if the inlet concentration remained constant during the measurements, which resulted in an average inlet concentration of 1.09 ± 0.02 g m^{-3}. In this case it is clear that there was a significant difference between the outlet and inlet concentration, RE = 41.6 %, which was caused by the presence of the fresh biomass degrading the hexane and the good dispersion of the air in the TPPB.

The NRT for hexane was again measured in this fresh emulsion by applying pulse injections in sample ports A and B. This resulted in a NRT of 35.3 s, which is 4.0 times higher than in the thick emulsion, indicating the better aeration of the fresh emulsion. The NRT is therefore a good indicator to monitor the biomass formation and the aeration conditions in a TPPB. A decrease in NRT can indicate that a part of the biomass needs to be purged in order to avoid a drop in the reactor performance and the decay of the bacteria.



(a) (b)

Figure 4.5: SIFT-MS monitoring of hexane concentration at inlet/outlet/inlet (a) before and (b) after inoculation. (---) indicates the time at which the outlet was monitored instead of the inlet and conversely.

The NRT is also a more accurate indicator for the gas residence time in the reactor than the EBRT, as it indicates the exact time that hexane is present in the TPPB. It is clear that the NRT of hexane, 35.3 s, is lower than the EBRT, 60 s. This indicates that the IL, which is calculated based on the EBRT, will be 1.7 times lower than the net IL based on the NRT.

4.1.3.3 Removal of a mixture in a TPPB

To illustrate the influence of a compound mixture on the performance of a TPPB, an air stream contaminated with DMS, toluene and hexane was fed to the reactor at an EBRT of 60 s. Plotting the EC of the different compounds as a function of the IL, see Fig. 4.6, shows that the biodegradation of toluene results in the highest RE with an average value of 72 ± 5 % for IL up to 120 g m^{-3} h^{-1}.

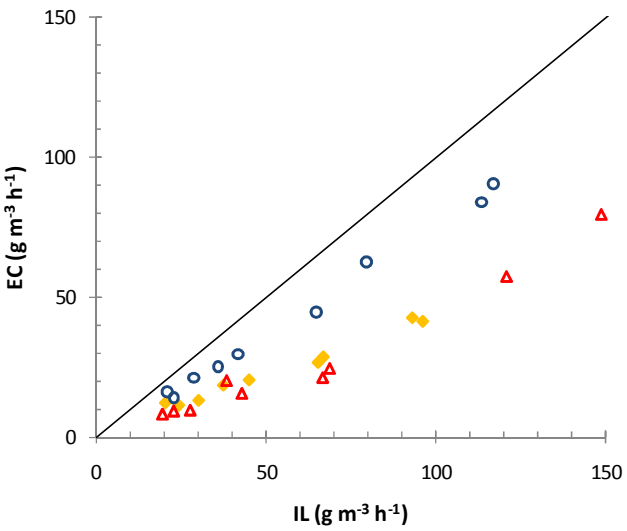


Figure 4.6: Elimination capacity (EC) vs. inlet load (IL) for (Δ) hexane, (○) toluene and (◆) DMS at an EBRT of 60 s.

The EC for DMS and hexane show about the same trend in the measured IL range, although both compounds have completely different Henry law coefficients. For DMS the average RE amounts 47 ± 6 % for IL up to 100 g m^{-3} h^{-1} and for hexane 42 ± 8 % for IL up to 150 g m^{-3} h^{-1}. At an IL of 100 g m^{-3} h^{-1} and an EBRT of 60 s EC of 45, 45 and 75 g m^{-3} h^{-1} are reached for respectively DMS, hexane and toluene. While biofilters are limited in degrading high inlet concentrations of VOC, because of the possible inhibitory effect on the biomass at the inlet of the filter, it is clear that a TPPB can deal with much higher inlet loads, since the emulsion in a TPPB is well mixed and dispersed. This was already reported by several authors when feeding the reactor with a single compound (Davidson and Daugulis, 2003; Montes et al., 2010; Muñoz et al., 2013), but this study indicates that even when feeding the reactor with a VOC mixture of 3 different compounds and at a total IL > 300 g m^{-3} h^{-1}, high RE can be reached. The EC of hexane in a mixture after refreshing the emulsion only differs little from the EC of hexane as single compound, see Fig. 4.7. At an IL of 150 g m^{-3} h^{-1} the EC of hexane amounts ± 98 g m^{-3} h^{-1} when feeding hexane as single compound and ± 80 g m^{-3} h^{-1} when feeding hexane in a mixture with toluene and DMS. This indicates that the addition of DMS and toluene does not really inhibit the degradation of hexane. These results indicate that the TPPB is a useful and reliable technique to treat a mixture of hydrophobic and hydrophilic VOC even at high IL.

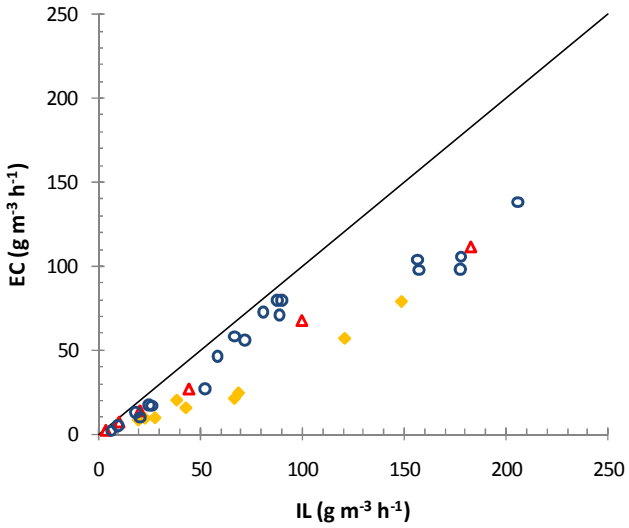


Figure 4.7: Elimination capacity (EC) vs. inlet load (IL) in a two-phase partitioning bioreactor at an EBRT of 60 s for hexane as single compound measured with (Δ) SIFT-MS and (○) GC and (◆) hexane in a mixture measured with GC.

4.1.4 Conclusions

The results obtained during this research illustrate that SIFT-MS is a suitable measuring technique to analyze online the performance of a TPPB and this in a short time period, as it is possible to adapt the inlet conditions much faster. Using the SIFT-MS it was possible to measure the NRT of a compound in the TPPB, which can be an indicator of the aeration in the bioreactor. A decrease in the NRT can indicate that part of the biomass needs to be purged in order to keep the aeration in the bottle optimal. When feeding only hexane to the TPPB, an EC of 138.2 g m^{-3} h^{-1} can be reached for an IL of 205.8 g m^{-3} h^{-1} at an EBRT of 60 s (RE = 67.1 %). Decreasing the EBRT, results in a decrease of the EC, which is possibly due to the lower contact time, but also to a decrease in air transfer efficiency when increasing the air flow. Feeding the TPPB with a mixture of DMS, hexane and toluene, at an EBRT of 60 s, results in an EC of respectively 45, 45 and 75 g m^{-3} h^{-1} for an IL of 100 g m^{-3} h^{-1}. This indicates that a TPPB is a reliable technique to treat high IL of hexane as single compound or in a VOC mixture containing compounds with different hydrophobicity.

4.2 SIMULTANEOUS BIODEGRADATION OF ACETONE, DIMETHYL SULPHIDE, N-HEXANE, TOLUENE AND LIMONENE IN A BIOFILTER AND A TWO-LIQUID-PHASE BIO(TRICKLING)FILTER IN SERIES

Summary

Waste air contaminated with a mixture of acetone, DMS, toluene, limonene and hexane was continuously fed to a biofilter, filled with compost (40 V%) and wooden dowels (60 V%), and a two-liquid-phase biofilter, filled with wooden dowels saturated with silicone oil, in series. Varying the pH in the first biofilter between 5.5 to 8.3 resulted in an optimal pH of 7.1, 6.6, 8.6 and 7.2 for respectively the degradation of acetone, DMS, toluene and limonene. The RE decreased with respectively 4.2 %, 16.1 %, 1.5 % and 6.7 % for acetone, DMS, toluene and limonene when applying a pH one unit lower than the optimal pH. This indicates that pH variations have the largest effect on the DMS degradation in this set-up. A dry-out period of 20 days was applied on the first biofilter in order to determine the influence of the moisture content of the packing material on the biofilter performance. After the dry out period the activity in the first reactor part decreased significantly, as this was the reactor part with the highest decrease in moisture content. For acetone, toluene, limonene and hexane, the RE increases with decreasing Henry law coefficient and the inhibitory effect of these compounds on the hexane degradation increases with decreasing Henry law coefficient. In a second part of this study, a 40/60 V% silicone oil/water emulsion was recirculated over the second biofilter, resulting in a two-liquid-phase biotrickling filter, in order to decrease the mass transfer resistance for hydrophobic compounds, which resulted in an increase of hexane removal. This emulsion also reduces the inhibitory effect when a mixture of hydrophilic and hydrophobic compounds is fed to the reactor.

4.2.1 Introduction

VOC can be defined as any organic compound having at 293.15 K a vapour pressure of 0.01 kPa or more, or having a corresponding volatility under the particular conditions of use (EU, 1999). This definition indicates that a large variety of organic compounds, with different properties can be classified under the term VOC, i.e. alkanes, alkenes, aromatics, sulphur compounds, esters, ethers, aldehydes… Biological gas treatment techniques such

as biofilters, biotrickling filters and bioscrubbers have been studied and used to remove VOC out of a waste air stream as alternatives for the traditional physical-chemical techniques (Estrada et al., 2011; Kennes et al., 2009; Vedova, 2008). These biotechniques are easy to construct and to operate and have low investment and operating costs (Estrada et al., 2011), but due to the difference in physical properties of the compounds, the performance of a bioreactor to treat a mixture of different VOC is often challenged. Especially for the most hydrophobic compounds the degradation will be lower as a result of the higher mass transfer resistance for these compounds to transfer from the gas to the liquid phase (Arriaga et al., 2006; Darracq et al., 2010), which limits the microbial activity potential (Arriaga and Revah, 2005a; Dumont et al., 2010; Muñoz et al., 2012). Also the presence of one compound can inhibit the degradation of another compound (Dixit et al., 2012; Gallastegui et al., 2011), which indicates the complexity of treating a mixture of different VOC in a bioreactor. The present study was set up in order to get more insight in the degradation of a complex VOC mixture, by feeding a biofilter with a mixture of five VOC with different properties, i.e,. a ketone (acetone), a sulphur compound (DMS), an aromatic compound (toluene), a terpene (limonene) and an alkane (hexane). In the first part of this study the influence of the Henry law coefficient, the pH and the humidification on the performance of a more conventional biofilter, filled with compost (40 V%) and wooden dowels (60 V%), was determined. During this first part a second biofilter (BF2), which was filled with 100 V% of wooden dowels, was put in series with the first biofilter (BF1). The wooden dowels were first soaked in silicone oil for 3 hours, before being used as packing material. Using a hydrophobic solvent as silicone oil into the bed of a biofilter can improve the performance of the biofilter considerably as long as the process is not bioreaction limited (Fazaelipoor et al., 2006).

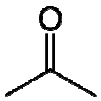
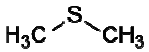
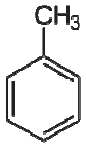
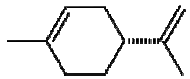
In a following part a silicone oil/water emulsion inoculated with activated sludge was recirculated over BF2, in order to improve the degradation of the more hydrophobic compounds in BF2. This emulsion was also used to supply nutrients, to humidify the column and to preserve the NAP in the reactor. Using a water/silicone oil emulsion inoculated with sludge to remove VOC out of a waste air stream, was already successfully applied in a Two-phase partitioning bioreactor (Muñoz et al., 2012; Muñoz et al., 2007). In a last part of this study, the compound mixture was adapted in order to check the influence of the presence of other compounds on the hexane removal in the biofilters.

Acetone, DMS, toluene, limonene and hexane are VOC which are often found in waste gases of industrial sources, but have different physical properties. Especially the difference in water solubility and Henry law coefficient is remarkable, see Table 4.2. Acetone, which is very soluble in water, has a Henry law coefficient which is about 4000

times lower than the one of hexane. This indicates that acetone will transfer much more easily from the gas phase to the liquid phase in comparison with hexane.

A 1:1:1:1:1 (wt) mixture of these 5 compounds was fed to the biofilter in order to research the reactor performance on the removal of a compound mixture with total different hydrophobicitiy.

Table 4.2: Compound properties.

Compound	**Acetone**	**DMS**	**Toluene**	**Limonene**	**Hexane**
Structure					
Functional group	Ketone	Sulphur compound	Aromatic compound	Terpene	Alkane
Solubility in H_2O at 25 °C (g L^{-1}) [b]	94	45	0.32	0.0034	0.016
Vapour pressure at 25 °C (mmHg) [b]	348	647	27.7	1.54	151
Boiling point (°C) [b]	46.5	29.5	110.6	175.4	68.5
Henry law coefficient (-) (C_g/C_l) [a]	0.012	0.048	0.43	3.3	44
Odour threshold (ppmv) [c]	42	0.003	0.33	0.038	1.5
Industrial sources	Paint, varnish, ink. coating industry [d]	Pulp and paper industry [e]	Solvent for polymer production [f]	Waste water treatment plant [g]	Solvent for polymer production [f]

[a] Calculated using the solubility and the vapour pressure

[b] (SciFinder); [c] (Nagata, 2003); [d] (Paca et al., 2010); [e] (Chan, 2006); [f] (Zamir et al., 2012); [g] (Lebrero et al., 2013a)

4.2.2 Materials and methods

4.2.2.1 Biofilter reactors

Both bioreactors were constructed out of 3 identical, cylindrical modules of Plexiglas with an internal diameter of 0.1 m. The length of each reactor was 0.6 m, resulting in an empty volume of 5.10E-3 m^3 per biofilter. Over the complete length of each reactor there were 4 different sampling ports to measure the VOC concentrations, i.e., inlet, outlet and 2 intermediate ports as shown in Fig. 4.8.

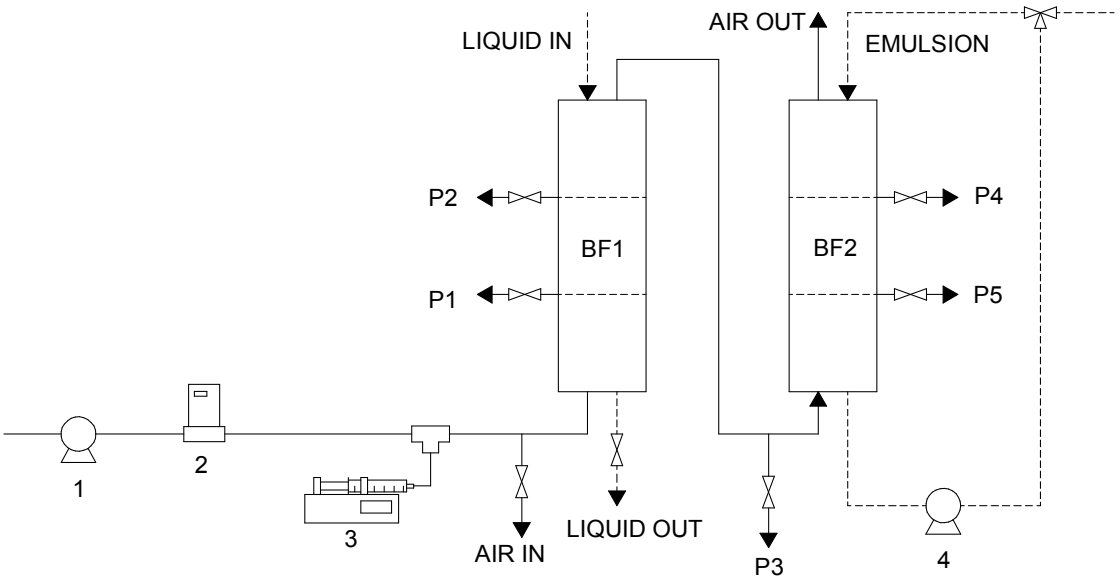


Figure 4.8: Schematic diagram of the two biofilters in series. (1) air pump, (2) mass flow and read-out unit, (3) syringe pump, (4) membrane pump and (P1-5) sample ports.

In biofilter 1 (BF1) a mixture of wooden dowels (length = 15 mm; diameter = 6 mm; 60 V%) and compost (40 V%) was used as carrier material on which the microorganisms could grow. Biofilter 2 (BF2) was filled with wooden dowels, which were first soaked in silicone oil in order to get a hydrophobic contact area. Air was loaded with a VOC mixture by using a syringe pump (New Era, infusion/withdraw NE 1000 Model) and was pumped through BF1 and BF2 from bottom to top. This flow direction was chosen, as H_2SO_4 will be formed in the water when degrading DMS. This sulphuric acid will lower the pH in the biofilter, but in this case only in the bottom parts, where the highest DMS removal will take place. This makes it easier to control the pH in the biofilter. BF1 and 2 were humidified once a day with respectively 150 and 50 ml water and 20 ml nutrients were added to each biofilter once a week to keep a C:N:P ratio of at least 100:5:1 (Shareefdeen and Singh, 2005). This ratio was weekly checked in BF1 by measuring the

nutrients in the leachate, i.e., total phosphate, total nitrogen and nitrate concentrations. The nutrients consisted out of a pH buffered nutrient solution (pH 7) containing KNO_3, 53.6 g L^{-1}, KH_2PO_4, 8.0 g L^{-1}, K_2HPO_4, 8.0 g L^{-1}, $MgSO_4 \cdot 7H_2O$, 0.5 g L^{-1}, P, Ca, Fe, Zn, Co, Mn, Mo, Ni, B and vitamins at trace doses. The activated sludge used to inoculate both reactors came from a wastewater treatment plant (Ossemeersen, Ghent) and was first preadapted during 4 weeks. In this adaptation period the aerobic sludge was put in a bottle of 1 L and continuously fed with an air stream of 1 L min^{-1} contaminated with a 1:1:1:1:1 (wt) mixture of acetone, DMS, toluene, limonene and hexane at a concentration of 0.1 g m^{-3} for each compound to acclimate the microbial cultures in the sludge.

In the second part of this study, an emulsion of silicone oil (40 V%, 47 V 20 Rhodorsil; VWR) and water and mineral medium (60 V%) was recirculated in BF2 by a membrane pump (Milton Roy) from top to bottom at a low flow rate of 7 ml min^{-1}, in order to humidify the reactor and to keep a good mixture between the water and the NAP in the biofilter. This emulsion was first inoculated with sludges from the same wastewater treatment plant and was preadapted in a two-phase partitioning bioreactor.

4.2.2.2 Process conditions

Both biofilters were operated under continuous loading during 183 days. An overview of the operational conditions, which were applied during this period, can be found in Table 4.3.

In the first 10 days of the experiment, a mixture of 1:1:1:1:1 (wt) acetone, DMS, toluene, limonene and hexane was fed to the biofilters. After this period the total inlet concentration was increased from 93 ± 3 mg m^{-3}, corresponding to an average concentration of 19 ± 3 mg m^{-3} for each compound, to 263 ± 48 mg m^{-3}, corresponding to an average concentration of 53 ± 2 mg m^{-3} for each compound. During the next 40 days (day 11 – 51), the pH was increased in BF1 from 5 to 8.3, by adding 0.01 M of K_2HPO_4 at the top of the reactor, in order to determine the influence of the pH on the reactor performance. The pH in BF2 was kept at 7 during the whole research. At day 52 the pH in BF1 was set at 6.6, by adding 0.01 M KH_2PO_4 at the top of the reactor, and no more nutrients and water was added to the biofilter during the next 20 days (day 52 – 72). After this dry-out period, 200 ml water and 50 ml nutrients were added to BF1. On day 74, 500 ml of water was added and recirculated over BF1 in order to increase the humidity in the biofilter. From day 75 the normal amount of water (150 ml per day) and nutrients (20 ml per week) were added to BF1. At day 82 a 40/60 V% silicone oil/water emulsion was recirculated over BF2 in order to increase the hydrophobicity.

From day 152 to 183 the composition of the compound mixture was changed frequently in order to determine the inhibitory effect of other compounds on the removal of hexane. To determine the maximal removal of hexane in the biofilters, the air was first polluted with hexane as single compound for 11 days (day 152 – 162). Afterwards a mixture of hexane with respectively toluene (day 163 - 165), acetone (day 166 - 170), DMS (day 171 - 177) and limonene (day 178 - 183) was added to the air stream.

Table 4.3: Operational parameters.

Day	C_{in} (mg m^{-3})	pH BF1	Compounds
1 - 10	93 ± 3	5 - 5.5	Acetone, DMS, toluene, limonene, hexane
11 - 29	263 ± 48	5 - 5.5	Acetone, DMS, toluene, limonene, hexane
30 - 51	263 ± 48	6 - 8.3	Acetone, DMS, toluene, limonene, hexane
52 - 82	263 ± 48	6.6	Acetone, DMS, toluene, limonene, hexane
82 - 151	263 ± 48	6.6	Acetone, DMS, toluene, limonene, hexane
152 - 162	138 ± 16	6.6	Hexane
163 - 165	279 ± 29	6.6	Hexane and toluene
166 - 170	205 ± 11	6.6	Hexane and acetone
171 - 177	248 ± 5	6.6	Hexane and DMS
178 - 183	171 ± 36	6.6	Hexane and limonene

4.2.2.3 Analytical techniques

The gas concentrations of the different compounds in the gas flow at the inlet, outlet and intermediate sampling ports, were monitored daily. Gas samples of 500 µl were taken at the different sampling ports using a 1.0 ml GASTIGHT® syringe and were analysed with a GC-FID (4890D Series, Agilent Technologies, USA) equipped with an HP-5 capillary column (30 m × 0.53 mm × 5 µm, Agilent Technologies, USA) and He as carrier gas used at a flow-rate of 5.2 ml min^{-1}. Temperatures for the injector and detector were kept constant at respectively 493 and 523 K. The temperature in the oven increased linearly from 308 K to 328 K (at 10 K per minute), stayed constant during 4 minutes, followed by a linear increase from 328 K to 413 K (at 40 K per minute), stayed again constant during 1 minute and increased linearly from 413 K to 498 K (at 50 K per minute).

The pH (Jenway 3310 pH-meter) of the leachate was measured daily, while the conductivity (Hanna Instruments, HI98312) was measured weekly. COD, total phosphate, total nitrogen and nitrate concentrations in the leachate were also measured weekly with Nanocolor® tube tests (Macherey–Nagel, Germany).

4.2.3 Results and discussion

4.2.3.1 Reactor performance

On the first day after inoculating the reactor, day 1, a RE > 99 % was already achieved for acetone, DMS, toluene and limonene, while the RE of hexane only reached 47 % at an EBRT of 40 s for each reactor and an average inlet concentration of 19 ± 3 mg m^{-3} for each compound. After 10 days of operating the biofilters, the hexane removal increased to 78.5 %. For acetone, DMS, toluene and limonene 90 % removal was already reached after an empty bed contact time of respectively 22 s, 37 s, 38 s and 50 s. In case of hexane, no degradation occurred in BF1, but an average RE of 65 ± 11 % was achieved in BF 2. On day 11 the average inlet concentration of each compound was increased to 53 ± 2 mg m^{-3}. In this case a RE > 99 % was only achieved for acetone and toluene after passing both reactors. For limonene and DMS the RE decreased respectively to 95 and 84 % and no significant removal of hexane was observed. For acetone, toluene and limonene 90 % removal was achieved after an empty bed contact time of respectively 20 s, 40 s and 50 s.

During these first 29 days, the pH decreased from 5.5 to 5, which was probably due to the oxidation of DMS resulting in the formation of H_2SO_4.

a) *Influence of the pH*

The effect of the pH on the performance of BF1, represented as RE, at an EBRT of 40 s and a total IL of 24 ± 4 g m^{-3} h^{-1} is shown in Fig. 4.9 for all compounds except for hexane, as there was no significant degradation in BF1 for hexane. For acetone, limonene, toluene and DMS the RE was monitored after passing respectively 1, 3, 2 and 3 reactor parts as in this case the RE was about the same for the 4 compounds. The different graphs show that there is an optimal pH for all compounds, which is around 7.1, 6.6 and 7.2 for respectively acetone, DMS and limonene. For toluene, the optimal pH is not reached in the measured pH range, but based on extrapolation it will probably be around 8.6. The majority of micro-organisms able to remove pollutants show an optimal growth in a certain pH range, which is usually around neutral pH. This is confirmed by the obtained values for the optimal pH to degrade acetone, DMS, toluene and limonene. pH values that differ from the optimum pH can affect the metabolism by altering the chemical balance of enzymatic reactions or by actually destroying the enzymes. A low pH value can even halt the chain of biological reactions.

To study the impact of a shift in pH away from the optimal pH on the reactor performance, the RE was determined at a pH which was one unit lower than the optimal pH. This resulted in a decrease in RE from 86.4 to 82.2 % for acetone, which corresponds

to a decrease of 4.2 % per pH unit. For DMS the RE decreases from 93.7 to 77.6 %, corresponding to a decrease of 16.1 % per pH unit. The RE for toluene decreases from 83.6 to 82.1 %, corresponding to a decrease of 1.5 % per pH unit, and for limonene from 96.9 % to 90.2 %, corresponding to a decrease of 6.7 % per pH unit. This indicates that a pH shift will have the highest impact on the degradation of DMS, while the impact on the degradation of acetone, toluene and limonene is rather low. Therefore the pH in BF1 was set on 6.6 as this is the optimal pH for DMS. This results in a RE of about 85.3, 93.7, 77.3 and 94.2 % for respectively acetone, DMS, toluene and limonene.

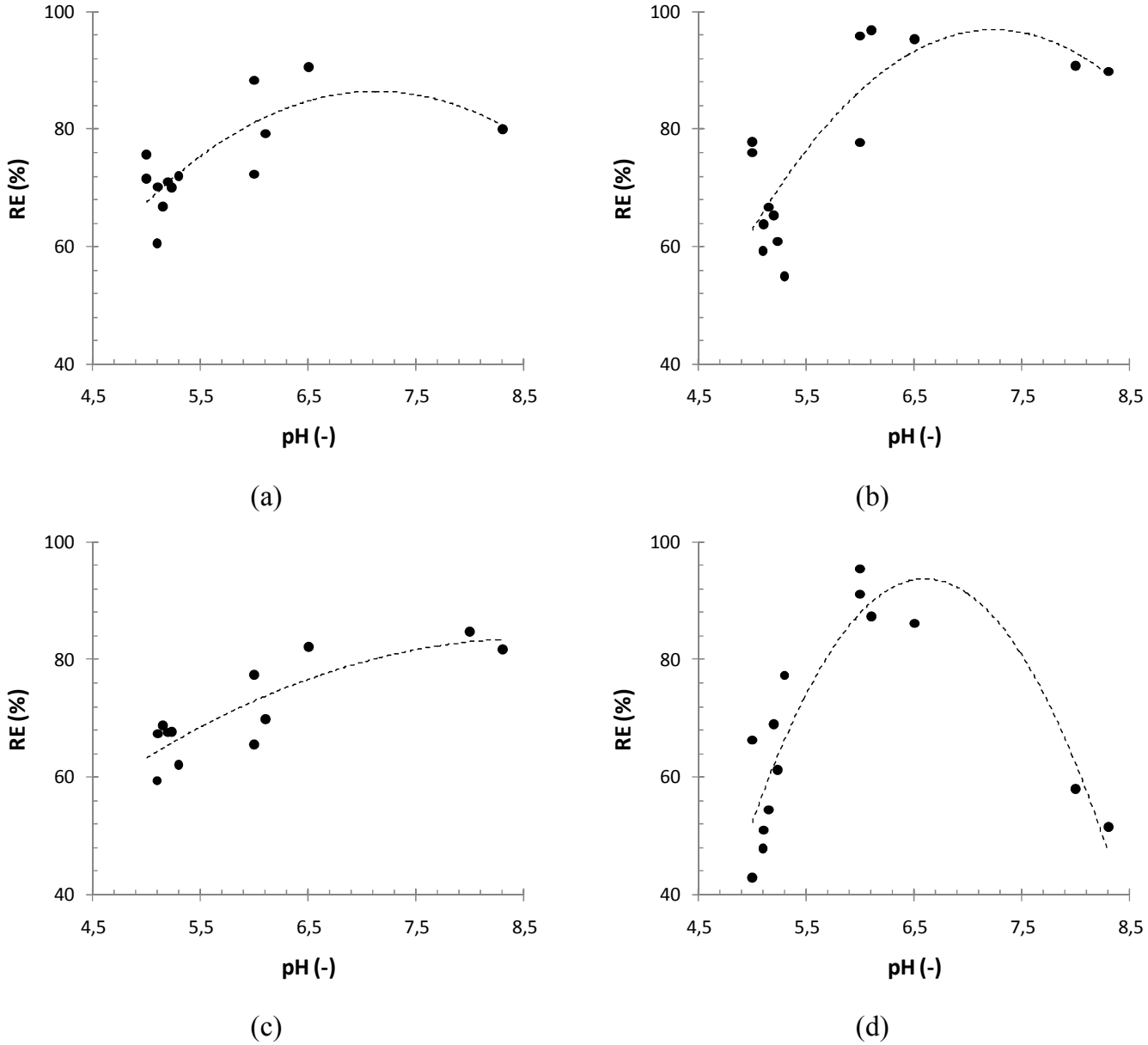


Figure 4.9: Influence of the pH on the removal efficiency (RE) of (a) Acetone after passing through 1 reactor part, (b) Limonene after passing through 3 reactor parts, (c) Toluene after passing through 2 reactor parts and (d) DMS after passing through 3 reactor parts.

b) *Influence humidity*

The humidity of the packing material is a key parameter influencing the activity of the bacteria in the bioreactor. If the humidity is too low; the bacteria will dry out, resulting in a decrease of activity and lower reactor performance. A humidity which is too high will create anaerobic parts in the reactor and increase the pressure drop (Campbell and Connor, 1997; Dorado et al., 2010). The effect of the humidity on the performance of BF1 was examined by shutting of the humidification and nutrient supply for 20 days. As microbial oxidation is an exothermic reaction, which results in an increase of bed temperature, moisture loss from the packing material will occur on a continuous basis and the filter bed will eventually dry out (Devinny et al., 1999). The dry-out of the packing material was first visible in the bottom part of the reactor, as this is the part with the highest biodegradation. Before measuring the concentrations after the dry-out period, 200 ml water and 50 ml nutrients were added to BF1, in order to provide the necessary nutrients to the bacteria.

The influence of the dry-out period on the degradation of the different compounds is shown in Fig. 4.10. For all 4 compounds the total reactor performance decreases after a dry-out period of 20 days. For acetone (Fig. 4.10(a)), limonene (Fig. 4.10(b)) and toluene (Fig. 4.10(c)) it is clear, that the dry-out period had the highest influence on the biodegradation in the first reactor part, 13.3 s of empty bed contact time. This can be linked with the high biodegradation in this part before the dry-out period and the lowering in moisture content in the first part of the reactor after the dry-out period. In case of DMS (Fig. 4.10(d)), this trend is not visible, as the highest biodegradation of DMS before the dry-out period occurred in the second and third part of the reactor instead of the first part. Before drying out the biofilter, the RE after 13.3 s of empty bed contact time (1 reactor part) amounted 92.9 %, 32.5 %, 38.0 % and 10.5 % for respectively acetone, limonene, toluene and DMS. After the dry-out period the RE of acetone, limonene and toluene fell back to 8.0 %, 0.5 % and 6.6 %, while the RE of DMS remained about equal, 7.6 %. The biodegradation in the second and third part of the reactor for toluene, DMS and limonene is not significantly influenced by the dry out period of 20 days, as this period was not long enough to decrease the moisture content significantly in these reactor parts. In case of acetone the biodegradation in the second and third reactor part increases significantly. Before the dry-out period about all the acetone is degraded by the first reactor part, so almost no biodegradation occurs in the following parts. After the dry out period the activity in the first reactor part decreases and more acetone is fed to the second and third part, which stimulates the biodegradation in these parts.

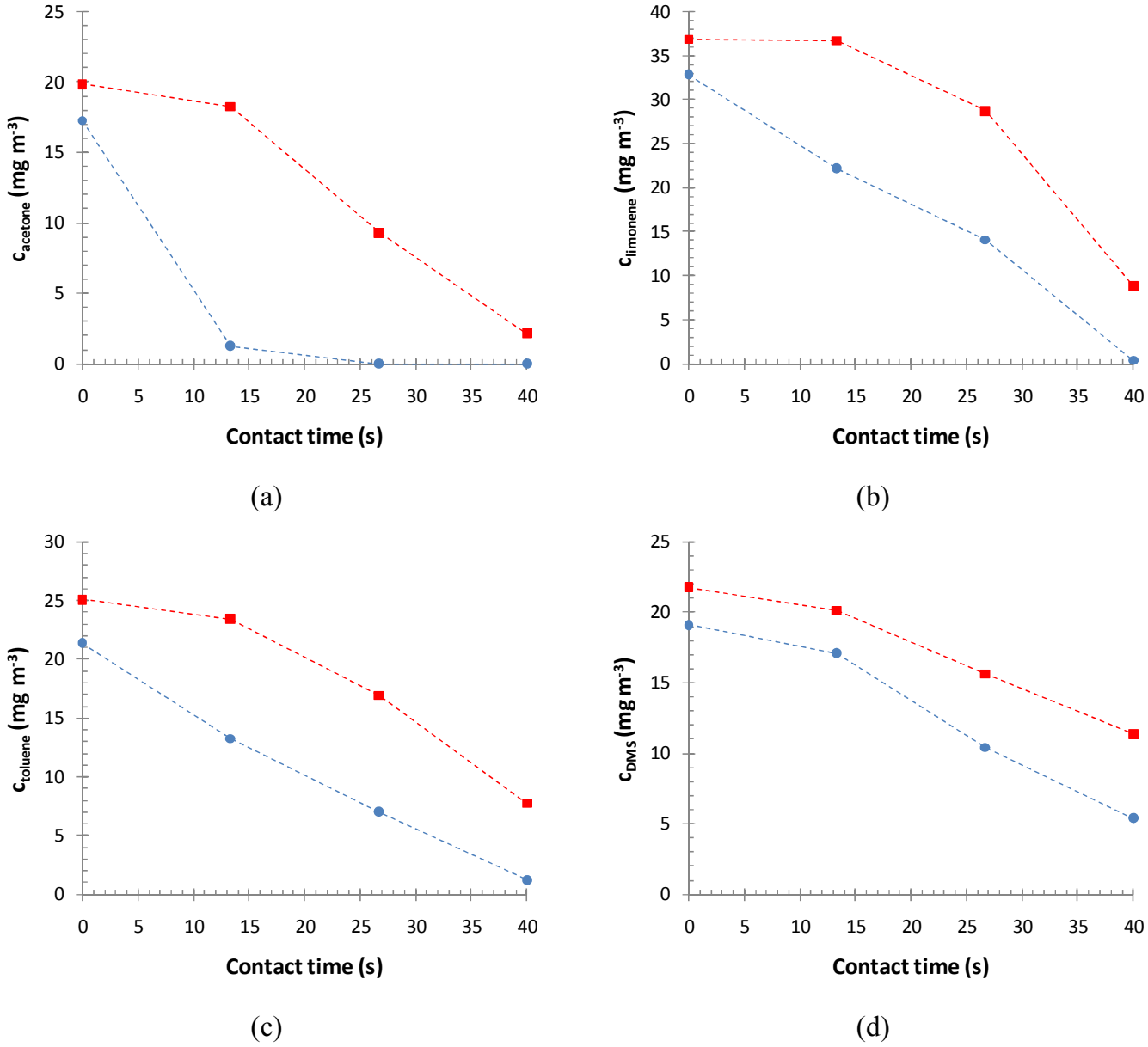


Figure 4.10: Influence of the humidification on the reactor performance for (a) acetone, (b) limonene, (c) toluene and (d) DMS. (●) When adding 150 ml water and 20 ml nutrients once a week and (■) after 20 days without any humidification.

c) *Influence of the Henry law coefficient*

The Henry law coefficient plays an important role in the elimination of VOC in biofilters (Deshusses and Johnson, 2000). A higher Henry law coefficient will lead to a higher mass transfer resistance from the air to the liquid phase, which may limit the efficiency of biological air filters. The influence of the Henry law coefficient on the degradation of the different compounds is shown in Fig. 4.11. For acetone, hexane, toluene and limonene it is clear that the RE decreases with increasing H. After passing one reactor part (empty bed contact time = 13.3 s), the RE amounts 86.4 %, 71.5 %, 56.0 % and 3.2 % for respectively

acetone (H = 0.012), toluene (H = 0.43), limonene (H = 3.3) and hexane (H = 44). To reach a fixed RE, the contact time increases with increasing H, e.g., a RE > 80 % is already reached for acetone after passing 1 reactor part, while for toluene and limonene respectively 2 and 3 reactor parts are needed. In case of DMS, the RE does not follow the same trend as the RE of the other compounds. A possible explanation for the lower RE is that the bacterial cultures which are responsible for the degradation of DMS are known to be slow growers (Hayes et al., 2010), which makes it harder to compete with the other compounds.

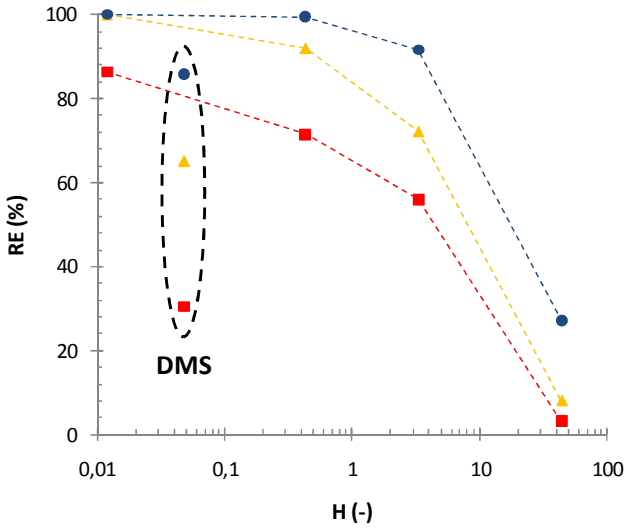


Figure 4.11: Influence of the Henry law coefficient on the removal efficiency (RE) of the compound after passing through (■) 1 part, (▲) 2 parts and (●) 3 parts.

4.2.3.2 Hexane degradation

a) *Silicone oil/water emulsion*

One of the objectives of this study was to improve the hexane degradation in a biofilter, when it was fed to the bioreactor with other more hydrophilic compounds. The use of a non-aqueous phase has already successfully been used in a TPPB to treat hydrophobic compounds, but this configuration is the most energy consuming among the biotechnologies (Muñoz et al., 2012). Therefore in the first part of this study BF2 was filled with wooden dowels which were first soaked into silicone oil in order to create a more hydrophobic surface area and to create a low-cost alternative for the TPPB. Recent studies already reported promising results by adding a NAP to the packing material of a biofilter, but these studies are scarce and were all performed on single compounds. Lebrero et al. (2014) reported an increase in EC from 10.5 ± 1.0 g m^{-3} h^{-1} to 22.9 ± 1.6 g m^{-3} h^{-1} when adding 10 % silicone oil to a compost based packing material at an IL of 29.4

± 1.9 g m^{-3} h^{-1} and an EBRT of 75 s. Fazaelipoor et al. (2006) obtained an EC of 114.9 g m^{-3} h^{-1} in a perlite biofilter without silicone oil at an EBRT of 147 s and an IL of 200 g m^{-3} h^{-1}. This EC increased to 167 g m^{-3} h^{-1} when the perlite bed particles were partially coated with silicone oil. The hexane degradation profile from this study through both biofilters is shown in Fig. 4.12.

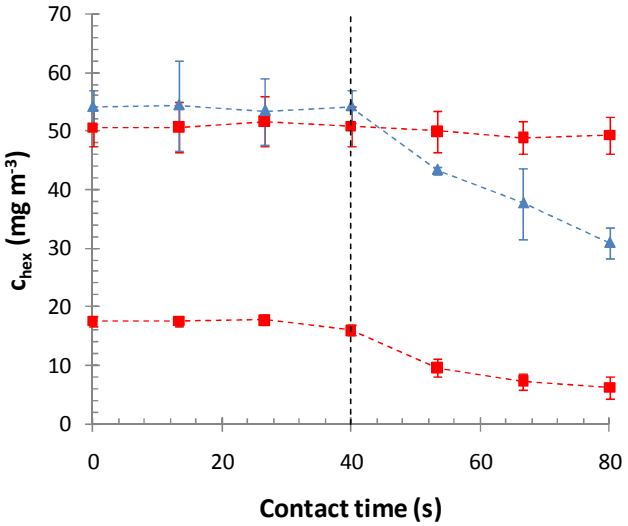


Figure 4.12: Hexane degradation profile for 2 biofilters in series (■) without recirculating a silicone oil/water emulsion over the second biofilter and a hexane inlet concentration of 17.6 ± 1.0 mg m^{-3} and 51 ± 3 mg m^{-3} and (▲) with recirculating a silicone oil/water emulsion over the second biofilter and a hexane inlet concentration of 54 ± 3 mg m^{-3}. (---) indicates the separation between the first and the second biofilter.

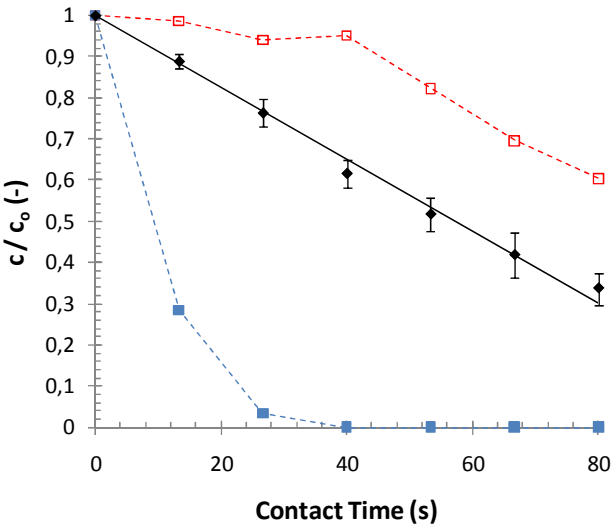
When hexane is fed in a mixture with acetone, DMS, toluene and limonene, there is no significant removal in the first biofilter even at the lowest hexane inlet concentration of 17.6 ± 1.0 mg m^{-3}. In BF2, with the wooden dowels saturated with silicone oil as packing material, an average RE of 64.7 % is reached for hexane. When increasing the average inlet concentration to 51 ± 3 mg m^{-3} per compound, no more significant removal of hexane occurs in BF2.

To increase the hexane degradation even further, an emulsion of silicone oil (40 V%) and water with mineral medium (60 V%) was recirculated resulting in a two-liquid-phase biotrickling filter. Montes et al. (2010) reported an increase in the biodegradation of α-pinene by applying a two-liquid-phase biotrickling filter. Also Rene et al. (2011) reported a 4 times higher maximal EC for styrene when adding 10 V% silicone oil to the trickling medium at an EBRT of 91.2 s. The emulsion used in this study was first inoculated with sludge and preadapted in a two-phase partitioning bioreactor, in which a RE of 70 % was reached for hexane at an inlet concentration of 2 g m^{-3}. After 3 days of recirculating the

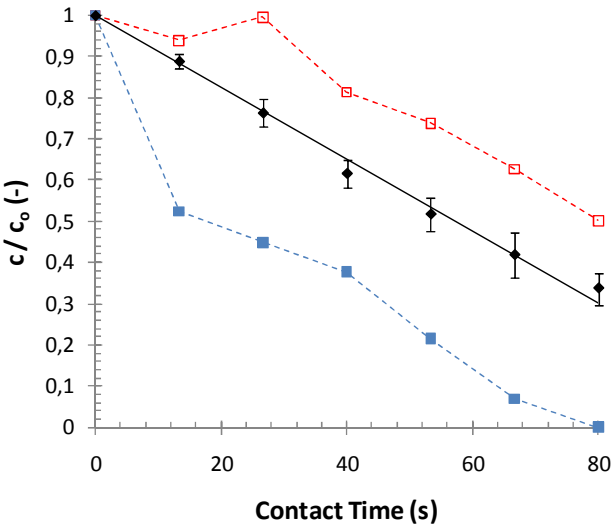
emulsion, a linear degradation profile of hexane was observed, which resulted in a total RE of 43 ± 2 %. This RE remained constant around 42.9 % during the following 66 days (day 85 – 151) for IL up to 10 g m^{-3} h^{-1} of hexane.

b) *Inhibitory effect*

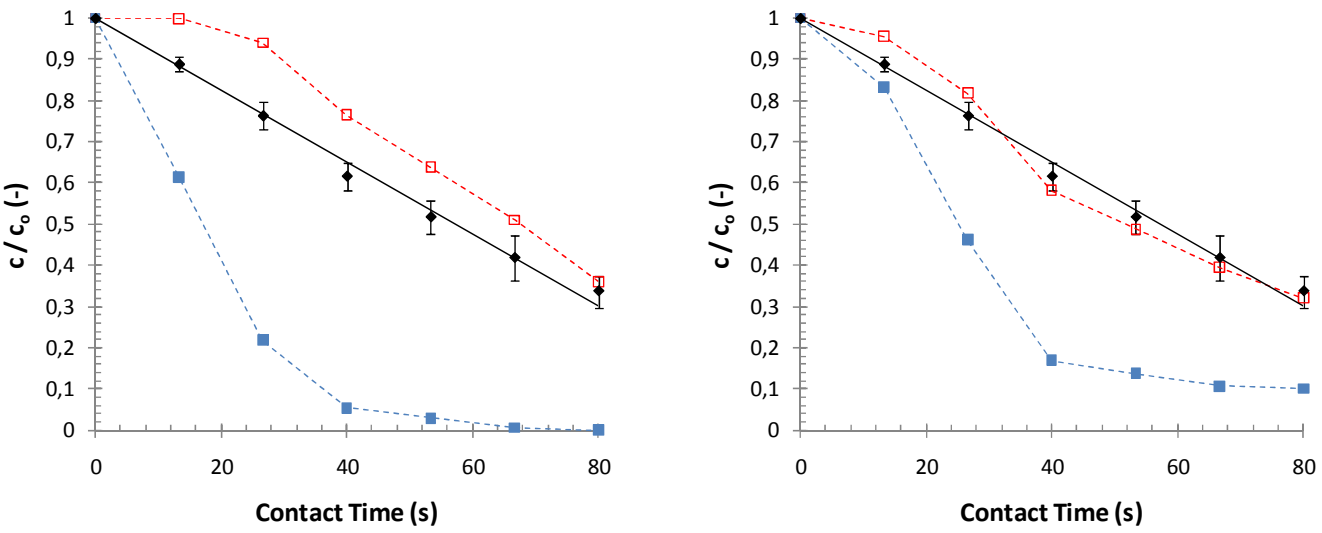
The presence of another compound can reduce the degradation of hexane. In order to determine this inhibitory effect the biofilters were first fed with hexane as single compound at an inlet concentration of 138 ± 16 mg m^{-3}. The hexane degradation profile over both biofilters, when fed as single compound is shown in Fig. 4.13. A linear degradation profile of hexane is observed with a total RE of 69.7 %. The linear degradation profile indicates that the maximal removal rate of hexane is constant, 1.21 mg s^{-1}, through both biofilters and that the biomass is homogeneous distributed in both reactors.



(a)



(b)



(c) (d)

Figure 4.13: Concentration profiles over the 2 biofilters in series indicating the inhibitory effect on the hexane removal (a) 72 hours after changing the feeding from (◆) only hexane to a mixture of (□) hexane and (■) acetone, 24 hours after changing the feeding from (◆) only hexane to a mixture of (b) (□) hexane and (■) limonene, (c) (□) hexane and (■) toluene and (d) 48 hours after changing the feeding from (◆) only hexane to a mixture of (□) hexane and (■) DMS.

To check the influence of another compound on the hexane removal, hexane was fed to the reactors in combination with respectively acetone (Fig. 4.13(a)), limonene (Fig. 4.13(b)), toluene (Fig. 4.13(c)) and DMS (Fig. 4.13(d)). After changing the feeding from hexane as single compound to a mixture of hexane and acetone, the RE of hexane after the first reactor part decreases from 11.6 %, hexane as single compound, to 5.1 %, 1.4 % and 0.2 % respectively 2, 72 and 96 hours after changing the feeding. For acetone the RE after the first reactor part increases, i.e., 48.4 %, 71.6 % and 72.0 % respectively 2, 72 and 96 hours after changing the feeding. When feeding the biofilters with hexane and toluene or with hexane and limonene, the RE after the first reactor part follows the same trend, with an increasing RE for limonene and toluene and a decreasing RE for hexane. In case of changing the feed to a mixture of DMS and hexane, the presence of DMS does not significantly affect the removal of hexane. Previous studies also indicated that volatile organic sulphur compounds (VOSC) like H_2S do not have an inhibitory effect on the simultaneous biological removal of toluene (Martinez et al., 2008), but do have an inhibitory effect on the simultaneous removal of another VOSC like DMS, with a higher affinity for H_2S than for DMS (Silva et al., 2012). A possible explanation is that the bacterial cultures responsible for the degradation of VOC like hexane, are not able to degrade VOSC like DMS, so no competition between these two compounds occur. In case of acetone, toluene and limonene, the inhibitory effect increases with decreasing Henry

law coefficient, e.g., acetone, which has the lowest H, needs to be removed completely, before any removal of hexane will occur. A plausible explanation is that acetone, toluene, limonene and hexane are probably degraded by the same consortia and competitive inhibitions occur. A higher Henry's law coefficient will result in a lower driving force for interphase mass transfer and lower pollutant availability to the biofilm. This was also visible in previous research applying a mixture of methyl ethyl ketone (MEK) and respectively hexane, $H_{hexane} >> H_{MEK}$, and 1-propanol, $H_{1\text{-propanol}} < H_{MEK}$ (Deshusses, 1997b). In this case the hexane did not inhibit the MEK degradation, while the addition of 1-propanol did lower the MEK degradation. Other studies also indicated competition in a biofilter between VOC like toluene and n-propanol (Dixit et al., 2012) or MEK and methyl-isobutyl ketone (Datta and Philip, 2012). The inhibitory effect of hydrophilic compounds on the degradation of hydrophobic compounds was also mentioned by Ikemoto et al. (2006).

4.2.4 Conclusions

This study determines the performance of a biofilter and a two-liquid-phase bio(trickling) filter in series when feeding it with a mixture of different VOC instead of only one compound. The performance of the biofilter fed with a mixture of acetone, DMS, toluene, limonene and hexane is influenced by the pH, the moisture content of the packing material and the Henry law coefficient of the different compounds. A pH shift from the optimal pH of the different compounds (all between 6.6 and 8.6), has the greatest influence on the DMS degradation, while the influence on the other compounds is much lower. The optimal pH of 6.6 for DMS is therefore chosen as optimal pH for the degradation of the complete mixture. Drying out the reactor during 20 days, results in a decrease in moisture content of the first reactor part, leading to lower RE for all the compounds. For acetone, hexane, toluene and limonene a longer contact time is needed to reach a fixed RE with increasing H. The RE of DMS does not follow this trend, which is possible due to different consortia responsible for the degradation of DMS. This can also be the reason that no inhibitory effect occurs when feeding a mixture of hexane with DMS although DMS has a much lower Henry law coefficient. If hexane is fed in a mixture with respectively acetone, toluene and limonene, the inhibitory effect on the hexane degradation will increase with a decreasing H. When feeding a biofilter with a mixture of compounds it is clear that compounds with a lower Henry law coefficient can inhibit the degradation of compounds with a higher Henry law coefficient. Adding a NAP to the biofilter (two-liquid-phase biofilter) or recirculating an silicone oil/water emulsion (two-liquid-phase biotrickling filter) increases the removal of hydrophobic compounds and

reduces the inhibitory effect when a mixture of hydrophilic and hydrophobic compounds is fed to the reactor. A two-liquid-phase biotrickling filter shows a better degradation for hydrophobic compounds than a two-liquid-phase biofilter, but consumes more energy, due to the higher pressure drop and the need of a recirculation pump.

4.3 TWO-PHASE PARTITIONING MEMBRANE BIOREACTOR A NOVEL BIOTECHNIQUE FOR THE REMOVAL OF DIMETHYL SULPHIDE, N-HEXANE AND TOLUENE FROM WASTE AIR

Summary

DMS, n-hexane and toluene removal from a waste air was carried out by a flat sheet composite MBR under continuous feeding conditions. The performance of this reactor was compared with the performance of a new type of MBR, the two-phase partitioning membrane bioreactor (TPPMB). In the TPPMB a 60/40 V% water/silicone oil emulsion inoculated with activated sludge was used as recirculation liquid in order to reach an acceptable removal for both hydrophobic and hydrophilic compounds. RE of respectively 76.8 ± 7.7 %, 77.6 ± 13.0 % and 12.1 ± 12.3 % were reached for toluene, DMS and hexane inlet concentrations ranging up to 2.6 g m^{-3} for each compound (IL ≤ 312 g m^{-3} h^{-1}) in a MBR. This indicates that a MBR is suitable to treat DMS and toluene, but unreliable to treat hexane when feeding the bioreactor with a mixture of these compounds. In a TPPMB RE of 85 ± 5 %, 62 ± 5 % and 53 ± 6 % were reached for toluene, DMS and hexane inlet concentrations ranging up to 2.8 g m^{-3} for each compound (IL ≤ 336 g m^{-3} h^{-1}) respectively. The RE for hexane is significantly higher in a TPPMB, while the variation on the hexane removal decreased, so the TPPMB is suitable and more reliable for degrading hexane than a MBR, when feeding a mixture of DMS, hexane and toluene.

4.3.1 Introduction

For the control of VOC emissions, biological gas treatment techniques such as biofiltration, biotrickling filtration and bioscrubbing have been studied and used as alternatives for the traditional physical-chemical techniques. A newer biotechnique for treatment of complex emissions is the use of a MBR, which has already been used

successfully at lab-scale (Álvarez-Hornos et al., 2011, 2012; Lebrero et al., 2013b). Using a MBR for waste gas treatment has the technological advantage that it is possible to separate the gas and liquid phases. In this way the conditions of both phases can be optimized much more easily. Pollutants diffuse through the membrane and are subsequently degraded by the microorganisms in the biofilm which are attached onto the dense side of the composite membrane. A MBR could potentially be more effective than conventional biosystems, although it still requires additional investigation and optimization with other compounds and with complex VOC mixtures. Nowadays only a mineral medium largely consisting out of water was used at the dense side of the membrane (Álvarez-Hornos et al., 2011, De Bo et al., 2003; Kumar et al., 2009; Lebrero et al., 2013b). For hydrophobic compounds, e.g. hexane, the water at the dense side, can still significantly decrease the mass transfer of these compounds, so no sufficient removal can occur. The first part of this study was performed to evaluate the performance of a MBR to treat a waste gas contaminated with a 1:1:1 (wt) mixture of DMS, n-hexane and toluene under various operating conditions, with inlet concentration ranging up to 3.6 g m^{-3} per compound.

DMS, hexane and toluene are VOC which are often found in waste gases of industrial sources, but with different properties. Especially the difference in water solubility is remarkable, see Table 4.4.

Table 4.4: Compound properties.

Compound	**DMS**	**Hexane**	**Toluene**
Group	Sulfide	Alkane	Aromatic
Solubility in H_2O at 25 °C (g L^{-1})	45 [b]	0.016 [b]	0.32 [b]
Vapour pressure at 25 °C (mmHg)	647 [b]	151 [b]	27.7 [b]
Henry law coefficient (-) (C_g/C_l) [a]	0.048	44	0.43

[a] Calculated using the solubility and the vapour pressure

[b] (SciFinder)

DMS is known to have a relative high solubility in water (low Henry law coefficient), but bacterial cultures responsible for the degradation of this compound are known to be slow growers (Hayes et al., 2010). Hexane has the highest Henry law coefficient and is the least soluble in water, while toluene is a VOC with a Henry law coefficient which is about 10 times higher than the one of DMS and about 100 times lower than the one of hexane. This Henry law coefficient is a very important characteristic which affects the performance of the reactor, since the transport of the VOC from the gas phase, through the membrane into the biofilm, which is composed of more than 90 % water, could be rate limiting (Zhu et

al., 2004). Hydrophilic compounds (lower Henry law coefficients) enter the biofilm much more easily, than hydrophobic compounds (higher Henry law coefficients) (Kim et al., 2005). In order to improve the mass transfer of more hydrophobic compounds, e.g. hexane, the mineral medium at the dense side of the membrane was replaced by a water/silicone oil emulsion in a second part of this research. Using a water/silicone oil emulsion inoculated with sludge to remove VOC out of a waste air stream, was already successfully applied in a TPPB (Muñoz et al., 2012; Muñoz et al., 2007), but has never been applied as such in a membrane bioreactor. Therefore the second part of this research was set up to compare the performance of a more conventional MBR with the performance of a novel biotechnique, i.e., a two-phase partitioning membrane bioreactor (TPPMB). In order to reach a sufficient mass transfer for hydrophobic, as for hydrophilic compounds, an optimal ratio between the water and the silicone oil was first determined. Using this optimal ratio, the TPPMB was first fed with a waste air stream only contaminated with hexane. Afterwards a mixture of 1:1:1 (wt) DMS, n-hexane and toluene was fed to the TPPMB in order to study the performance of the reactor on the removal of a mixture of compounds with total different hydrophobicitiy.

4.3.2 Materials and methods

4.3.2.1 Membrane bioreactor system

A commercially available flat composite membrane (GKSS Forschungszentrum Geesthacht, Germany) consisting of a porous polyacrylonitrile support layer, 50 µm, and coated with a very thin dense PDMS top layer, 1.5 µm, was used. An overview of the reactor set-up can be found in Fig. 4.14. The MBR which consisted of two identical compartments made of Perspex, was placed in an isothermal chamber at 23 °C. Each compartment of the reactor had four channels with a length of 20 cm, a width of 5 mm and a depth of 2 mm, resulting in a volume of 8 ml at each side of the membrane. The membrane was clamped between the two compartments, resulting in a contact area of 40 cm^2. Dry air was polluted with the VOC mixture by using a syringe pump (New Era, infusion/withdraw NE 1000 model, USA) and was flowing along the porous side of the composite membrane. The air flow was adjusted by using a mass flow controller (Brooks Instruments, USA) and was introduced countercurrent with the recirculation liquid at the dense side of the membrane, which was adjusted by a membrane pump (LMI, Milton Roy, USA). The recirculation bottle was placed in a thermostatic water bath at 23 °C and stirred at 500 rpm (IKA RCT basic, Germany).

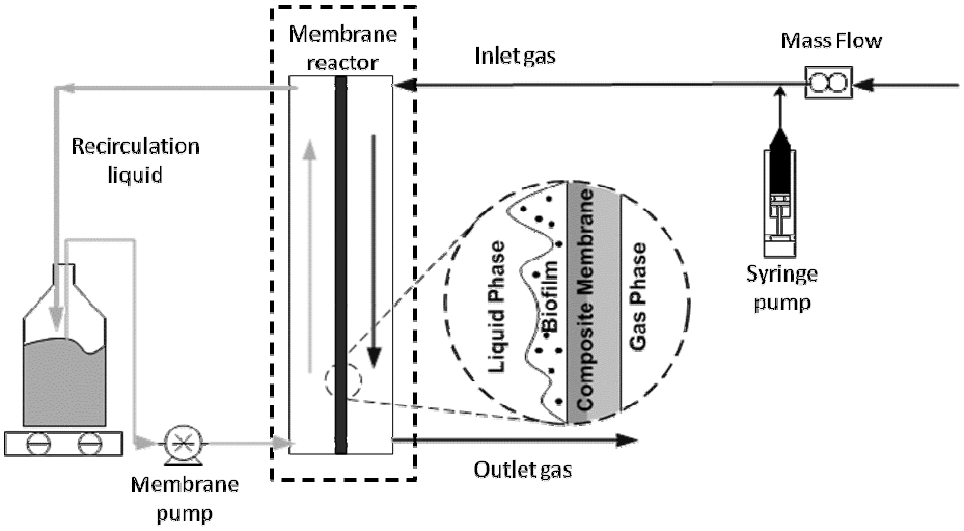


Figure 4.14: Schematic diagram of the flat sheet membrane bioreactor (Álvarez-Hornos et al., 2012).

The necessary macro and micronutrients were supplied using a pH buffered nutrient solution (pH 7) containing KNO_3, 10.7 g L^{-1}, KH_2PO_4, 3.0 g L^{-1}, K_2HPO_4, 3.0 g L^{-1}, $MgSO_4 \cdot 7H_2O$, 0.5 g L^{-1}, P, Ca, Fe, Zn, Co, Mn, Mo, Ni, B and vitamins at trace doses. The volume of nutrients added was kept at a C:N:P ratio of 100:5:1 (Shareefdeen and Singh, 2005). This ratio was weekly checked by measuring the nutrients in the leachate. The MBR was inoculated with a mixed microbial culture obtained from an activated sludge (Ossemeersen WWTP, Ghent) and was first preadapted during 30 days with the compounds to be treated in order to acclimate the mix of microbes in the sludge. During this adaptation period the aerobic sludge was put in a bottle of 1 L and continuously fed with an air stream of 1 L min^{-1} contaminated with a 1:1:1 (wt) mixture of DMS, n-hexane and toluene at a concentration of 0.1 g m^{-3} for each compound. Inoculation of the MBR occurred by recirculating 500 ml of the preadapted activated sludge at the dense side of the membrane during 24 hours. In this period a biofilm could be formed upon the surface of the membrane. In a first part of the experiment, water with mineral medium was recirculated at the dense side of the membrane, while in a second part an emulsion of water with mineral medium and silicone oil (47 V 20 Rhodorsil; VWR) was used as recirculated liquid.

4.3.2.2 Process conditions

The membrane bioreactor was operated under continuous loading for 13 months. During this period several operational conditions were tested (see Table 4.5).

Table 4.5: Operational parameters for membrane biofilter experiments, with EBRT the empty bed residence time.

Day	Compound	C_{in} per compound (g m^{-3})	EBRT (s)	Liquid flow (ml min^{-1})	liquid	Biomass
0 - 112	Hex - DMS - Tol	0 - 2.6	30	22	100 V% water	Yes
113 - 189	Hex - DMS - Tol	0 - 1.9	20	22	100 V% water	Yes
190 - 210	Hex - DMS - Tol	0.3 - 1.0	20	45	100 V% water	Yes
211 - 275	Hex - DMS - Tol	0 - 1.7	30	22	80/20 V% water/oil	Yes
276 - 282	Hex - DMS - Tol	0 - 2.7	30	22	No liquid (air)	No
283 - 302	Hex - DMS - Tol	0 - 3.0	30	22	100/0 V% water/oil	No
303 - 308	Hex - DMS - Tol	0 - 3.6	30	22	80/20 V% water/oil	No
309 - 321	Hex - DMS - Tol	0 - 2.7	30	22	60/40 V% water/oil	No
322 - 350	Hex - DMS - Tol	0 - 2.9	30	22	40/60 V% water/oil	No
351 - 364	Hex - DMS - Tol	0 - 2.7	30	22	20/80 V% water/oil	No
365 - 377	Hex	0 - 3.2	30	22	60/40 V% water/oil	Yes
378 - 386	Hex	0 - 2.5	18	22	60/40 V% water/oil	Yes
386 - 407	Hex - DMS - Tol	0 - 2.8	30	22	60/40 V% water/oil	Yes

The first 210 days of the experiment, only water with mineral medium was used as recirculated liquid and a 1:1:1 (wt) mixture of DMS, n-hexane and toluene was fed continuously to the reactor at the porous side of the composite membrane. In this first part of the experiment DMS, n-hexane and toluene concentrations were varied from 0 to 2.6 g m^{-3} at gas EBRT of 20 and 30 s. At the dense side, the flow rate of the liquid was changed from 22 ml min^{-1} to 45 ml min^{-1}, in order to check the influence of the liquid flow rate on the reactor performance. Finally the water at the dense side was replaced by an emulsion of water with silicone oil in an 80/20 V% ratio for 65 days. During these experiments the inlet and outlet concentrations were measured as well as the CO_2 production at the outlet of the membrane.

To determine the mass transfer of the different compounds through the membrane as such (Kumar et al., 2009; Lebrero et al., 2013b), the bioreactor was operated during 1 week without any liquid recirculation at the dense side of the membrane. In this period the contaminated air passed at the porous side of the membrane and clean air passed countercurrent at the dense side of the membrane. DMS, n-hexane and toluene concentrations were increased daily from 0 to 2.7 g m^{-3} at a gas EBRT of 30 s. The inlet and outlet concentrations of the different compounds at the porous side of the composite membrane were monitored in order to calculate the mass transfer of these compounds through the membrane.

In the next 80 days of the experimental study, a water/silicone oil emulsion without any biomass inoculation was recirculated at the dense side of the membrane, in order to determine the influence of the liquid on the mass transfer of the different compounds. During this part of the experiment, the water/silicone oil V% ratio was adjusted with an oil V% ranging from 0 to 80 V%, to find an optimal ratio at which a sufficient mass transfer of all three the compounds occurs. DMS, n-hexane and toluene concentrations were varied from 0 to 3.6 g m^{-3} at a gas EBRT of 30 s for each water/silicone oil V% ratio. To have an indication of the mass transfer resistance caused by the mineral medium in a conventional MBR, a 100 V% mineral medium without any biomass was applied first at the dense side of the membrane. Once the optimal water/silicone oil V% ratio was determined, it was applied on the water/silicone oil emulsion used in the next parts of the experiment.

During the last 40 days of the experiment, the optimal water/silicone oil emulsion of 60/40 V% was used at the dense side of the membrane and inoculated with biomass. First only hexane was fed to the reactor at an EBRT of 30 and 18 s and with concentrations ranging from 0 to 3.2 g m^{-3}. Finally the performance of the TPPMB reactor was determined when feeding it with a mixture of DMS, n-hexane and toluene at an EBRT of

30 s and concentrations from 0 to 2.8 g m^{-3} for each compound. As the Henry law coefficients of these three compounds are ranging from 0.048, for DMS, to 44, for hexane, the removal of this mixture will give a good indication of the performance of a TPPMB for hydrophilic and hydrophobic compounds.

4.3.2.3 Analytical techniques

The gas concentrations of the different compounds in the gas flow were monitored daily by taking gas samples of 500 µl using a 1.0 ml GASTIGHT® syringe at the gas inlet and outlet of the reactor. Analysis of these samples were performed by using a GC-FID (4890D Series, Agilent Technologies, USA) equipped with an HP-5 capillary column (15 m × 0.53 mm × 1.5 µm, Agilent Technologies, USA) and He as carrier gas used at a flow-rate of 2 ml min^{-1}. The CO_2 gas concentration at the outlet was determined by using a CARBOCAP® carbon dioxide analyser (GM70 model, Vaisala, Finland).

4.3.3 Results and discussion

4.3.3.1 Performance of the MBR

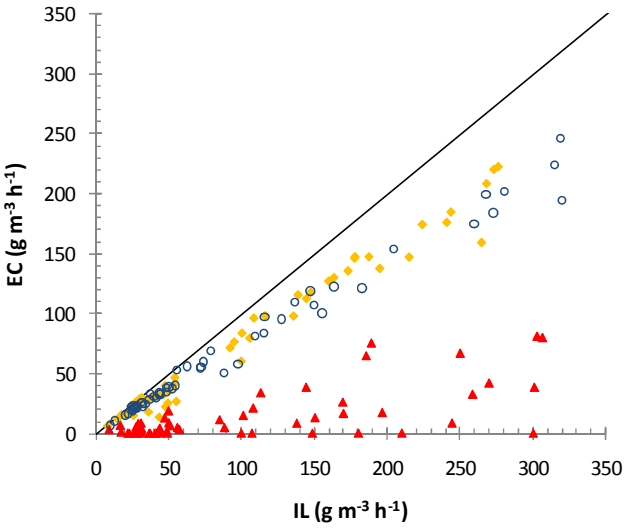


Figure 4.15: Elimination capacity (EC) of (◆) DMS; (○) toluene and (▲) hexane as a function of the inlet load (IL) at an empty bed residence time of 30 s and water as liquid medium.

In a first part of this experimental work, the performance of a conventional flat sheet membrane bioreactor is evaluated at an EBRT of 30 s. The IL, EC and RE were monitored daily. Plotting the EC of the different compounds in function of the IL, both expressed in

g compound per reactor volume (m^3) and per hour, see Fig. 4.15, shows that the biodegradation of DMS and toluene are quite similar, while the removal of hexane is significant lower. For DMS and toluene the EC increases about linearly with increasing IL (for IL up to 300 g m^{-3} h^{-1}), resulting in an about constant RE of 77.6 ± 13.0 % and 76.8 ± 7.7 % for DMS and toluene respectively. At an IL of 276 g m^{-3} h^{-1} the biofilter reaches a maximal EC (EC_{max}) of 223 g m^{-3} h^{-1} for DMS in the measured IL range. For toluene the EC_{max}, 246 g m^{-3} h^{-1}, is reached at an IL of 319 g m^{-3} h^{-1}. At these EC_{max} values for DMS and toluene, the graphs are still quite linear, so higher EC values could probably be reached at higher IL. This indicates that a MBR is suitable to treat DMS and toluene. Comparing these EC_{max} values, with the ones found in literature, see Table 4.6, it is clear that for DMS about the same EC_{max} value is reached as in similar researches with the same type of membrane and at a comparable EBRT. In case of toluene, the EC_{max} found in this study is higher than the EC_{max} reached with the same type of membrane when fed with a mixture of ethyl acetate, toluene and hexane. When only toluene is fed to the MBR, an EC_{max} of 625 g m^{-3} h^{-1} was found by Kumar et al. (2009), which is much higher than the value reached in this study, but at an IL of 300 g m^{-3} h^{-1}, about the same EC, 267 g m^{-3} h^{-1}, was reached as in this study.

Table 4.6: Summary and comparison of the maximal elimination capacity (EC_{max}) for DMS and toluene, with PDMS polydimethylsiloxane and EBRT the empty bed residence time.

DMS

Technique	Compound(s)	EBRT (s)	EC_{max} (g m^{-3} h^{-1})
PDMS composite membrane	DMS, toluene and hexane	30	223
PDMS composite membrane (*Hyphomicrobium* VS)	DMS	24	200 [a]
PDMS composite membrane (*Hyphomicrobium* VS)	DMS	24	258 [b]

TOLUENE

Technique	Compound(s)	EBRT (s)	EC_{max} (g m^{-3} h^{-1})
PDMS composite membrane	DMS, toluene and hexane	30	246
PDMS composite membrane	Toluene	20	625 [c]
PDMS composite membrane	Ethyl acetate, toluene and hexane	60	75 [d]

[a] (De Bo et al., 2003); [b] (Kumar et al., 2010); [c] (Kumar et al., 2009); [d] (Álvarez-Hornos et al., 2012)

For hexane the EC also increased with increasing IL, but the RE was less stable and varied from 0 to 30 % and this for the complete range of the measured IL, which makes the MBR unreliable to treat hexane. Álvarez-Hornos et al. (2012) also concluded that a PDMS composite MBR is unable to degrade n-hexane when a mixture of 1:1:1 ethyl acetate:n-hexane:toluene was supplied at an EBRT of 60 s.

4.3.3.2 Influence of EBRT and liquid flow rate on MBR

A decrease in EBRT from 30 s to 20 s results in a significant decrease of the reactor performance. The decrease in EBRT had the highest impact on the DMS degradation. In this case the RE lowers from 81 %, at an IL of 276 g m^{-3} h^{-1} (EC = 223 g m^{-3} h^{-1}) for an EBRT of 30 s, to 51 % at an IL of 280 g m^{-3} h^{-1} (EC = 142 g m^{-3} h^{-1}) for an EBRT of 20 s. For toluene the RE decreases from 71 %, at an IL of 315 g m^{-3} h^{-1} (EC = 224 g m^{-3} h^{-1}) for an EBRT of 30 s, to 50 % at an IL of 324 g m^{-3} h^{-1} (EC = 163 g m^{-3} h^{-1}) for an EBRT of 20 s. In case of hexane, the lower EBRT did not affect the performance of the MBR and the RE still varied between 0 and 30 % for IL ranging from 8 to 305 g m^{-3} h^{-1}.

Increasing the flow rate of the liquid medium from 22 ml min^{-1} to 45 ml min^{-1} at the dense side of the membrane decreases the performance of the reactor for the removal of DMS and toluene. At a liquid flow rate of 22 ml min^{-1} and an EBRT of 20 s, the RE for DMS was around 80 % for IL ranging between 60 and 140 g m^{-3} h^{-1}, while the RE decreased to values around 30 %, when increasing the liquid flow rate up to 45 ml min^{-1}. For toluene the RE decreased from 70 % to 40 %. A possible explanation could be found in the fact that at higher liquid flow rates, more biomass will be swept away by the liquid, decreasing the thickness of the biofilm attached at the dense side of the membrane, resulting in a performance decrease.

4.3.3.3 CO_2 production

During the first 210 days of the experiment, the CO_2 concentration in the outlet gas stream of the reactor was measured. A relationship between, the amount of Carbon-CO_2 present in the outlet air stream and the amount of the Carbon which is removed by eliminating the compounds was found, indicating that the removal of the compounds is caused by biodegradation. Linear regression of this experimental data results in a value of 0.34 ± 0.02 g m^{-3} of C-CO_2 per g m^{-3} of C-Compounds, which means that at least 34 % of the C is incorporated in CO_2. This value is quite low, as the CO_2 only is measured at the porous side of the membrane, while it is formed at the dense side of the membrane and will only partially transfer from the dense side to the porous side of the membrane. The retained CO_2 will circulate with the mineral medium and can escape as CO_2 along the headspace of

the liquid medium. Another part of the carbon will also be incorporated in additional biomass. To ensure that no VOC were leaving the reactor along the headspace of the liquid medium, a gas sample of the headspace was analyzed daily, but no VOC were retrieved.

4.3.3.4 Mass transfer resistance

Even though a hydrophobic membrane was used, the results show that the removal of the hydrophobic compound, hexane, remains low and unstable (RE < 30 %), see Fig. 4.15.

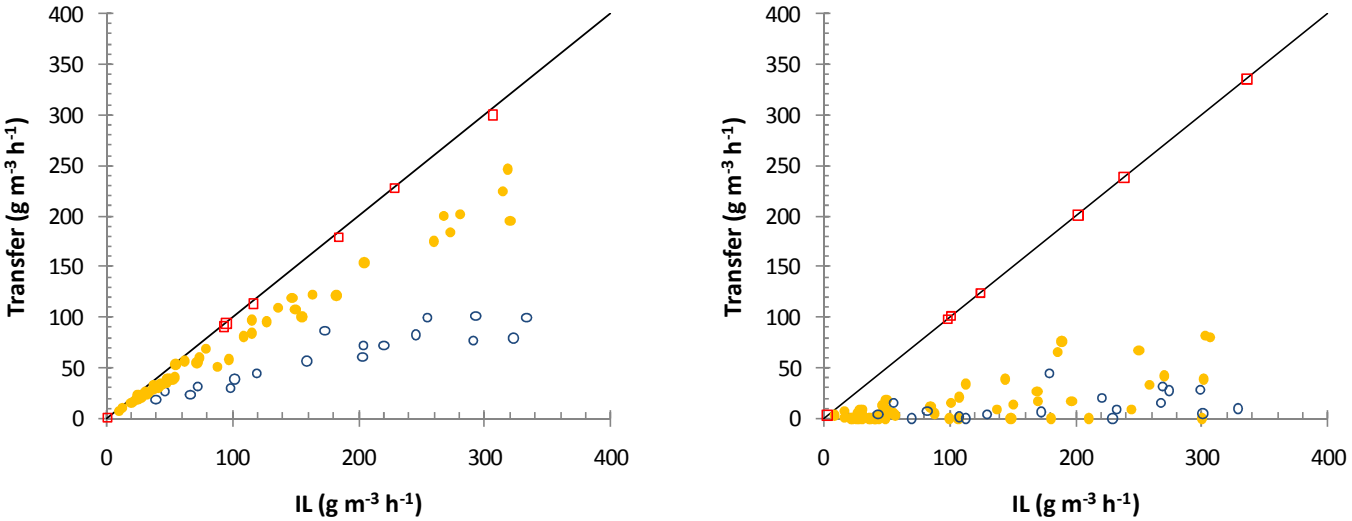


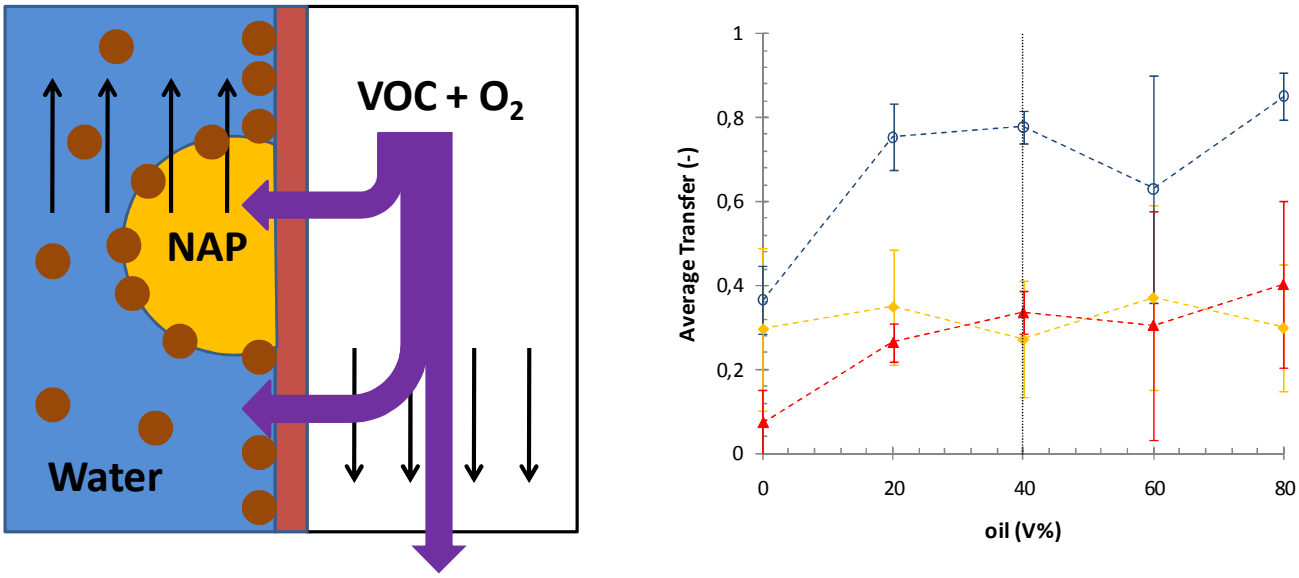
Figure 4.16: (a) Transfer of toluene through the membrane as a function of the inlet load (IL) with (□) dry air; (●) water with biomass and (○) water without biomass as liquid medium, empty bed residence time (EBRT) = 30 s.
(b) Transfer of hexane through the membrane as a function of the IL with (□) dry air; (●) water with biomass and (○) water without biomass as liquid medium, EBRT = 30 s.

For DMS and toluene, which are much more hydrophilic (lower Henry law coefficient), the MBR shows a very good performance. In order to determine the resistance which causes this low removal of hexane, the mass transfer resistance over the actual membrane and the mass transfer resistance caused by the water at the dense side of the membrane were determined. By replacing the liquid medium, by non-polluted dry air at the dense side of the membrane, it was possible to measure the mass transport of the three compounds through the membrane at an EBRT of 30 s. When plotting the transfer of these compounds in function of the IL, with IL ranging up to 350 g m^{-3} h^{-1}, see Fig. 4.16, it is clear that about 98 ± 1 %, 99 ± 1 % and 99.8 ± 0.4 % for respectively toluene, hexane and DMS transfers from the porous side to the dense side of the membrane. This indicates that

the membrane itself does not provide any significant mass transfer resistance for the different compounds to move from one compartment to the other in the measured range of IL.

When replacing the air at the dense side of the membrane by 100 V% mineral medium without inoculation, the mass transfer resistance increases significantly due to the addition of a water layer at an EBRT of 30 s, see Fig. 4.16. In case of toluene, see Fig. 4.16(a), only 37 ± 8 % of the compound will be able to move from the gas phase at the porous side of the membrane to the liquid phase at the dense side. This value is lower than the RE of 76.8 ± 7.7 % which can be reached with the addition of biomass, as the biomass will act as a biological catalyst in the MBR. DMS will follow the same trend as toluene when mineral medium is circulated at the dense side of the membrane, with a transfer percentage of respectively 77.6 ± 13.0 % and 32.6 ± 15.6 % with and without inoculation of the mineral medium. For hexane, see Fig. 4.16(b), which has the highest Henry law coefficient, the presence of water at the dense side of the membrane had the highest influence. In this case, the transfer dropped to a value which varied between 0 and 10 %. This demonstrates that the low biodegradation of hexane, is partially due to the high transfer resistance caused by the water layer.

In order to decrease the mass transfer resistance for hydrophobic compounds like hexane, an emulsion of water and silicone oil was used at the dense side of the membrane. In this new reactor type, see Fig. 4.17(a), the more hydrophilic compounds will transfer from the gas phase into the water, while the more hydrophobic compounds can transfer from the gas into the NAP. Increasing the amount of silicone oil from 0 V% to 40 V%, see Fig. 4.17(b), results in an increase of mass transfer of hexane from the gas at the porous side of the membrane to the liquid at the dense side. When using a 60/40 V% water/silicone oil emulsion, the transfer of hexane increases from 7 ± 8 % to a more stable value of 34 ± 5 %. Using the water/oil emulsion at the dense side of the membrane does not affect the mass transfer of the DMS significantly and even increases the mass transfer of toluene. For toluene the transfer percentage reaches 78 ± 4 % when applying a 60/40 V% water/silicone oil emulsion. As a higher volume fraction of silicone oil, > 40 V%, does not result in a significant higher transfer percentage and as the silicone oil is more expensive and does not contain any nutrients or biomass, the 60/40 V% water/silicone ratio is considered as optimal ratio.



(a) (b)

Figure 4.17: (a) Mass transfer model describing the total VOC/O_2 transferred from the gas phase to the non-aqueous phase (NAP) and aqueous phase in a two-phase-partitioning membrane bioreactor.
(b) Average transfer of (◆) DMS; (○) toluene and (▲) hexane vs. partition of oil in water/oil emulsion for inlet loads ranging up to 350 g m^{-3} h^{-1} at an empty bed residence time of 30 s (without biomass).

4.3.3.5 Performance of the TPPMB

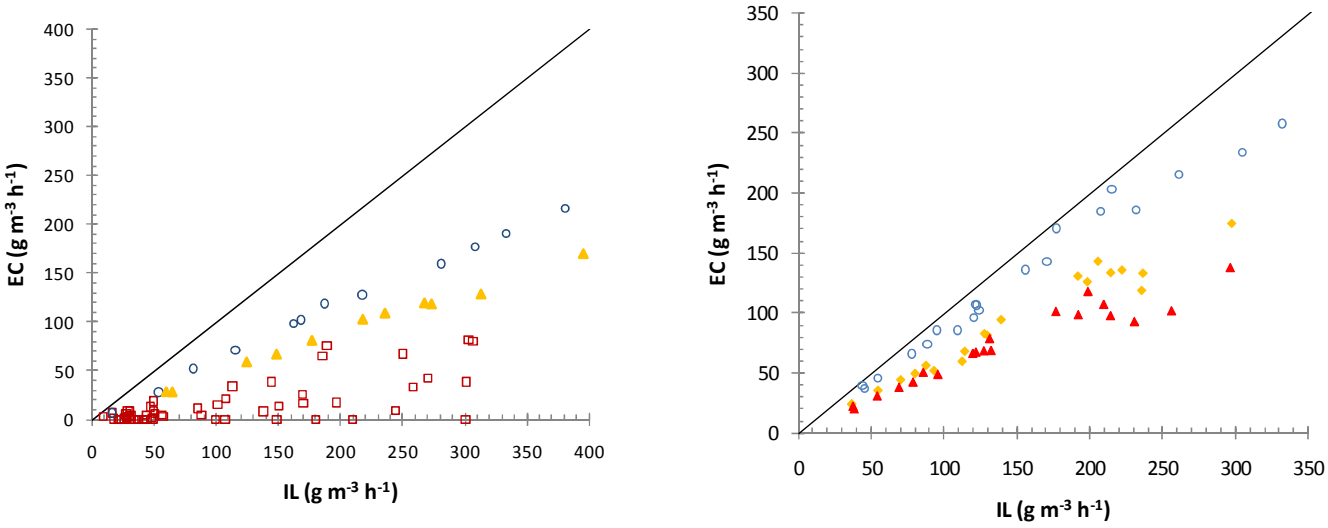
a) *Only Hexane*

Using a water/silicone oil 60/40 V% emulsion inoculated with biomass at the dense side of the membrane, results in a more stable and higher RE of 58 ± 6 %, for treating an air stream contaminated with only hexane at an EBRT of 30 s and IL up to 400 g m^{-3} h^{-1} (c_{in} = 3.3 g m^{-3}), see Fig. 4.18(a). In a TPPMB the hexane can transfer from the gas phase through the membrane into the silicone oil. As some of the bacteria are attached at the surface between the silicone oil and the water, see Fig. 4.17(a), the hexane can more easily reach these bacteria (lower mass transfer resistance in silicone oil) and can be used as carbon source. Even at an EBRT of 18 s the RE still reaches a value of 44 ± 2 % and this for IL ranging up to 400 g m^{-3} h^{-1} (c_{in} = 2.0 g m^{-3}).

b) *Compound mixture*

To illustrate the influence of a compound mixture on the performance of a TPPMB and in order to compare this performance with the one of a conventional MBR, an air stream contaminated with DMS, toluene and hexane was fed to the reactor at an EBRT of 30 s.

Plotting the EC of the different compounds as a function of the IL, see Fig. 4.18(b), shows that the biodegradation of toluene results in an average RE of 85 ± 5 % for IL up to 350 g m^{-3} h^{-1}, which is higher than the one reached with a conventional MBR. This higher RE is reasonable as the mass transfer resistance for toluene is lower in a TPPMB than in a MBR. For DMS the average RE in a TPPMB with a 60/40 V% water/silicone oil emulsion amounts 62 ± 5 % for IL up to 300 g m^{-3} h^{-1}, which is slightly lower than in a MBR. In case of hexane, the RE in a TPPMB reaches 53 ± 6 % for IL up to 300 g m^{-3} h^{-1}, which is about similar as the RE reached when only hexane is fed to the reactor. This indicates that the presence of toluene, which is more hydrophilic, does not inhibit the degradation of hexane, which is more hydrophobic. This confirms the conclusion made in section 4.2, which suggest that the addition of a NAP decreases the inhibitory effect of hydrophilic compounds on the degradation of more hydrophobic compounds. This RE is also higher and more reliable (less fluctuations) than the RE reached in a conventional MBR, which indicates that the TPPMB is a useful and reliable technique to treat hexane as single compound and in a mixture.



(a) (b)

Figure 4.18: (a) Elimination capacity (EC) of hexane as a function of the inlet load (IL) with recirculation of (□) 100 V% water and (○) a 60/40 V% water/oil emulsion at an EBRT of 30 s and (▲) a 60/40 V% water/oil emulsion at an empty bed residence time (EBRT) of 18 s (with biomass).
(b) EC of (◆) DMS; (○) toluene and (▲) hexane as a function of the IL at an EBRT of 30 s and a 60/40 V% water/oil emulsion as liquid medium.

4.3.4 Conclusions

This research compares the performance of a conventional flat sheet MBR with the one of a flat sheet TPPMB using a 60/40 V% water/silicone oil emulsion as recirculation liquid. Applying a MBR to treat an air stream contaminated with a 1:1:1 (wt) mixture of DMS, n-hexane and toluene at an EBRT of 30 s, results in RE of 77.6 ± 13.0 % and 76.8 ± 7.7 % for DMS and toluene respectively and this for IL up to 300 g m^{-3} h^{-1}. In this range of IL, the RE of hexane varies continuously between 0 to 30 %, which makes the MBR unreliable to treat hexane when feeding the bioreactor with a mixture of DMS, hexane and toluene. Using a TPPMB to treat an air stream contaminated with the same VOC mixture at an equal EBRT of 30 s, increased the RE of toluene to 85 ± 5 %, but decreased the RE of DMS to 62 ± 5 %. In case of hexane, the RE in a TPPMB reaches a much more stable and higher value of 53 ± 6 %. This makes the TPPMB a reliable technique to treat hexane as well as single compound as in a mixture.

Chapter 5 General conclusions and future research

5.1 CONCLUSIONS

In this thesis, the performance of several conventional and innovative air treatment biotechnologies was evaluated. Different studies already indicated the good performance of biotechnologies to treat single compounds in a polluted air stream, but studies on the removal of mixtures with different properties are scarce. This thesis provides valuable information to bridge this knowledge gap as it focuses on the removal of VOC mixtures containing compounds with different hydrophobicity using a conventional biotechnique, i.e. biofiltration (**chapter 3** and **section 4.2**) and using innovative biotechniques, i.e. a TPPB (**section 4.1**), a two-liquid-phase biofilter and two-liquid-phase biotrickling filter (**section 4.2**) and a TPPMB (**section 4.3**). A TPPMB is a complete novel biotechnique which combines a TPPB reactor with a MBR. A main advantage of a TPPMB relative to the TPPB is the fact that the liquid phase and air phase are separated, so the air transfer does not depend on the distribution of the air in the emulsion, which is also less energy consuming.

The results from the first experimental part of this work, **chapter 2**, show that a biofilter can be used successfully to treat an air stream contaminated with EB. In this part a novel packing material, macadamia nutshells, was used which especially differs in moisture content and water retaining capacity from the more conventional packing materials like soil, compost and woodchip. Despite the lower moisture content and water retaining capacity, macadamia nutshells are very suitable as packing material due to the lower biodegradability, which makes it less susceptible to deterioration, increasing the life time of the material and decreasing the pressure drop.

When a mixture of acetone, DMS, toluene, limonene and hexane is fed to a biofilter, **section 4.2**, it is clear that a VOC with a high Henry law coefficient needs a longer contact time in order to be degraded. A high Henry law coefficient increases the transfer resistance for the compound to diffuse from the gas phase to the liquid phase which limits the applicability of a biofilter to treat waste air emissions loaded with a mixture of VOC with different Henry law coefficients. Acetone as well as toluene and limonene, all having a lower Henry law coefficient than hexane, have an inhibitory effect on the removal of hexane. Although DMS also has a very low Henry law coefficient, it does not inhibit the removal of hexane, which is probably due to other microbial consortia responsible for the degradation of DMS.

The data obtained in **chapter 2** and **section 4.2** also indicate that the performance of a biofilter is influenced by the moisture content, the temperature and the pH. A decrease in moisture content will lead to a decrease in reactor performance. For the temperature and the pH an optimal value can be found for each compound to reach a maximal degradation. In case of EB the best removal can be found at 312 K. For a biofilter fed with acetone, DMS, toluene, limonene and hexane, the optimal pH for the different compounds all range between 6.6 and 8.7, i.e., around the neutral pH.

The EBRT also influences the performance of a bioreactor as mentioned in **chapter 2**, **section 4.1** and **section 4.3**. In a biofilter and a TPPMB a decrease in EBRT will result in a decrease in reactor performance as the contact time between the gas phase and the liquid phase decreases. In a TPPB the decrease in performance is not only due to a shorter contact time, but also to a decrease in air transfer efficiency when increasing the air flow, which results in a higher influence of the EBRT.

In **chapter 3** and **section 4.1**, SIFT-MS was used in order to measure the performance of the different bioreactors in a short period of time and to obtain more information about the transient behaviour of a bioreactor on VOC pulse injections, which is not possible to measure with a GC-FID. When measuring the reactor performance of a TPPB in **section 4.1**, it was clear that the same performance was obtained much faster by using SIFT-MS, ± 4 concentration measurements per second, as with the GC, but GC measurements are still necessary to determine the absolute concentrations and to obtain a correction factor for the concentrations monitored by the SIFT-MS.
The analysis of pulse injections at the inlet of a biofilter, **chapter 3**, indicated that a decrease in reactor volume or an increase in Henry law coefficient decreases the gas velocities at which mass transfer resistance becomes significant. By applying pulse injections it is also possible to measure the NRT of a compound in a bioreactor online. This NRT is a more accurate indicator of the gas residence time relative to the EBRT as it

indicates the exact time for a compound to migrate through the reactor. This NRT depends on the compound type and the conditions in the bioreactor (e.g. reactor type, volume, porosity...). In a biofilter, **chapter 3**, a higher Henry law coefficient will result in a lower retention time, NRT. In a biofilter the NRT of an inherent compound (RE ≈ 0 %) can be used to determine the online porosity of the filter. The determination of the biofilter porosity by using SIFT-MS is not only new and straightforward; it also results in a more accurate value for the porosity than the more conventional static method as it is measured online and takes into account the actual conditions in the biofilter, i.e. humidity, moisture content, particle size and distribution...
In a TPPB, **section 4.1**, the NRT can be used as a parameter indicating when biomass needs to be purged or when the aqueous medium needs to be refreshed in order to maintain a good reactor performance.
In general can be concluded that SIFT-MS reduces the analytical limitations significantly.

In order to decrease the process limitations, the use of a NAP in several biotechnologies was evaluated in **chapter 4**. From the results it was clear that applying a NAP in a bioreactor decreases the mass transfer resistance for hydrophobic compounds and the inhibitory effect of the hydrophilic compounds on the degradation of hydrophobic compounds. This results in a stable and better overall performance of the bioreactors for hydrophobic compounds like hexane, see Fig. 5.1.

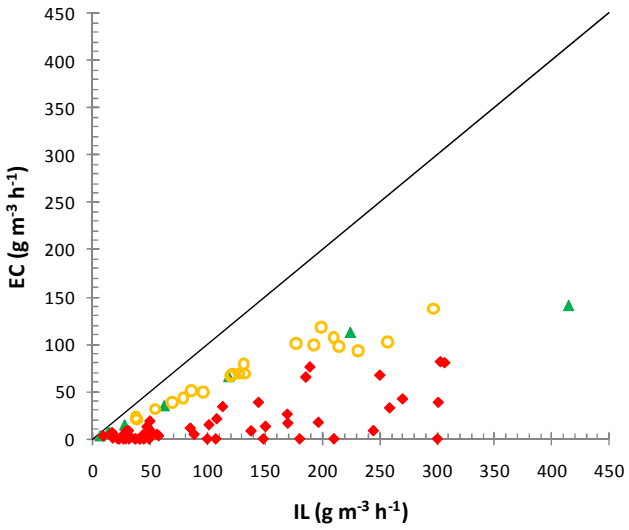
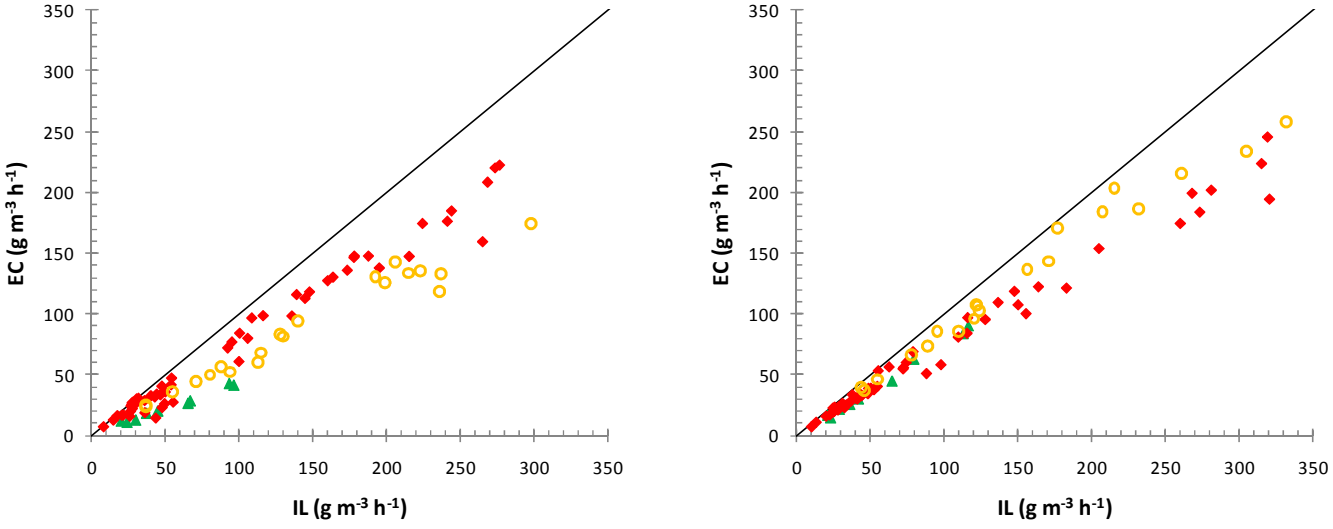


Figure 5.1: Elimination capacity (EC) vs. inlet load (IL) for hexane at an empty bed residence time of 30 s (▲) in a two-phase partitioning bioreactor, (◆) in a membrane bioreactor and (○) in a two-phase partitioning membrane bioreactor.

In a membrane bioreactor without the addition of silicone oil, there is a high scatter on the EC. Also in a conventional biofilter, see section 4.2 figure 4.12 (first reactor), the removal of hexane was negligible. In a TPPB and TPPMB, where silicone oil is added to the aqueous phase, the EC is more stable and higher, see Fig. 5.1. The addition of a NAP to the liquid phase does not affect the removal efficiency of the bioreactors for the more hydrophilic compounds like toluene and DMS, see Fig. 5.2, as both techniques, TPPMB (with silicone oil) and MBR (without silicone oil), are equally efficient in reducing DMS and toluene at an EBRT of 30 s. Only in the TPPB a higher EBRT is necessary to reach the same EC for DMS as for toluene. But one needs to be careful with comparing the EC of different reactor set-ups as the empty reactor volume used to calculate the EBRT does not always reflect the active reactor volume, e.g. in a biofilter the empty reactor volume is highly different from the real active volume.



(a) (b)

Figure 5.2: (a) Elimination capacity (EC) vs. inlet load (IL) for DMS (▲) in a two-phase partitioning bioreactor (TPPB) at an empty bed residence time (EBRT) of 60 s, (◆) in a membrane bioreactor (MBR) at an EBRT of 30 s and (○) in a two-phase partitioning membrane bioreactor (TPPMB) at an EBRT of 30 s.
(b) EC vs. (IL) for toluene (▲) in a TPPB at an EBRT of 60 s, (◆) in a MBR at an EBRT of 30 s and (○) in a TPPMB at an EBRT of 30 s.

In a TPPMB an overall RE of 65 % was reached when treating a mixture of DMS, toluene and hexane with a total inlet concentration of 7.7 g m^{-3} at an EBRT of 30 s. In a TPPB an overall RE of 60 % was reached when treating the same mixture with a total inlet concentration of 6.0 g m^{-3} at an EBRT of 60 s and an RE of 65 % for treating hexane as single compound with an inlet concentration of 21.5 g m^{-3} and an EBRT of 120 s.

When plotting these results in Fig. 5.3 it is clear that the use of a NAP in a bioreactor increases the applicability of bioreactors. The addition of a NAP will increase the mass transfer of hydrophobic compounds to the biomass and will increase the residence time of the compound in the bioreactor. The presence of a NAP will therefore not only reduce the application limitations, but also increases the biodegradability of the hydrophobic compounds, which makes Fig. 5.3 more reliable to use when dealing with VOC mixtures.

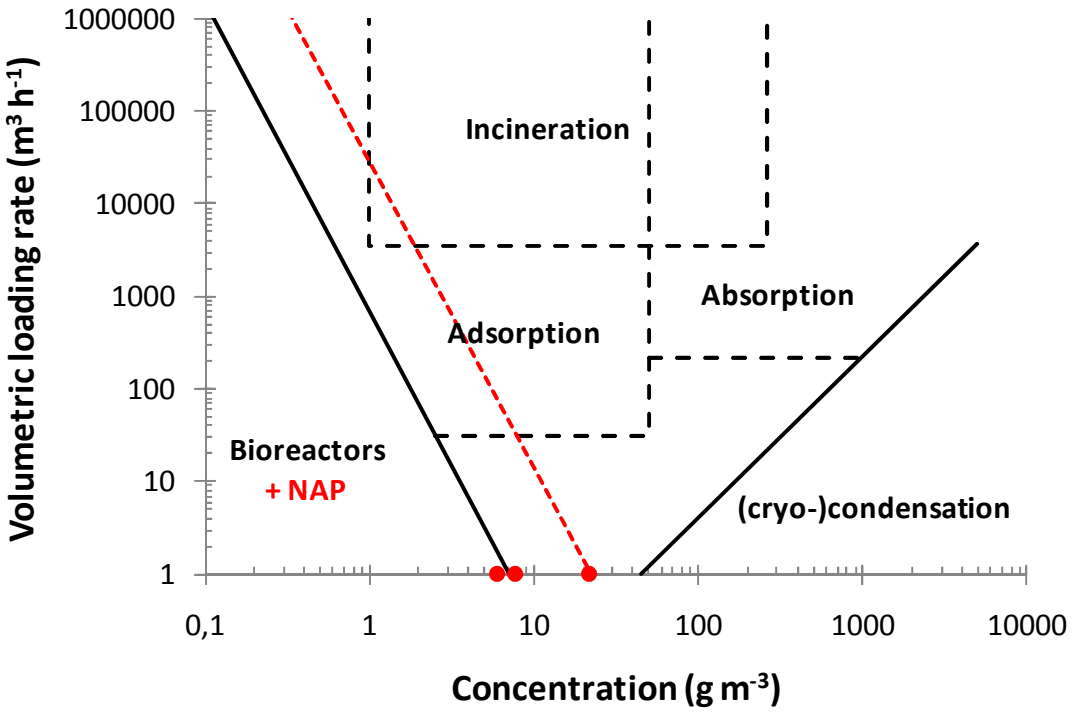


Figure 5.3: Application limit range of major biological and non-biological air pollution control technologies based on Kennes et al. (2001).

Overall this research indicates that the conventional biotechniques are suitable to treat single compounds like EB, but to treat VOC mixtures of different compounds, higher residence times are needed as the degradation of the more hydrophobic compounds can be inhibited by the presence of more hydrophilic compounds. In order to decrease these application limitations a NAP can be applied in combination with an aqueous phase, which improves the reliability and the performance of biotechnologies treating emissions loaded with a mixture of VOC. The addition of a NAP to the bioreactor will not only decrease the inhibitory effect, but also improves the reactor performance, so lower residence times (higher flows) can be applied. This effect is much higher in a TPPB and TPPMB than in a two-liquid-phase bio(trickling)filter where the RE only increases a little.

Some advantages and disadvantages of the different applied biotechniques are summarized in Table 5.1.

Table 5.1: Comparison of the applied bioreactors (**BF** = biofilter; **TLPBF** = two-liquid-phase biofilter; **TLPBTF** = two-liquid-phase biotricklingfilter; **TPPB** = two-phase partitioning bioreactor; **MBR** = membrane bioreactor; **TPPMB** = two-phase partitioning membrane bioreactor; **NAP** = non-aqueous phase and **RE** = removal efficiency)

	BF	**TLPBF**	**TLPBTF**	**TPPB**	**MBR**	**TPPMB**
NAP	NO	YES	YES	YES	YES	YES
RE of hydrophobic compounds	-	+/-	+	++	-	++
Energy consuming	+	+	-	- -	-	-
Space occupation	- -	- -	- -	+	+	+
Control of operation parameters	-	-	+/-	+	+ +	+ +

A main disadvantage of using a NAP relative to the use of a conventional bioreactor is the additional cost for the NAP and for the disposal of it when the packing material needs to be renewed or when a part of the leachate needs to be purged. Also the energy cost is an important factor to take into account before choosing a suitable bioreactor set-up. In a two-liquid-phase biotricklingfilter, the energy cost will be higher than in a conventional biofilter as an additional pump is needed to circulate the emulsion continuously. Next to this, the emulsion needs to be well stirred in order to create a good mixture between the aqueous phase and the NAP, which is also the case in the TPPB and TPPMB. In the TPPB, the air needs to be blown through the liquid phase which is very energy consuming. A main advantage of a TPPMB and MBR relative to the TPPB is the fact that the liquid phase and air phase are separated, so the air does not have to be blown through the liquid (only part of the gas will diffuse through the membrane). The transfer through the membrane is namely based on the permeability of the compounds, which is about 100 times higher for DMS than for oxygen. Also less emulsion is needed in a TPPMB reactor relative to a TPPB in order to obtain a similar contact time, which decreases the energy consumed by the stirrer.

A main disadvantage of a biofilter, a two-liquid-phase biofilter and a two-liquid-phase biotricklingfilter is the high space occupation due to the lower active area per reactor volume. In a TPPR the whole reactor volume can be used if the air is well distributed, which leads to smaller reactors. Also in a MBR and a TPPMB, the active area per reactor volume is higher, decreasing the footprint of the reactor.

In a MBR and TPPMB, the liquid phase is completely separated from the gas phase, what makes it possible to optimise the working conditions for the bacteria (pH, temperature, nutrients), which is much more difficult in a biofilter as there is no continuous liquid flow.

Taking into account the pros and cons of the different biotechniques leads to a small preference for the TPPMB as best technique to treat VOC mixtures. This techniques shows a good removal of hydrophobic and hydrophilic compounds, has a high active area per reactor volume (smaller footprint, less emulsion needed) and allows to control the working conditions very easily.

5.2 FUTURE RESEARCH

The use of pulse injections to determine the NRT and to gain more information on mass transfer resistance and reaction limitation in a biofilter should be investigated on pilot or industrial scale to test the practical feasibility. In **section 4.2**, pulse injections were performed on three different compounds, but in order to confirm the results and conclusions pulse injections of more compounds (e.g. acetone and limonene) would be interesting.

The use of a NAP in the different biotechnologies discussed in **chapter 4** were all performed at lab-scale and till now no research has been done on pilot or industrial scale. Future research should focus on the applicability of a NAP on larger scale and on the possibility to reuse the NAP in the set-up when renewing the packing material or the emulsion in order to avoid disposal of the NAP and to decrease the operating costs.

In this work, the different compounds were selected based on their Henry law coefficient. Future studies should also focus on real compositions of industrial emissions. Also a more biological approach should be performed to gather more information on the relation between different compounds, as the inhibitory effect does not only depend on the hydrophobicity but also on the type of microorganisms which are responsible for the degradation. E.g. in Figure 4.9 (see chapter 4.2) DMS only starts to degrade in the second part of the bioreactor at normal humidification conditions when almost all the acetone is removed. This could indicate that the presence of acetone has an inhibitory effect on the removal of DMS, as both compounds can be degraded by methylotrophic bacteria.

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Curriculum Vitae

Personal Information

Name:	Diëgo Volckaert
Address:	Sittingbournelaan 36
	8900 Ieper
Phone:	0497862889
E-mail:	Diego_vol@hotmail.com
Place and Date of Birth:	Ieper, 4th of August 1985 (Belgium)
Marital Status:	Married

Education

2010 - 2014:	**Doctor (PhD) of Applied Biological Sciences**
	Ghent University
2003 – 2007:	**Master in Industrial Sciences: Chemistry**
	KHBO Oostende
	(Thesis: "Onderzoek naar de werking van een biologische afvalwaterzuivering")
1997 – 2003:	**Sciences – Mathematics**
	O.L.V. ter Nieuwe Plant Lyceum Ieper

Additional courses

2010:	Environmental Chemistry
2010:	Microbial Ecological Processes
2010:	Modeling and Simulation of Biosystems
2010:	Statistical Data Processing
2010:	Reaction Kinetics and Reactors
2010:	Techniques for Chemical Analysis

Teaching activities

Supervision of the practical work of the master of Bioengineering students (Faculty of bioscience Engineering, Ghent University

Techniques for Chemical Analysis: Column Chromatography

Environmental Chemistry + Analysis and abatement of Air Pollution: GC-MS

Teaching assistant for "Membrane processes in Environmental Technology" to the master degree students (Prof. H. Van Langenhove, Faculty of Bioscience Engineering, Ghent University

Teaching assistant for the Module "environmental technology" for the training of Environmental Coordinator A (IVPV)

Tutoring experience

2010 - 2011:	Chidnapa Kittikoon, Control of Thai VOC emission by using biofilter packed with macadamia nutshells
2012 - 2013:	Joren Bruneel, Evaluatie van de simultane verwijdering van aceton, dimethylsulfide, hexaan, tolueen en limoneen door twee biofilters in serie
2012 - 2013:	Sander Wuytens, Behandeling van een gasmengsel dimethylsulfide, hexaan en tolueen met behulp van een membraanbioreactor
2012 – 2013:	Deba Enomah Lucy Ebude, Treatment of hydrophobic volatile organic compounds using the two-phase partitioning bioreactor
2012 - 2013:	Elnaz Fathi, Online SIFT-MS measurements of a biofilter response to VOC inlet concentration changes

Work Experience

Thesis	
2006:	Thesis at **Bayer Antwerpen comm. V. (Chemical Industry)**: Research Lab (Central Laboratory)
R&D Lab worker	
2007 – 2008:	Technologic Centre of **Bekaert (Metal Industry)**: R&D lab for Electrochemistry
R&D Assistant	
2008 - 2010:	R&D department of **Ysco (Food Industry)**: Packaging development

Published Articles

Álvarez-Hornos, F.J., Volckaert, D., Heynderickx, P.M., Van Langenhove, H. 2011. Performance of a composite membrane bioreactor for the removal of ethyl acetate from waste air. Bioresour. Technol., 102, 8893-8898.

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Articles Under Review

Volckaert, D., Heynderickx, P.M., Fathi, E., Van Langenhove, H. SIFT-MS a novel tool for monitoring and evaluating a biofilter performance. (Submitted to Chemical Engineering Journal)

Review Experience

Reviewer for Biochemical Engineering Journal

Conferences and Symposiums

1st European Congress of Applied Biotechnology, Berlin (Germany), September 25-29 2011

Poster:

Álvarez-Hornos, F.J., Volckaert, D., Martínez-Soria, V., Penya-roja, J.M., Marzal, P., Gabaldón, C. Start-up evaluation of a peat biofilter treating waste gas contaminated with ethyl acetate by using two strategies: without inoculation and with inoculation.

Proceeding + Oral presentation:

Álvarez-Hornos, F.J., Volckaert, D., Heynderickx, P.M., Van Langenhove, H. Removal of ethyl acetate from air in a membrane bioreactor.

4th Conference on Biotechniques for air pollution control, La Coruña (Spain), October 12-14 2011

Poster:

Álvarez-Hornos, F.J., Volckaert, D., Heynderickx, P.M., Van Langenhove, H. Removal of ethyl acetate, n-hexane and toluene from waste air in a membrane bioreactor under continuous and intermittent feeding conditions.

Proceeding + Oral presentation:

Volckaert, D., Álvarez-Hornos, F.J., Heynderickx, P.M., Van Langenhove, H. Ethylbenzene removal under mesophilic conditions in a multiple-stage biofilter with macadamia nutshells as carrier material.

10th Conference on Biofiltration for Air Pollution Control, San Francisco, California (USA), March 4-7 2013

Proceeding + Oral presentation:

Volckaert, D., Álvarez-Hornos, F.J., Heynderickx, P.M., Van Langenhove, H. Online SIFT-MS measurement of a biofilter response to dimethylsulfide concentration step changes

Treto Fdez, H., Rodriguez Rico, I., Volckaert, D., Heynderickx, P.M., Van Langenhove, H. Removal Kinetic of Dimethyl Sulfide in a Biofilter with sugarcane bagasse as a packing material

5th International Conference on Biotechniques for Air Pollution Control and Bioenergy, Nîmes (France), September 11-13 2013

Proceeding + Oral presentation:

Volckaert, D., Wuytens, S., Van Langenhove, H. Removal of dimethylsulfide, n-hexane and toluene from wast air in a flat membrane bioreactor under continuous conditions

Volckaert, D., Heynderickx, P.M., Fathi, E., Van Langenhove, H. SIFT-MS a logical tool for monitoring and evaluating a biofilter performance

European Symposium on Advances in SIFT-MS, Breda (Netherlands), February 3-4 2014

Oral presentation:

Volckaert, D., Heynderickx, P.M., Fathi, E., Van Langenhove, H. SIFT-MS a logical tool for monitoring and evaluating a biofilter performance

Language Skills

Dutch:	Native language
English:	Very good
French:	Good
German:	Basics

Software knowledge

Microsoft Office:	Good
Solid Edge:	Good
Java, C++, LabView:	Basics
Statistix, Aspen Plus:	Basics