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Studying Bioavailability Limitations in Processes That Involve Gaseous Phases

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Abstract

Air pollution and human exposure to low-quality air containing contaminants are the most critical environmental threats to public health worldwide. Indeed, air pollution alone caused approximately 8.1 million deaths in 2021 in the world and 0.7 million deaths in children under 5 years, which represents 15% of all global deaths in children under five. The economic cost and social impact of air pollution are high worldwide, while its harmful effects create disproportionate disease burdens in less affluent portions of society. Moreover, as global CO_2 mitigation falters, reductions in methane emissions are imperative to controlling near-term global warming and improving air quality. The voluntary Global Methane Pledge launched at COP 26 in November 2021 is supported by about 160 countries and aims at reducing methane emissions from human activity by 30% from 2020 levels by 2030. Despite these initiatives, methane emissions are not falling. Air pollution control using more sustainable methods has become increasingly important and its development and implementation requires urgent focus in the near future.

Biological gas treatment methods are increasingly used for air pollution control and gas purification as they are considered a more sustainable alternative to traditional physical-chemical gas treatment methods. Biological removal of gaseous contaminants relies on the ability of microorganisms to degrade these contaminants and thus the effectiveness of these methods largely depends on the bioavailability of the contaminants for the microorganisms. However, bioavailability of contaminants in traditional biological gas treatment systems is often hampered. Bioavailability governs the rate of bioconversions of these gaseous contaminants and may be the result of limited mass transfer to the microorganisms or microbial inhibition by the contaminant or its metabolites. Contaminants that are hydrophobic or present in low concentration, or that inhibit biodegradation, result in poor removal rates in traditional biological gas purification systems. The wider application of biological gas treatment methods to replace less sustainable physical-chemical methods requires improvements to overcome limitations related to bioavailability, particularly for gaseous streams containing hydrophobic contaminants and contaminants present at relatively low concentrations.

This PhD thesis obtained an enhanced understanding of bioavailability limitations of especially hydrophobic contaminants at relatively low concentrations in gas treatment bioprocesses. More specifically, methods to enhance the bioavailability of (1) gaseous hydrophobic contaminants in the context of indoor air quality (IAQ) and (2) dilute methane to reduce greenhouse gas (GHG) emissions have been investigated from an experimental and theoretical point of view. Conventional biological gas treatment systems operate as laminar contactors. The laminar flow in conventional biological gas treatment systems is a flow regime characterized by high diffusion and low advection and is the opposite of turbulent flow. Improved convection by advection (i.e., the transport by the larger-scale motion of currents in a medium, for example through mixing) would improve mass transfer. In this context, capillary reactors when operated under segmented (Taylor) flow regime provide an internal liquid recirculation that combines enhanced mass transfer with low pressure drops, two important factors affecting cost effectiveness for many industrial applications.

Several long-term experimental studies were undertaken to investigate constraints of bioavailability and possible design and operational strategies to overcome them. First the treatment in a capillary reactor of gaseous compounds that are model compounds for hydrophobic indoor air contaminants was evaluated (Chapter 5). This process was further investigated through the addition of a second non-aqueous liquid phase with a high affinity for these contaminants (Chapter 6) and through the co-abatement of gaseous contaminants and CO_2 (Chapter 7). The abatement of dilute methane using the concept of a capillary bioreactor was investigated with the focus on liquid optimisation (Chapter 8) and reactor operation (Chapter 9). Overall, bioavailability limitations related to biological gas treatment have been investigated in general terms, with an emphasis on the underlying principles and technically feasible methods to overcome bioavailability limitations of especially hydrophobic contaminants in a capillary bioreactor.

The removal efficiency of the model air contaminants hexane, toluene and α-pinene, selected based on their different hydrophobicity and biodegradability, was on average 58, 90 and 44% (with maximum removals of up to 75, 99 and 75%, respectively), at an average gas contact time in the capillary channels of less than 1 second. This extremely low gas contact time is at least one and closer to two orders of magnitude lower than that of conventional biological air treatment systems. An active contaminant-degrading culture could be sustained in the system treating hexane, toluene and α-pinene, while no accumulation of biofilm inside the capillary channels was observed. The bioreactor system showed stable operation for 100-days and was robust against three common upset scenarios (failures of air supply, water recirculation, and power supply) most likely facilitated by the highly diverse bacterial community that was observed.

The toluene, α-pinene and hexane removals were further enhanced up to 99, 98, and 55%, respectively, when 10% (v/v) silicone oil with a viscosity of 20 cSt was dispersed in the recirculating liquid. The addition of silicone oil increased the removal efficiency of α-pinene from 45 ± 6% to 98 ± 2% over two days, likely due to the fact that silicone oil alleviated biokinetic inhibition by acting as a buffer for this compound and their metabolites. For toluene, the removal efficiencies gradually increased after silicone oil addition from 81 ± 3% to 99 ± 1% over eight weeks, likely due to microbial adaptation. The removal efficiency of hexane did not increase after silicone oil addition, potentially due to inhibition of hexane or its metabolites as the bioreactor was deliberately operated without replenishment of the recirculation liquid. Interestingly, visually all the biomass adhered to the silicone oil phase rather than residing in the water phase.

The feasibility of a capillary bioreactor as a platform for the biological gaseous co-abatement of CO_2 and hydrophobic VOCs was confirmed. An instant reduction of the outlet CO_2 concentration compared to the inlet CO_2 concentration was observed after the introduction of microalgae into the capillary bioreactor. A net CO_2 consumption was observed achieving complete carbon sequestration from the removed VOCs with additional CO_2 removed from the inlet ambient air.

Furthermore, different bench experiments elucidated that the liquid phase in a capillary bioreactor can be optimized to enhance the bioavailability of dilute methane. Synthetic surfactants were investigated to assess their potential to enhance bioavailability and

mass transfer, both with and without the presence of silicone oil. Three non-ionic surfactants were selected for their widespread availability and common use in many households or industries. The surfactants BRIJ 58 and SDBS, in contrast to TWEEN 60, showed to be able to significantly enhance bioavailability of dilute methane at the concentrations tested. The lower apparent gas-liquid partition coefficient of methane and the enhanced cell hydrophobicity of the methane oxidizing consortium appear to be the main mechanisms underlying methane biodegradation. The surfactant BRIJ 58 was found to enhance the gas-liquid mass transfer in a capillary channel, but the effect was significant only when combined with silicone oil. The enhanced emulsification of the oil by the surfactant appeared to be the main mechanism for this enhancement, rather than the modification of the gas-liquid partial coefficient of methane. The amount of silicone oil added impacted mass-transfer significantly when comparing 10% v/v versus 25% v/v, regardless of the oil viscosity. But the viscosity of the silicone oil (and thus the overall viscosity of the emulsion) appeared to be critical to maintain optimum turbulent (Taylor) flow conditions, with a lower viscosity being better as confirmed in the abiotic methane mass transfer rate experiments.

When the removal of gaseous methane was investigated in different capillary bioreactor configurations, the addition of only surfactant or only silicone oil did not show any enhancement in methane removal. However, when the capillary bioreactor containing silicone oil and the surfactant BRIJ 58 were combined the treatment of dilute methane significantly advanced. Its performance was improved to an average elimination capacity of 231 ± 30 g methane per m^3 internal capillary channel per hour at an efficiency of 51 ± 2% and an empty channel gas contact time of 23 seconds. This is a large improvement as for conventional biological methane treatment methods approximately six minutes is required for similar removal efficiencies. Moreover, the potential of silicone oil as a buffer for methane was confirmed in a test that showed no deterioration in methane removal in the capillary bioreactor following the methane supply interruption of six days. Remarkably, no accumulation of biomass on the walls of the capillary glass channels was observed during the entire period of more than 300-days operation of the capillary bioreactor. The shear-stress appeared to be high enough to prevent biomass growth on the inside wall of the capillary channels which was further explained by the pulsating shear stress created by the segmented (Taylor) gas-liquid flow. It appears that a capillary bioreactor, when operated with internal gas recirculation and thus decoupling optimal conditions for mass transfer from the gas contact time, may be a useful platform for further exploring the abatement of dilute methane.

This study can serve as a stepping stone to future research and wider spread application of promising new strategies for biological gas treatment. These methods aim to address key challenges in improving air quality, reducing GHG emissions, and enhancing the economic viability of gas-phase biorefineries. Such biorefineries are often hampered by bioavailability issues such as the mass transfer limitation of the contaminant from the gas to the liquid phase containing the microorganisms responsible of its bioconversion, or microbial inhibition by the contaminant or its metabolites.

Resumen

La contaminación atmosférica y la exposición humana a aire de baja calidad que contiene contaminantes son las amenazas medioambientales más graves para la salud pública en todo el mundo. De hecho, sólo la contaminación atmosférica causó aproximadamente 8,1 millones de muertes en 2021 en el mundo y 0,7 millones de muertes en niños menores de 5 años, lo que representa el 15% de todas las muertes mundiales en niños de esta edad. El coste económico y el impacto social de la contaminación atmosférica son elevados en todo el mundo, mientras que sus efectos nocivos provocan enfermedades de manera prioritaria en los sectores más desfavorecidos de la sociedad. Además, dado que la mitigación del CO_2 a escala mundial se tambalea, es imperativo reducir las emisiones de metano para controlar el calentamiento global a corto plazo y mejorar la calidad del aire. El Compromiso Mundial sobre el Metano, de carácter voluntario, lanzado en la COP 26 en noviembre de 2021, cuenta con el apoyo de unos 160 países y tiene como objetivo reducir las emisiones de metano procedentes de la actividad humana en un 30% con respecto a los niveles de 2020 para 2030. A pesar de estas iniciativas, las emisiones de metano no disminuyen. El control de la contaminación atmosférica mediante métodos más sostenibles es cada vez más importante y su desarrollo y aplicación requieren una atención urgente en un futuro próximo.

Los métodos biológicos de tratamiento de gases se utilizan cada vez más para el control de la contaminación atmosférica y la depuración de gases, ya que se consideran una alternativa más sostenible a los métodos físico-químicos tradicionales. La eliminación biológica de contaminantes gaseosos depende de la capacidad de los microorganismos para degradarlos. Por tanto, la eficacia de estos métodos está directamente relacionada con la biodisponibilidad de los contaminantes para dichos microorganismos. Sin embargo, en los sistemas biológicos tradicionales de tratamiento de gases, esta biodisponibilidad suele verse limitada, bien por una transferencia de masa limitada a los microorganismos o por la inhibición microbiana debida al contaminante o sus metabolitos, lo que influye en la tasa de bioconversión de los contaminantes gaseosos. Por ello, los contaminantes hidrófobos o presentes en bajas concentraciones, o aquellos que inhiben la biodegradación, dan lugar a tasas de eliminación deficientes en los sistemas tradicionales de depuración biológica de gases. Así, la implementación de métodos biológicos para sustituir a los métodos físico-químicos menos sostenibles requiere mejoras para superar las limitaciones relacionadas con la biodisponibilidad, en particular para las corrientes gaseosas que contienen contaminantes hidrófobos y/o presentes en concentraciones relativamente bajas.

Esta tesis doctoral ha permitido comprender mejor las limitaciones de biodisponibilidad de contaminantes especialmente hidrófobos a concentraciones relativamente bajas en bioprocesos de tratamiento de gases. Más concretamente, se han estudiado desde un punto de vista experimental y teórico métodos para mejorar la biodisponibilidad de (1) contaminantes gaseosos hidrófobos en el contexto de la calidad del aire interior y (2) metano diluido para reducir las emisiones de gases de efecto invernadero (GEI). Los sistemas biológicos convencionales de tratamiento de gases funcionan como contactores laminares. El régimen de flujo laminar está caracterizado por una alta difusión y una baja advección, siendo opuesto al flujo turbulento. La mejora de la convección por

advección (es decir, el transporte por el movimiento a mayor escala de las corrientes en un medio, por ejemplo, a través de la mezcla) mejoraría la transferencia de masa. En este contexto, los reactores capilares, cuando funcionan en régimen de flujo segmentado (Taylor), proporcionan una recirculación interna del líquido que combina una transferencia de masa mejorada con bajas caídas de presión, dos factores importantes que afectan a la rentabilidad de muchas aplicaciones industriales.

Se realizaron varios estudios experimentales de larga duración para investigar las limitaciones de biodisponibilidad y las posibles estrategias operativas y de diseño para superarlas. En primer lugar, se analizó el tratamiento en un reactor capilar de compuestos gaseosos modelo de contaminantes hidrófobos típicos de aire de interior (capítulo 5). Este proceso se estudió más a fondo mediante la adición de una segunda fase líquida no acuosa con una alta afinidad por estos contaminantes (Capítulo 6), analizando posteriormente la eliminación simultánea de los contaminantes gaseosos y CO_2 (Capítulo 7). Se estudió la reducción de metano diluido utilizando el concepto de biorreactor capilar, centrándose en la optimización de la fase líquida (Capítulo 8) y el funcionamiento del reactor (Capítulo 9). En general, se han estudiado las limitaciones de biodisponibilidad en el tratamiento biológico de gases, con especial atención a los principios subyacentes y los métodos técnicamente viables para superar dichas limitaciones, en particular en el caso de contaminantes hidrófobos en un biorreactor capilar.

La eficacia de eliminación promedio de los contaminantes modelo hexano, tolueno y α-pineno (seleccionados en función de su diferente hidrofobicidad y biodegradabilidad) fue del 58, 90 y 44%, con eliminaciones máximas de hasta aproximadamente el 75, 99 y 75%, respectivamente, con un tiempo medio de residencia del gas en los canales capilares de aproximadamente 0,5 segundos. Este tiempo de residencia del gas, extremadamente bajo, es al menos un orden de magnitud y casi dos órdenes de magnitud inferior al de los sistemas biológicos convencionales de tratamiento del aire. Durante toda la operación, se pudo mantener un cultivo activo de degradación de hexano, tolueno y α-pineno, mientras que no se observó acumulación de biopelícula en el interior de los canales capilares. El biorreactor funcionó de forma estable durante 100 días y fue robusto frente a tres alteraciones habituales, probablemente gracias a la gran diversidad de la comunidad bacteriana observada. La eliminación de tolueno, α-pineno y hexano aumentó hasta el 99, 98 y 55%, respectivamente, cuando se dispersó en el líquido recirculante un 10% (v/v) de aceite de silicona con una viscosidad de 20 cSt. La adición de aceite de silicona aumentó la eficacia de eliminación del α-pineno del 45 ± 6% al 98 ± 2% en dos días, probablemente debido a que el aceite de silicona alivió la inhibición microbiológica al actuar como buffer para los COV y sus metabolitos. En el caso del tolueno, las eficiencias de eliminación aumentaron gradualmente tras la adición de aceite de silicona del 81 ± 3% al 99 ± 1% en ocho semanas, lo que se atribuyó a la adaptación microbiana. La eficiencia de eliminación del hexano no aumentó tras la adición de aceite de silicona, debido potencialmente a la inhibición causada por el hexano o por sus metabolitos, ya que el biorreactor fue operado sin reposición del líquido de recirculación. Es interesante señalar que, visualmente, toda la biomasa se adhirió a la fase de aceite de silicona en lugar de residir en la fase acuosa.

Se confirmó la viabilidad de un biorreactor capilar como plataforma para la eliminación simultánea biológica de CO_2 y COVs hidrófobos. Se observó una reducción instantánea de la concentración de salida de CO_2 en comparación con la concentración de CO_2 de entrada tras la introducción de microalgas en el biorreactor capilar. El consumo neto de CO_2 confirmó la completa eliminación del CO_2 generado por la oxidación de los COV y la fijación de CO_2 adicional procedente del aire ambiente de entrada.

Los experimentos en batch confirmaron que la fase líquida en un biorreactor capilar puede optimizarse para mejorar la biodisponibilidad de metano diluido. Se investigaron surfactantes sintéticos para evaluar su potencial para mejorar la biodisponibilidad y la transferencia de masa, tanto con presencia de aceite de silicona como sin ella. Se seleccionaron tres surfactantes no iónicos por su amplia disponibilidad y uso común en muchos hogares o industrias. Los surfactantes BRIJ 58 y SDBS, a diferencia del TWEEN 60, demostraron ser capaces de aumentar significativamente la biodisponibilidad del metano diluido a las concentraciones ensayadas. El menor coeficiente aparente de partición gas-líquido del metano y la mayor hidrofobicidad celular del consorcio oxidante del metano parecen ser los principales mecanismos subyacentes a la biodegradación del metano. Se observó que el surfactante BRIJ 58 mejoraba la transferencia de masa gas-líquido en un canal capilar, pero el efecto sólo era significativo cuando se combinaba con aceite de silicona. La emulsificación mejorada del aceite por el surfactante parecía ser el principal mecanismo de esta mejora, más que la modificación del coeficiente parcial gas-líquido del metano.

La cantidad de aceite de silicona añadida influyó significativamente en la transferencia de masa al comparar 10% v/v frente a 25% v/v, independientemente de la viscosidad del aceite. La viscosidad del aceite de silicona (y, por tanto, la viscosidad global de la emulsión) demostró ser crítica para mantener unas condiciones óptimas de flujo turbulento (Taylor), siendo mejor una viscosidad más baja, como se confirmó en el experimento abiótico de tasa de transferencia de metano.

Cuando se estudió la eliminación de metano gaseoso en diferentes configuraciones de biorreactores capilares, la adición de sólo surfactante o sólo aceite de silicona no mostró ninguna mejora en la eliminación de metano. El biorreactor capilar que contenía aceite de silicona y BRIJ 58 tratando metano diluido obtuvo los mejores resultados con una capacidad media de eliminación de 231 ± 30 g de metano por m^3 de canal capilar interno por hora, con una eficiencia del 51 ± 2% y un tiempo de residencia del gas en el canal vacío de 34 segundos. Además, el potencial del aceite de silicona como buffer para el metano se confirmó en una prueba, donde no se observó deterioro en la eliminación de metano en el biorreactor capilar tras la interrupción de la alimentación durante seis días. Tampoco se detectó acumulación de biomasa en las paredes de los canales de vidrio capilar durante los más de 300 días de funcionamiento del biorreactor capilar. La tensión de cizallamiento parecía ser lo suficientemente alta como para impedir el crecimiento de biomasa en la pared interior de los canales capilares. Se demostró por tanto que un biorreactor capilar, cuando funciona con recirculación interna de gas y desvincula así las condiciones óptimas para la transferencia de masa del tiempo de residencia del gas, puede ser una plataforma útil para la eliminación de las emisiones de metano diluido.

Este estudio sienta las bases para futuras investigaciones y una aplicación más amplia de nuevas estrategias prometedoras de métodos biológicos de tratamiento de gases. Estas estrategias tienen como objetivo superar las limitaciones relacionadas con la mejora de la calidad del aire, la reducción de las emisiones de GEI y la mejora de la viabilidad económica de las biorrefinerías en fase gaseosa. Estas biorrefinerías a menudo se ven obstaculizadas por problemas de biodisponibilidad del contaminante, derivadas de la limitación de la transferencia de masa del mismo desde el gas a la fase líquida que contiene los microorganismos responsables de su bioconversión, o bien de la inhibición microbiana por el contaminante o sus metabolitos.

Samenvatting

Luchtverontreiniging en blootstelling eraan zijn wereldwijd één van de meest kritieke milieubedreigingen voor de volksgezondheid. Luchtvervuiling alleen al veroorzaakte in 2021 ongeveer 8,1 miljoen doden in de wereld en 0,7 miljoen doden onder kinderen jonger dan 5 jaar, wat neerkomt op 15% van alle wereldwijde sterfgevallen bij kinderen onder de vijf jaar. De economische kosten en de sociale impact van luchtverontreiniging zijn wereldwijd hoog, terwijl de schadelijke effecten ervan onevenredige ziektelasten veroorzaken in minder welvarende delen van de samenleving. Bovendien, nu de wereldwijde vermindering van CO_2-uitstoot hapert, is een vermindering van de methaanuitstoot absoluut noodzakelijk om de opwarming van de aarde op korte termijn te beheersen en de luchtkwaliteit te verbeteren. De vrijwillige Global Methane Pledge, die tijdens COP 26 in november 2021 werd gelanceerd, wordt ondersteund door ongeveer 160 landen en heeft tot doel de methaanemissies door menselijke activiteiten voor 2030 met 30% te verminderen ten opzichte van het niveau van 2020. Ondanks deze initiatieven daalt de methaanuitstoot niet. De bestrijding van luchtverontreiniging met behulp van duurzamere methoden is steeds belangrijker geworden en de ontwikkeling en implementatie ervan vereist in de nabije toekomst dringende aandacht.

Biologische gasbehandelingsmethoden worden steeds vaker gebruikt voor de beheersing van luchtverontreiniging en gaszuivering, omdat ze worden beschouwd als een duurzamer alternatief voor traditionele fysisch-chemische gasbehandelingsmethoden. Biologische gasbehandelingsmethoden gebruikt het natuurlijke vermogen van micro-organismen om verontreinigingen af te breken en de effectiviteit van deze methoden hangt dus grotendeels af van de biologische beschikbaarheid van de verontreinigingen voor de micro-organismen. De biologische beschikbaarheid van verontreinigingen in traditionele biologische gasbehandelingssystemen wordt echter vaak belemmerd. Biologische beschikbaarheid bepaalt de snelheid van bioconversies van de gasvormige verontreinigingen en kan het resultaat zijn van beperkte massaoverdracht naar de micro-organismen. Verontreinigingen die hydrofoob (waterafstotentend) zijn, of aanwezig zijn in lage concentraties, of die de biologische afbraak remmen, resulteren vaak in een slechte verwijdering in traditionele biologische gaszuiveringssystemen. De bredere toepassing van biologische gasbehandelingsmethoden ter vervanging van minder duurzame fysisch-chemische methoden vereist verbeteringen om metname de biologische beschikbaarheid te bevorderen voor gasvormige stromen die hydrofobe verontreinigingen bevatten.

Dit proefschrift verwierf een verbeterd inzicht van de biologische beschikbaarheidsbeperkingen van met name hydrofobe verontreinigingen in bioprocessen voor gasbehandeling. Specifiek zijn methoden bestudeerd om de biologische beschikbaarheid van (1) gasvormige hydrofobe verontreinigingen te verbeteren in de context van de binnenluchtkwaliteit en (2) lage methaan concentraties om de uitstoot van broeikasgassen te verminderen vanuit een experimenteel en theoretisch oogpunt. Conventionele biologische gasbehandelingssystemen werken als laminaire gas-vloeistof contact reactoren. De laminaire stroming in conventionele biologische gasbehandelingssystemen is een stromingsprofiel dat wordt gekenmerkt door hoge diffusie en lage advectie en is het tegenovergestelde van turbulente stroming. Verbeterde convectie door advectie (d.w.z. het transport door de grootschaligere beweging van stromen in een medium, bijvoorbeeld door menging) zou de

massaoverdracht verbeteren. In deze context bieden capillaire reactoren mogelijkheden, vooral wanneer ze worden bedreven middels een specifiek gas-vloeistof stromingsprofiel (de zogenaamde gesegmenteerd gas-vloeistof stroming of wel Taylor-flow). Dit stromingsprofiel bevat een interne vloeistofrecirculatie die een verbeterde massaoverdracht combineert met een lage energieverbruik, twee belangrijke factoren die van invloed zijn op de kosteneffectiviteit voor veel industriële toepassingen.

Er werden verschillende experimentele langetermijn-studies uitgevoerd om de beperkingen van de biologische beschikbaarheid te onderzoeken en zo mogelijke ontwerp- en operationele strategieën te ontwikkelen om deze beperkingen te overwinnen. De behandeling van vervuilde lucht in een capillaire reactor wordt als eerste besproken (Hoofdstuk 5). Dit proces werd verder bestudeerd door de toevoeging van een tweede niet-waterige vloeibare fase met een hoge affiniteit voor deze verontreiningen (Hoofdstuk 6) en door de gelijktijdige biologische behandeling van CO_2 (Hoofdstuk 7). De reductie van verdund methaan met behulp van het concept van een capillaire bioreactor werd bestudeerd met de nadruk op vloeistofoptimalisatie (Hoofdstuk 8) en reactorwerking (Hoofdstuk 9). Samenvattend zijn de beperkingen van de biologische beschikbaarheid in verband met biologische gasbehandeling bestrudeerd in algemene termen en specifieke experimenten uitgevoerd in capillaire bioreactoren om deze beperkingen beter te begrijpen en te overwinnen voor twee soorten hydrofobe verontreinigingen.

De verwijderingsefficiëntie van de modelluchtverontreinigingen hexaan, tolueen en α-pineen, geselecteerd op basis van hun verschil in waterafstootbaarheid en biologische afbreekbaarheid, was gemiddeld 58, 90, en 44% (met maximale verwijderingen tot respectievelijk ongeveer 75, 99, en 75%) bij een gemiddelde gascontacttijd in de capillaire kanalen van minder dan 1 seconde. Deze extreem korte gascontacttijd is ten minste één, maar dichter bij twee ordes van grootte lager dan die van conventionele biologische luchtbehandelingssystemen. De actieve microbiële cultuur in het systeem werd gekwantificeerd en vertoonde een rijke diversiteit. Geen accumulatie van biofilm in de capillaire kanalen werd waargenomen, hetgeen belangrijk voor de operationele stabiliteit op de langere termijn. De bioreactor vertoonde een stabiele werking gedurende 100 dagen en was robuust tegen drie veelvoorkomende verstoorde scenario's (onderbreking van de luchttoevoer, de water recirculatie, en de stroom/energie), hoogstwaarschijnlijk gefaciliteerd door de zeer diverse bacteriële gemeenschap die werd waargenomen.

De verwijdering van tolueen, α-pineen en hexaan werd verder verbeterd tot respectievelijk 99, 98 en 55% wanneer 10% (v/v) siliconenolie werd toegevoegd aan de recirculerende vloeistof. De toevoeging van siliconenolie verhoogde de verwijderingsefficiëntie van α-pineen van 45 ± 6% tot 98 ± 2% in twee dagen tijd, mogelijk doordat de olie de biokinetische remming ophefte door te fungeren als een buffer voor de verontreiniging en/of zijn afbraakproducten. Voor tolueen nam de verwijderingsefficiëntie geleidelijk toe over een periode van acht weken van 81 ± 3% tot 99 ± 1% na de toevoeging van olie, mogelijk door microbiële aanpassing. De verwijderingsefficiëntie van hexaan nam niet toe na toevoeging van olie, waarschijnlijk als gevolg van remming van hexaan of zijn afbraakproducten, aangezien de recirculatievloeistof in de bioreactor opzettelijk niet werd

ververst. Verrassend was dat visueel alle biomassa zich aan de olie fase hechtte in plaats van in de waterfase te verblijven.

De haalbaarheid van een capillaire bioreactor als platform voor de gelijktijdige biologische gasvormige verwijdering van CO_2 en de waterafstotende verontreinigingen werd bevestigd. Een onmiddellijke vermindering van de CO_2-concentratie werd waargenomen na de introductie van micro-algen in de capillaire bioreactor. Er werd een netto CO_2-verbruik waargenomen waarbij volledige koolstofvastlegging uit de verwijderde verontreiningen werd bereikt, terwijl extra CO_2 uit de verontreinigende lucht werd verwijderd.

Vervolgens hebben verschillende experimenten aangetoond dat de vloeibare fase in een capillaire bioreactor kan worden geoptimaliseerd om de biologische beschikbaarheid van methaan te verbeteren. Synthetische oppervlakte-actieve stoffen werden onderzocht op hun potentieel om de biologische beschikbaarheid en massaoverdracht te verbeteren, zowel met als zonder olie. Drie oppervlakte-actieve stoffen werden geselecteerd vanwege hun wijdverbreide beschikbaarheid en algemeen gebruik in veel huishoudens of industrieën. De oppervlakte-actieve stoffen BRIJ 58 en SDBS bleken, in tegenstelling tot TWEEN 60, in staat om de biologische beschikbaarheid van verdund methaan aanzienlijk te verbeteren bij de geteste concentraties. De lagere schijnbare gas-vloeistof verdelingscoëfficiënt van methaan en de verbeterde bacteriele celhydrofobiciteit van de methaan-oxiderende bacterien bleken de belangrijkste mechanismen te zijn die ten grondslag liggen aan de verbeterende beschikbaarheid van methaan. De oppervlakte-actieve stof BRIJ 58 bleek de gas-vloeistofmassaoverdracht in een capillair kanaal te verbeteren, maar het effect was alleen significant in combinatie met de olie. De verbeterde emulgering van de olie door de oppervlakte-actieve stof bleek het belangrijkste mechanisme voor deze verbetering te zijn, en niet de verhoging van de methaan gas-vloeistof verdelingscoëfficiënt.

De hoeveelheid toegevoegde olie had een aanzienlijke invloed op de massaoverdracht, ongeacht de viscositeit van de olie. Maar de viscositeit van de olie (en dus de algehele viscositeit van de emulsie) bleek van cruciaal belang te zijn om optimale turbulente (Taylor) stromingsomstandigheden te behouden, waarbij een lagere viscositeit beter was, zoals bevestigd in een abiotisch experiment dat de methaan massaoverdrachtssnelheid vastlegde.

Toen de verwijdering van gasvormig methaan werd bestudeerd in verschillende capillaire bioreactor configuraties, vertoonde de toevoeging van alleen oppervlakte-actieve stof of alleen siliconen-olie geen verbetering van de methaanverwijdering. De capillaire bioreactor met siliconen-olie en BRIJ 58 voor de behandeling van verdund methaan presteerde veruit het beste met een gemiddelde verwijderingscapaciteit van 231 ± 30 g methaan per m^3 intern capillair kanaal per uur met een efficiëntie van 51 ± 2% en een gas contacttijd van 23 seconden. Dit is een grote verbetering ten opzichte van conventionale biologische methoden voor methaan verwijdering, waar voor vergelijkbare verwijderingsrendementen typisch rond de zes minuten nodig zijn. Bovendien werd het potentieel van de olie als buffer tijdens de methaan afbraak bevestigd in een test die geen verslechtering van de methaanverwijdering in de capillaire bioreactor aantoonde na de onderbreking van de methaantoevoer van zes dagen. Verrassend was dat er geen ophoping van biomassa op de wanden van de capillaire kanalen werd waargenomen gedurende de gehele periode van 300 dagen. De schuifspanning bleek hoog genoeg te zijn om de groei van

biomassa aan de binnenwand van de capillaire kanalen te voorkomen en was verder verklaard door de pulserende schuifspanning als gevold van het gesegmenteerde (Taylor) gas-vloeistof stromingsprofiel. Het lijkt erop dat een capillaire bioreactor, wanneer deze wordt gebruikt met interne gasrecirculatie en zo optimale omstandigheden voor massaoverdracht loskoppelt van de gascontacttijd, een nuttig platform kan zijn voor verder onderzoek naar de verwijdering van methaan emissies.

Deze studie kan worden gebruikt als opstap naar een bredere toepassing van veelbelovende nieuwe strategieën voor biologische gasbehandelingsmethoden om de uitdagingen aan te pakken die verband houden met het verbeteren van de luchtkwaliteit, het verminderen van de uitstoot van broeikasgassen en het vergroten van de economische levensvatbaarheid van bio-raffinaderijen, die momenteel worden belemmerd door de biologische beschikbaarheid van de verontreinigingen.

List of Publications

The following publications are presented as part of this thesis. The publications are all published in international Q1 journals[1] indexed in ISI Web of Knowledge.

- Kraakman, N.J.R., Bordel, S., Lebrero, R., Muñoz, R., (2025). Dilute Methane Biofiltration through Multi-channel Taylor Flow Capillary Bioreactors. ***Journal of Water Process Management*** (submitted for publication).

- Kraakman, N.J.R., Villarreal-Heras, L., González-Martín, J., Cantera, S., Muñoz, R., Lebrero, R. (2024). Enhancing Dilute Methane Treatment Through Liquid Phase Alteration in a Capillary Bioreactor. ***Chemical Engineering Journal*** (submitted for publication).

- Kraakman, N.J.R., González-Martín, J., Sanchez Garcia, C., Cantera, S., Lebrero, R., Muñoz, R. (2024). **Multi-channel Capillary Bioreactor for Hydrophobic VOC and CO_2 Abatement – Process Intensification Through Silicone Oil Addition**. *J. of Environmental Chemical Engineering.* 12, 113695.

- Kraakman, N.J.R., González-Martín, J., Rodriguez, E., Lebrero, R., Deshusses, M.A., Muñoz, R. (2023) **Hydrophobic Air Pollutants Removal at One Second Gas Contact in a Multi-channel Capillary Bioreactor**. *J. of Environmental Chemical Engineering*, 11. 110502.

- Kraakman, N.J.R., González-Martín, J., Pérez, C., Lebrero, R., Muñoz, R. (2021) **Recent Advances in Biological Systems for Improving Indoor Air Quality**. *Reviews in Environmental Science and Bio/Technology*. 20 :363–387.

- Bordel, S., Kraakman, N.J.R., Munoz, R. (2024) **Theoretical analysis of gas-liquid mass transfer in Taylor Flow capillary reactors.** *Chemical Engineering Science*. 119949.

- González-Martín, J., Kraakman N.J.R., Pérez, C., Lebrero, R., Muñoz, R. (2020) **A state–of–the-art review on indoor air pollution and strategies for indoor air pollution control**. *Chemosphere* 262.

[1] Q1 journal = a journal within 25% of journals with the highest CiteScores. Journals are grouped into subject category and ranked according to the Journal Impact Factor (JCR) or citation weighting (SJR).

PART I

INTRODUCTION

1. JUSTIFICATION AND OBJECTIVES OF THIS RESEARCH

1.1 Justification and Main Drivers

Air pollution treatment and gas conversion methods that use biological processes need improvements in design and/or operation to overcome current limitations in mass transfer of (1) hydrophobic contaminants or (2) contaminants present at low concentrations, as both cause limited bioavailability. The improvements would provide benefit in the following applications, which are all in urgent need of more cost-effective sustainable solutions:

- Air pollution and human exposure to low-quality indoor air are the most critical environmental threats to public health worldwide according to the World Health Organization and the Health Effects Institute (Health Effects Institute, 2024; World Health Organization, 2016). Recent reports have indicated that, at a global scale, 1 out of 10 deaths are attributable to air pollution. Indeed, air pollution alone caused approximately 8.1 million deaths in 2021 in the world and 0.7 million deaths in children under 5 years, which represents 15% of all global deaths in children under five. In addition, the economic cost and social impact of air pollution are high worldwide, while its harmful effects create disproportionate disease burdens in less affluent portions of society. Air pollution control using more sustainable methods has become increasingly important and their development and implementation requires urgent focus in the near future.

- The indoor concentration of air pollutants is almost always higher than the outdoor concentration of air pollutants, while an average adult in the US spends 86% of their time indoors (houses, workplaces, schools, shopping centres, public buildings) and an additional 6% inside vehicles or public transport. The health threats of indoor air contaminants caused by long-term exposure have become more apparent over the last decades as buildings are progressively sealed against the outside climate conditions to obtain heating and cooling energy cost savings, and as a result also of stricter safety guidelines. Modern buildings accumulate higher indoor air contaminant concentrations because they increasingly rely on mechanical ventilation with greatly reduced outdoor air ingress. There is currently no single physical-chemical technology able to remove all indoor air pollutants in a cost-effective way. New biological purification methods may be able to provide this, but low concentrations of especially hydrophobic contaminants often limit their bioavailability for effective biological treatment, which requires improvements in current technology designs.

- As global CO_2 mitigation falters, reductions in methane emissions are imperative to controlling near-term global warming and improving air quality. The voluntary Global Methane Pledge launched at COP 26 in November 2021 is supported by about 150 countries and aims to reduce methane emissions from human activity by 30% from 2020 levels by 2030. Despite these initiatives, methane emissions are not falling (Methane Tracker, 2024). Furthermore, approximately 55% of all the anthropogenic methane emissions have a concentration below 5% v/v, the lower explosive limit of

methane in air mixtures, and are therefore incompatible for energy recovery or for cost-effective physical-chemical abatement. Fortunately, bioprocesses have shown to be able to combat dilute methane emissions, but their efficiency is hampered by bioavailability due to mass transfer limitation of the hydrophobic methane from the gas phase to the liquid phase containing the microorganisms.

- Gaseous process streams containing contaminants can negatively affect the utilisation of produced valuable gaseous streams such as biogas or biohydrogen (renewable energy vectors). Similarly, the economic viability of gas-phase biorefineries converting gaseous streams containing methane, carbon monoxide or hydrogen into higher value products (e.g., fertilisers or biodegradable polymers, alternative for the current plastics which are all derived from fossil fuels and not degradable causing accumulation of microplastics in the environment) is typically hindered by the mass transfer of the compounds from the gas to the liquid phase containing the microorganisms responsible for the conversion. This limitation restricts the scale-up of these processes for achieving a cost-competitive gas bioconversion (Amabile et al., 2020). Improved methods are required that can enhance gas-liquid mass transfer and eliminate current limitations in bioavailability for gas-phase biorefineries to be more cost-effective.

Biological gas treatment methods are considered a 'green' technology compared to conventional physical-chemical methods, because of the relative low carbon footprint without the continuous input of resources such as harsh chemicals, adsorbents, or combustion fuel. Biological gas treatment is generally also safe as it is operated at ambient pressure and temperatures, does not involve a concentration step with risk of smouldering or fire, and eliminates health and safety risks associated with the storage and handling of chemicals. Adsorption processes (mainly activated carbon filtration) and thermal oxidative processes (incineration) strongly dominate the field of industrial air and gas purification, but require typically ongoing inputs of resources, which makes them far less sustainable. Moreover, thermal oxidative processes can lead to health-damaging smog from its NOx-emissions and generate GHG emissions: carbon dioxide, methane slip and nitrous oxide (which has a considerable greenhouse potential and is known to be formed during thermal oxidative processes when the combustion temperature is lower than 1000°C). The wider application of biological gas treatment methods to replace less sustainable physical-chemical methods, requires improvements to overcome limitations related to bioavailability, particularly for gaseous streams containing hydrophobic contaminants and contaminants present at relatively low concentrations.

1.2 Main Objectives and Hypothesis

Microorganisms have natural potential to convert gaseous contaminants into less hazardous compounds and even added value bioproducts. However, bioavailability of contaminants in traditional biological gas treatment systems is often hampered as a result of the limited mass transfer to the microorganisms. Bioavailability governs the rate of bioconversions of these gaseous contaminants. Thus, contaminants that are hydrophobic or low in concentration or that inhibit biodegradation entail poor removal rates in traditional biological gas purification

systems. The focus of this study is therefore on the bioavailability of gaseous contaminants that are hydrophobic (i.e., methane, hexane, α-pinene, toluene) or present at relatively low concentrations (i.e., contaminants in indoor air, dilute methane).

The traditionally applied biological gas treatment methods (biofilters and biotrickling filters) may also be called laminar contactors. Laminar flow occurs when a gas or liquid flows in parallel layers, with minimal disruption between the layers. Laminar flow is a flow regime characterized by high diffusion and low advection and is the opposite of turbulent flow. Improved convection by advection (e.g., through mixing) would improve mass transfer, and mixing is therefore typically applied in liquid reactors to enhance reactions including mass transfer. However, mixing requires energy input, which is a critical parameter for the design of process equipment and for the operating costs.

Research efforts are needed in the search of less energy-intensive biological gas treatment methods that enhance mass transfer rates and overcome existing mass transfer barriers of traditional approaches. Capillary gas-liquid reactors for chemical reactions have shown to combine enhanced mass transfer through mixing with minimum energy consumption, but studies on capillary gas-liquid bioreactors are limited, mostly dealing with short single capillary channels, relatively short test duration or limited in operating conditions or not focused on treating hydrophobic gaseous compounds. The research in this PhD Thesis is undertaken to improve the fundamental understanding of a multi-capillary channel gas-liquid bioreactor and its removal mechanisms of model hydrophobic gaseous contaminants at short gas contact times. The **hypothesis** is that capillary channel gas-liquid bioreactors exhibit a superior performance compared to traditional biological gas treatment methods, enabling the expansion of their application field for more sustainable processes for air pollution control and gas purification.

Principles are ideas based on scientific rules and laws that are generally accepted by scientists. The overarching objective of this study is to help establishing new principles as a stepping stone to future development and wider spread application of promising new biological gas treatment strategies to help tackling the challenges mentioned above in **Section 1.1**.

1.2 Sub-objectives

- Identify constraints of bioavailability in gaseous bioprocesses.
- Investigate and prioritise possible methods to overcome these constraints.
- Design and build a bench-scale multi-channel capillary reactor.
- Map the different gas-liquid flow regimes including segmented (Taylor) flow.
- Measure the mass -transfer in the capillary reactor at different operating conditions.
- Explore the removal of hydrophobic indoor air contaminants in the capillary reactor.
- Optimise its performance and quantify resilience against common operating upsets.
- Collect information to improve the bench-scale multi-channel capillary reactor.
- Test the potential of a non-aqueous liquid phase (silicone oil).
- Explore the potential of co-abatement of VOC and CO_2 using microalgae.
- Test the removal of dilute methane in the capillary reactor.
- Incubate mixtures of methanotrophs to adapt to silicone oil and synthetic surfactants.
- Test the bioavailability of dilute methane to adapted methanotroph cultures.

- Determine the cell hydrophobicity of the adapted methanotroph cultures.
- Quantify emulsion capacity/stability of different surfactant-oil-in-water emulsions.
- Quantify mass-transfer of methane in a single capillary channel under Taylor-flow.
- Quantify mass-transfer of methane in a single capillary channel with different liquids.
- Select surfactant to add to liquid phase in a capillary bioreactor treating methane.
- Explore the removal of dilute methane in the capillary reactors different in set-up and operating condition:
    - different capillary channels
        - internal diameters (1.7mm and 2.4mm)
        - lengths (1.5m and 1.0m)
    - different operational modes
        - changes in gas-liquid slug velocities, gas-liquid ratios, methane inlet loading rates, gas contact times, with/without internal gas recirculation.
    - different liquid characteristics
        - with/ without surfactants
        - with/ without silicone oil
- Optimise its performance, quantify resilience and conditions relevant for reliable long-term performance:
        - increased surfactant concentrations
        - increased silicone oil concentrations
        - sudden methane load increases
        - methane supply interruption
        - nutrient requirements
        - biomass control
- Evaluate energy requirements.
- Compile conclusions and recommendation for further research.

1.3 Outline of Thesis

Biological techniques for the purification of hydrophobic gaseous contaminants or gaseous contaminants at relatively low concentrations were investigated from a theoretical and experimental viewpoint. **Chapter 2** is a high-level introduction to air pollution and gaseous contaminants relevant to this study. **Chapter 3** discusses existing biological air treatment methods with the focus on two application areas where the treatment is hampered by bioavailability limitations of hydrophobic compounds present at relatively low concentrations: indoor air quality and dilute methane abatement. **Chapter 4** reviews gas-liquid mass transfer aspects of biotechnology for gas treatment in general terms, with an emphasis on the underlying principles. **Chapter 1 till Chapter 4** are all part of **Part I *Introduction***.

Part II, **III and IV** are experimental studies to investigate constraints of bioavailability and possible ways to overcome them. **Part II** *Capillary Channels and Hydrophobic Contaminants* investigates the treatment of model compounds for hydrophobic indoor air contaminants in a capillary reactor (**Chapter 5**). This process was further investigated in **Part**

III *Process Intensification,* through the addition of a second non-aqueous liquid phase (**Chapter 6**) and through the co-abatement of gaseous contaminants and CO_2 (**Chapter 7**). The abatement of dilute methane using the concept of a capillary bioreactor was explored in **Part IV** *Dilute Methane Mitigation using Multi-Channel Capillary Bioreactor*, with the focus on liquid optimisation (**Chapter 8**) and reactor operation (**Chapter 9**).

Part V *Conclusions and Outlook* provides the main conclusions (**Chapter 10**), while the last chapter (**Chapter 11**) provides recommendations for future work.

2. AIR POLLUTION AND GASEOUS CONTAMINANTS

Chapter overview

This chapter is a high-level introduction to air pollution and gaseous contaminants relevant to this study. It explains why air pollution and human exposure to low-quality air containing contaminants are one the most critical environmental threats to public health with high economic cost and social impact worldwide.

It also explains why this study is partly focussed on indoor air contaminants since indoor air quality has not been as acknowledged as outdoor air pollution has. People spent between 80% (developed countries) and 90% (EU-28) indoors and thus source ~10,000 Litres per day from indoor sources such as houses, workplaces, schools, shopping centres and public buildings. The health threats of indoor air contaminants caused by their long-term exposure have become more apparent over the last decades as buildings are progressively sealed against the outside climate conditions to obtain heating and cooling energy cost savings.

Moreover, the need for methane mitigation is increasing dramatically as research indicates that methane has greater climatic impact than previously thought (O'Connor et al, 2010) and, as global CO_2 mitigation falters, it now appears that aggressive methane mitigation is a lower cost means to reduce climate change. With about 60% of global methane emissions caused by human activities, there is a burning need to reduce methane emissions worldwide, which requires the development of cost-effective and sustainable methane abatement techniques.

2.1 Brief Introduction to Air and Gas Contaminants

Air Quality Threat

Air pollution and human exposure to low-quality air containing contaminants are among the most critical environmental threats to public health worldwide according to the World Health Organization (World Health Organization, 2016). Recent reports have indicated that, at a global scale, 1 out of 10 deaths are attributable to air pollution. Indeed, air pollution alone caused approximately 6.7 million deaths in 2019 in the world (**Figure 3-1**).

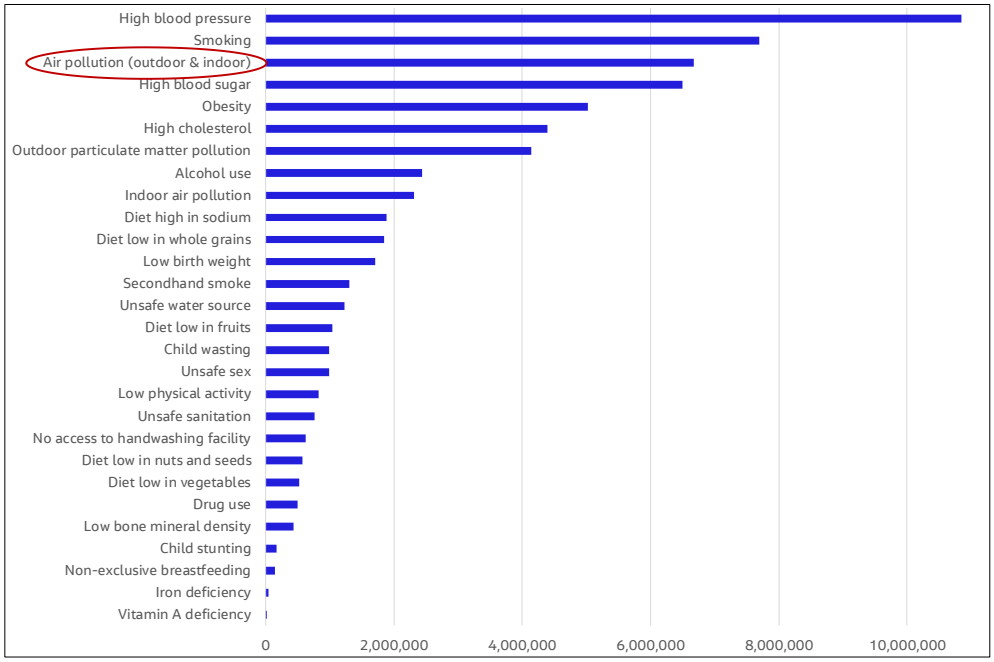


Figure 3-1 The estimated annual deaths in the world attributed to risk factors. (IHME, 2019).

Air contaminants are chemical compounds in the ambient air at concentrations negatively affecting not only human health but also the environment, including the health of animals, plants, crop yield, climate, and man-made infrastructures such as buildings. Air contaminants may be categorised as particle matter (PM), volatile organic and inorganic compounds (VOCs and VICs), and greenhouse gases (GHGs). VOCs and VICs vaporize quickly having a low boiling point (< 250 ºC), and low water solubility at room temperature. Beside direct health impacts, VOCs and VICs can react under the influence of ultraviolet sunlight to produce ozone and secondary aerosols leading to smog.

Gaseous contaminants are often difficult to detect, and their effect is often visible only years after being emitted. The economic cost and social impact of air pollution are high worldwide. For example, the yearly cost of illnesses and premature deaths attributed to air pollution for the European Region alone was estimated to be US$1.575 trillion (WHO, 2015). Its harmful effects create disproportionate disease burdens on the less affluent portions of society. Air pollution has become an increasing concern especially since the industrial revolution and is a problem of the twentieth century that will remain for at least several decades in the future. Although concerns about air pollution have lagged somewhat behind water pollution in the past, today, air quality has been given prominence. This is in part due to

the increasing awareness about its effect on human health and the environment we live in, including the Earth 's climate. Therefore, environmental regulations have been established, which resulted in a variety of air and gas treatment technologies being developed to reduce the concerns and to meet these regulations.

Air contaminants are present in both outdoor and indoor environments and are the result of emissions from various emission sources, including industrial processes, waste processing facilities, transportation, agricultural activities, among other including household activities. Even long-term exposure to low contaminant levels (parts per billion concentrations or ppb_v) can result in health problems including rashes, light headedness, headaches, and life-threatening diseases, among them different types of cancer (World Health Organization, 2016).

Process Gas Contaminants

Process gas contaminants can be present in gaseous streams at concentrations negatively affecting the utilisation of produced gaseous streams. Examples of gaseous streams requiring purification prior to utilisation are:

- Hydrogen sulphide (H_2S) in biogas, which causes corrosion or produce harmful SO_x at combustion engines fuelled by biogas,
- Carbon dioxide (CO_2) in biogas, which reduces the energy value of the gas and prevents injection in the national gas grids,
- Siloxanes in biogas, which causes scaling in combustion engines causing damage,
- Carbon monoxide (CO) in synthesis gas produced by thermal gasification of organic matter which reduces the energy value of the fuel hydrogen (H_2) gas.
- Tars in syngas, which reduces its potential transformation into chemical building blocks.

Gas Biorefineries

Gas treatment can be integrated in the downstream processes to not only recover useful products like renewable energy (biogas or hydrogen), but also to upgrade (waste) gases into higher value products. This includes the production of fertilisers (e.g., ammonium from waste streams containing ammonia) or raw materials (e.g., elemental sulphur or sulphuric acid from waste streams containing hydrogen sulfide or carbon disulfide). Syngas, CO_2, biogas, or methane can be upgraded to produce valuable products such as the methanol or biodegradable polymers such as polyhydroxy-alkanoates (PHAs) to make bioplastics (Lopez et al., 2018). This is a promising sustainable alternative for the current plastics, which are all derived from fossil fuels and not degradable causing accumulation of (micro-) plastics in the environment.

These gas-phase biorefineries rely on the mass transfer of the compounds from the gas to the liquid containing the microorganisms converting the compounds, which is key for upscaling these processes to achieving fast enough conversion rates to be economically viable (Amabile et al., 2020; Lecker et al., 2017).

2.2 Air Contaminants in Occupied Spaces

Indoor Air Quality

The indoor concentration of air pollutants is almost always higher than the outdoor concentration of air pollutants because outdoor-sourced contaminated air enters indoor occupied spaces and combines with indoor-sourced contaminants. Indoor air pollution has not been as acknowledged as outdoor air pollution has, especially in highly industrialized or dense traffic areas. However, the health threats of indoor air contaminants from long-term exposure have become more apparent over the last decades as buildings are progressively sealed against the outside climate conditions to obtain heating and cooling energy cost savings (EEA 2019) and comply with stricter safety guidelines. Modern buildings accumulate higher indoor air contaminant concentrations because they increasingly rely on mechanical ventilation with greatly reduced outdoor air ingress.

At a global level, the World Health Organization (WHO) estimated that each year 3.8 million people die prematurely from illnesses ascribed to indoor air pollution, much of this due to cooking or heating, which represents 7.7% of the global mortality (WHO 2018). For most European countries the economic cost to society of household air pollution is significant in terms of gross domestic product (WHO 2015), with, for example, annual expenses of up to €20,000 million in France (Anses 2014). Moreover, health problems such as respiratory illnesses, allergies and even cancerous diseases associated with poor indoor air quality (IAQ) are compounded by sick building syndrome (Burge 2004). Additional to health impacts, poor IAQ has been shown to reduce workplace productivity by 10-15% (Cincinelli et al. 2016).

Between 80% (developed countries) and 90% (EU-28) of the average 250 million litres of air a person breathes during their life (about 10,000 Litres per day) is sourced from indoor sources such as houses, workplaces, schools, shopping centres, public buildings or means of transport (Royal College of Physicians, 2016). Similarly, the USA Human Activity Pattern Survey found that an average adult spends 86% of their time indoors and an additional 6% inside vehicles or public transport (Marć et al. 2018). In addition, IAQ has been classified as a priority concern for children's health (EU Environmental Agency 2019) and identified as one of the USA's largest environmental threats (Guieysse et al. 2008).

Indoor Air Contaminants

Indoor air contaminants include particulate matter, bioaerosols and over 400 different chemical compounds, while contaminant sources and emission rates may rapidly change over time (Luengas et al. 2015). Indoor contaminant sources include permanent sources (building materials, carpets, paints, varnishes, etc.) and occasional sources (furniture, cleaning and disinfection products, cooking, personal care products, tobacco smoke, etc.), while outdoor contaminants intrusion mostly depends on human activities (road traffic, industry, etc.) (Hubbard et al. 2005). **Table 2-1** summarizes the most relevant indoor air contaminants, their typical sources and commonly used measurement methods.

Table 2-1 Common Indoor Air Contaminants.

Indoor Air Contaminants	Typical Contaminant Sources[1]	Common Measurement Methods[2]
Particle Matter ($PM_{2.5}$ and PM_{10})	Indoor sources: ovens, heaters or stoves, fireplaces, and tobacco smoke. Outdoor anthropogenic sources: combustion processes, industry, and traffic. Outdoor natural sources: dust from sandstorms or sea salt, pollen, or fire ash.	Real-time direct reading instrument; light scattering airborne particle counter
Bioaerosols	Pets, mould, insects, sick occupants, (de)humidifiers or improper air filters (and may be attached to Particle Matter).	Impactor (air sampler directed onto a growth surface intending microbial colony enumeration) or metagenomic techniques
Volatile Organic Compounds (VOCs)		
Formaldehyde	Resins, glues, paints, paper products, cosmetics, electronic equipment, cleaning agents and fabrics. Construction materials such as insulation foams and wooden-based materials in floorings or furniture (note that emissions from some of these materials, e.g., plywood, usually decay within several weeks after installation).	ISO 16000-3, ASTM D5197, NIOSH 2016, EPA TO-11 (or 11A) or EPA Method IP-6 (or 6A).
BTEX	Indoor sources: combustion devices, tobacco smoke, construction materials (polymeric furnishings, carpets, paints, wooden furniture, resins, coatings, and adhesives), cosmetics, cleaning products and pharmaceuticals. Outdoor sources: traffic and industrial activity.	Tenax sorbent followed by thermal desorption and GC-MS or MS-FID as per ISO 16000-6, ASTM D5197 or EPA TO-17
Trichloroethylene	Lubricants, varnishes, paint removers, adhesives and typewriter correction fluids and some bleach household products and other cleaning agents.	
Terpenes	Perfumery products, deodorizers and cleaning products, air fresheners, deodorants, fragrances, and shampoos. Terpenes can also originate from furniture or flooring made from pine wood.	
Volatile Inorganic Compounds (VICs)		
Carbon monoxide (CO)	Indoor sources: defective cooking and heating devices, fireplaces, tobacco smoke and vehicle gases from attached garages. Outdoor sources: dense traffic or high industrialized districts.	Real-time direct reading instruments
Nitrogen oxides (NO_x)	Indoor sources: gas appliances like stoves, ovens or heaters. Outdoor sources: power generation, industries, and traffic.	
Ozone (O_3)	Photocopier machines, laser printers and other electronic devices with high voltage. Outdoor sources: photochemical reactions in the presence of VOC, NO_x and UV light.	
Carbon dioxide (CO_2)	Occupants producing CO_2 as well as fireplaces and some cooking and heating devices.	
Radon	Radon is a radioactive gas that is released through the decay of radium in soils and rocks that may enter indoor air spaces of buildings.	Real-time devices using alpha-particle sensitive material

[1] WHO 2015; Rösch et al. 2014.

[2] International WELL Building Institute, 2019

CO_2 as Indoor Air Contaminant

Because occupants produce CO_2, its concentration in indoor spaces occupied by humans and/or animals is higher than CO_2 concentrations outdoors. Above concentrations of 1,000 ppm_v CO_2 is defined as an indoor air pollutant by the American Society of Heating,

Refrigerating and Air-Conditioning Engineers (ASHREA 2019) and in most green building certification schemes threshold CO_2 concentrations are considered (Wei et al. 2015). With the growing trend of constructing airtight buildings to provide energy consumption savings, the difference in indoor–outdoor CO_2 concentration increases as the ventilation rate per person decreases (i.e., rate of outdoor air supply to an indoor space). Given the current global average outdoor concentration of about 400 ppm_v, CO_2 levels in urban areas can be expected to be higher (Persily 1997) and CO_2 concentrations inside occupied indoor spaces typically vary from outdoor levels up to several thousand ppm_v (Persily et al. 2008). High CO_2 concentrations in office buildings are achieved especially in the afternoons and in meeting rooms where sometime important decisions are made.

Several studies have shown that human performance is directly influenced by CO_2 concentration. Indeed, a decline in workplace productivity and student academic performance have been shown with elevated CO_2 levels (Satish et al. 2012; Bakó-Biró et al. 2004; Seppänen et al. 2006; Shaughnessy et al. 2006). Satish et al. (2012) showed moderate but statistically significant adverse effects of 1,000 ppm_v CO_2 in six out of a nine scales of human decision-making performance and a large reduction in seven scales at 2,500 ppm_v when compared to a baseline level of 600 ppm_v. Two previous studies with only 10 participants showed that they performed proofreading significantly more poorly at CO_2 concentrations of 4,000 ppm_v and marginally but significant differences were recorded at 3,000 ppm_v versus 600 ppm_v. The difference in reading performance was observed in the errors found, not in the reading speed. The quality of sleep is also affected by the CO_2 concentration in the sleeping room, alongside the next day performance (Strøm-Tejsen et al. 2016). In addition, negative symptoms like dry eyes, sore throat, nose congestion (related to the mucous membranes) and drowsiness, short breath, cough, and panting (related to the lower respiratory tract) have been associated with elevated CO_2 levels (Erdmann and Apte 2004).

Although many elevated CO_2 concentrations are the result of insufficient supply of ambient outside air as per current professional standards, even the ventilation rates in the leading ASHRAE standard (ASHREA 2019) can result in CO_2 concentrations higher than 1,000 ppm_v in generously occupied spaces (Satish et al. 2012).

Indoor Air Quality Control Strategies

A comprehensive understanding of indoor air contaminants (type, concentration and variability in space and time) is relevant for the development of effective control strategies both in terms of prevention and active abatement. Prevention should be considered as the first step for improving IAQ and therefore, some measures have recently been implemented to eliminate certain contaminant sources. The European Directive 99/77/EC restricted harmful construction materials (e.g., asbestos) and products containing hazardous components (e.g., halogenated pesticides), and workplaces and public places now commonly ban smoking in many countries. Such control at the source is achievable when sources are known, whereas new hazardous substances are often detected. It is therefore technically difficult and economically prohibitive to completely prevent indoor air contaminants at all times (Guieysse et al. 2008; Luengas et al. 2015). Additionally, increasing concern with greenhouse gas emissions has led many countries to commit to zero energy buildings and to prioritize energy performance during major renovations of existing buildings (European Directive 2010/31/EU). New building design standards such as Passivhaus involve well-insulated and sealed construction,

which removes or reduces natural ventilation, increasing the risk of gas and particulate indoor air contaminants accumulation (Broderick et al. 2017). This conflict between energy efficiency and IAQ standards points to an increased need for development of effective in-situ indoor air purification systems.

Active purification units can be installed to lower or eliminate hazardous levels of indoor air contaminants. Mechanical and electronic filtration as well as adsorption and ozonation comprise most commercially available systems. These physical-chemical technologies have been traditionally installed as portable units or as part of the central heating and ventilation system (Luengas et al. 2015; González-Martín et al. 2021). However, these systems still have multiple drawbacks including being less effective at low concentrations of air contaminants. The simplest and most used method for PM removal is mechanical filtration, which is based on circulating air through a fibrous material that retains particulate contaminants. However, frequent filter replacements are required to maintain the capture efficiency and prevent the re-emission of particulate contaminants. On the other hand, electrical filtration attracts and retains negatively charged particles on a plate of opposite polarity. Unfortunately, by-products such as ions, ozone or other compounds may be generated during electronic filtration (Luengas et al. 2015; Hubbard et al. 2005). Adsorption involves the retention of contaminants on a surface and occurs because all molecules employ attractive forces, especially molecules at the exterior of solid materials (e.g., pore walls of activated carbon), and these surface molecules seek to adhere to other molecules. Regular replacement of adsorbent materials is required to prevent contaminants re-emission and to maintain efficiency levels. Potentially harmful microorganisms can be also accumulated and re-emitted. Finally, electronic ozonization relies on the generation of O_3 from ambient O_2 by high-voltage discharge or UV radiation. However, Luengas et al. (2015) also found that despite the abatement efficiencies of electric ozonisers are superior to other physical-chemical methods, VOCs and VICs can react with O_3 (a strong oxidant) during ozonisation and form hazardous secondary contaminants. In addition, health issues may arise from potentially toxic indoor levels of O_3, which has a typical exposure limit of only 0.1 ppm_v for 8 hours (Luengas et al. 2015; Hubbard et al. 2005; Chen et al. 2005).

2.3 Greenhouse Gases – Methane

The Need for Methane Mitigation

The global economic output (as measured in gross domestic product or GDP) is estimated to double between 2020 and 2040, with greenhouse gas emissions rising by ~ 30% (IEA, 2021). However, even emissions at the current level are already leading to unquestionable environmental changes and global warming **(Figure 2-2)**.

The need for methane mitigation is increasing dramatically as research indicates that methane has greater climatic impact than previously thought (O'Connor et al, 2010) and as global CO_2 mitigation falters. In this context, aggressive methane mitigation is a lower cost means to reduce climate change while the mitigation cost is a function of emission sources (WMO, 2011; Harmsen et al., 2019). Methane is responsible for ~ 30% of the rise in global

temperatures since the Industrial Revolution. Although emissions of methane are much smaller than those of CO_2 by mass, methane is about 28 times more potent than CO_2 per unit mass when averaged over the (most common) 100-year time scale. Over a 20-year time scale, which is relevant to the near-term threat of climate change, methane is 72 times more potent. Reductions in methane emissions are imperative to controlling near-term global warming and improving air quality (Methane Tracker, 2024). "Strong, rapid and sustained reductions in CH_4 emissions would also limit the warming effect resulting from declining aerosol pollution and would improve air quality" (IPCC, 2021).

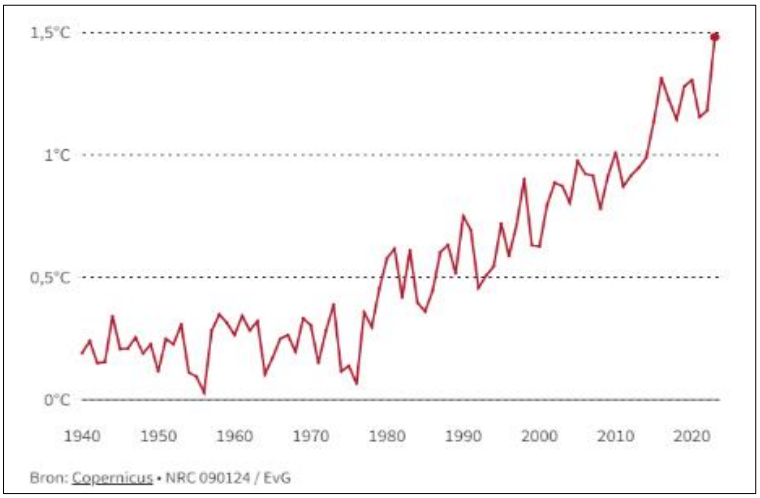


Figure 2-2 Yearly average temperature deviation from the years 1850 and 1900.

The voluntary Global Methane Pledge, launched at COP 26 in November 2021, is supported by about 150 countries and aims to reduce methane emissions from human activity by 30% from 2020 levels by 2030. Some countries have also released national methane action plans and many countries are in the process of doing so. Despite these initiatives, methane emissions are not falling (Methane Tracker, 2024 or World Meteorological Organization, 2023)

Atmospheric methane concentrations have increased from a pre-industrial value of about 715 ppb_v up to 1732 ppb_v in the early 1990s to an average global methane concentration is 1911.8 ± 0.6 ppb_v as of 2022, the highest concentration reported within the last 800,000 years (Myhre et al., 2013).

Methane – Emission Sources

About 60% of global methane emissions are caused by human activities according to the 2021 assessment by the Climate and Clean Air Coalition and the United Nations Environment Programme (CCAC, 2021). The methane emissions vary largely in emission rate and are emitted from various industries and sectors, of which the following are major contributors:

- fossil fuels (35%), where the oil and gas industry accounts for 23%, and coal mining for 12%.
- waste (20%), mainly landfills and wastewater, and
- agriculture (40%), where manure and enteric fermentation represent 32%, and rice cultivation represents 8%.

The largest sources of emissions are natural gas and oil systems and enteric fermentation. Methane emissions from natural gas and oil systems are the result of system leaks, inefficiencies, and process upsets, while methane emissions from enteric fermentation refers to methane formation (methanogenesis) in the guts of ruminant livestock (cattle, goats, sheep).

The difference between the emission sources related to anthropogenic activities and natural sources is not clear, as they are interrelated because land-use changes and climate change influence emissions from natural wetland system. Activities that contribute to methane emissions all essentially operate by one of three mechanisms:

- *Creation of conditions for methanogenesis (app. 60%)*

  The biological formation of methane leads to emissions from enteric fermentation, rice cultivation, landfills, manure, wastewater treatment, and agricultural soils.
- *Extraction and release of fossil methane (app. 30%)*

  The extraction and release of fossil methane includes leaks and venting during extraction and distribution of oil and natural gas, and from coal mining. The leakage from natural gas systems is expected to grow due to the fast growth of natural gas extraction from shale formations, which tend to be leakier than conventional gas extraction.
- *Release of products of incomplete combustion (app. 9%)*

  The release of products of incomplete combustion includes emissions from stationary and mobile combustion of fossil fuel, biomass burning at small scale for cooking (primarily in the developing world) and several sources included prescribed burning of savannas, burning of forests for clearing, and field burning of agricultural wastes.

Anaerobic digestion for the conversion of organic waste to energy has significantly expanded over the last decades but unfortunately results in liquid effluents containing a substantial amount of dissolved methane (Gloria et al., 2016). The release of methane from the liquid effluent (about 20 g CH_4 m^{-3} from sludge digested at 30 °C) may hinder the wider acceptance of anaerobic digestion in the near future and require control as part of controlling greenhouse gas emissions in sewage treatment plants (STPs) now-a-days called water resource recovery facilities (WRRFs). Modern landfills are equipped with covers including a compacted clay layer and a membrane liner to minimize leachate production and protect groundwater resources. They are equipped with a gas collection system and atmospheric vents with some of the largest landfills provided with energy recovery systems. However, as the amount of methane generated from the landfill decreases over time, the efficiency of the energy recovery system is limited to the first years after covering the landfill.

Some of the sources are confined, where the gas is physically contained or in a managed flow, while other sources are unconfined, where the gas is emitted over an area of land or water. **Table 2-2** shows methane concentrations for some major sources emitting methane. Examples of dilute methane emissions are the emission from landfills (0–20% v/v), from ventilated coal mines (0.1–1% v/v), from liquid manure storage tanks (0–3% v/v), or

animal houses (0-0.015% v/v) (BCME, 2010; Limbri et al., 2013; Huang et al., 2011; Melse and van der Werf, 2005).

Table 2-2 Methane concentrations at major emission sources (Stolaroff et al, 2012).

Source	Methane concentration
Ambient air (current average)	1.9 ppm_v
Arctic air	2 – 8 ppm_v
Urban air	2 – 10 ppm_v
Cattle feedlot, open	2 – 10 ppm_v
Swine feeding or dairy milking ventilation air	10 – 300 ppm_v
Enclosed manure storage headspace	140 – 28,000 ppm_v
U.S. landfill, at surface	< 500 ppm_v by regulation
Coal mine ventilation gas (VAM)	0.1 – 1 % typical, < 1 % by regulation
Anaerobic digester gas	35 - 65%
Landfill drainage gas	40 – 60 % at peak production
Coal post-mining drainage gas	30 – 95%
Coal pre-mining drainage gas	60 – 95%
Natural gas, at wellhead	75 – 99%

Methane – Mitigation Measures

The burning need to reduce methane emissions worldwide requires the research and development of cost-effective and sustainable methane abatement techniques. Different measures for mitigation of methane waste gas emissions are discussed in this section. Modern waste reduction strategies follow the "Reduce, Reuse, Recycle" hierarchy, with nowadays the fourth component Rethink added. Applied to methane emissions management, methane formation should be prevented or reconsidered when it can't be used for energy generation. When formed, methane should be prevented from escaping, and when escape is inevitable, then conversion should be considered. Examples of these measures are as follows:

- *Prevent formation of methane:*
    - Ventilation air methane (VAM) emitted from mines can be reduced by increasing drainage during pre-operating stage and utilizing the drainage gas.
    - Landfill emissions can be reduced by separating household waste and processing it separately (e.g., divert organic waste for anaerobic digestion and paper for recycling).
    - The biomass burning at small scale for cooking (primarily in the developing world), which accounts for about 3% of the total global methane emission, can be controlled through the use of more efficient cooking stoves or switching to different fuels.
    - The emissions through enteric fermentation can be reduced by consuming less meat and can also be slightly reduced by changing the diet of cattle, and by vaccines, and animal selection (Hristov et al., 2013).
    - The methane formed from organic matter by biological conversion (methanogenesis) can be reduced by limiting the biological process (e.g.,

keeping a landfill relatively dry, periodically drain rice patches or aerate agricultural soils in general). In addition, biocides were found to reduce methanogenic conversions in soil as well as in the guts of cattle, although this effect was generally temporary.
    - Cooling has shown to be moderately effective when used for manure collected under animal houses.
- *Prevent escape of methane:*
    - Natural gas leaks and venting can be reduced by ensuring that equipment is properly operated and frequently calibrated and tested.
    - Emissions from landfills or manure ponds can be reduced by placing a cap over them.
- *Convert methane to less harmful components:*
    - Manure ponds can be upgraded to anaerobic digesters and promote methanogenesis and utilise the methane for energy.
    - Stimulating biological oxidation (methanotrophic conversion) by aeration (e.g., turning composting piles at composting facilities).
    - Apply engineered bio-covers on landfills to capture and oxidize methane before it emits into the atmosphere.
    - Use abatement technologies to treat methane.

When methane is completely oxidized to carbon dioxide, the contribution to global warming is significantly reduced. About 90% of the impact on the greenhouse effect is reduced when methane is converted to CO_2 as methane is considered about 25 times more potent on mass basis, but only 9 times more potent on a molar basis. The difficulty is that dilute methane contained in ventilation gases from many sources like mines, landfills, livestock and chemical plants is often too lean for self-sustaining combustion. Abatement of methane emissions is possible by direct combustion as long as the minimum concentration is 20% (v/v) or 130 g m^{-3} (Haubrichs and Widmann, 2006). As more than 55% of anthropogenic methane emissions have a concentration below the lower explosive limit of methane in air mixtures of 5% v/v, they are incompatible for energy recovery or for chemical oxidation processes devoted to the removal of methane. Most technologies are therefore not economically viable when the methane concentration is below 5% v/v (Pecorini and Iannelli, 2020). For example, activated carbon filtration is not suitable because of the low affinity of methane for the adsorbents. Recent advances in catalytic chemistry may provide opportunities and could result in new application to treat dilute methane but are still premature (Pratt et al., 2018).

3. BIOLOGICAL GAS TREATMENT METHODS

Chapter overview

Biological gas treatment methods are increasingly used for air pollution control and gas purification processes as they are considered a more sustainable alternative to traditional physical-chemical gas treatment methods. They are considered a 'green' technology because of the relatively low carbon footprint without the continuous input of resources such as harsh chemicals, adsorbents, or combustion fuel. Biological gas treatment is generally also safe as it is operated at ambient pressure and temperature, does not involve a concentration step with risk of smouldering or fire, and eliminates health and safety risks associated with the storage and handling of chemicals.

However, the wider application of biological gas treatment methods to replace less sustainable physical-chemical methods requires improvements to overcome limitations related to especially bioavailability, particularly for gaseous streams containing hydrophobic contaminants. In this chapter the existing biological methods of air treatment are discussed with the focus on two application areas characterized by its treatment hampered by bioavailability limitations due to hydrophobic compounds present at relatively low concentrations: indoor air quality and dilute methane abatement.

3.1 Biological Gas Treatment Processes

Introduction

Efforts to improve air quality, reduce GHG emissions, and change from energy- and resource-intensive production processes to low-emission, high energy and resource efficient alternatives have become compulsory and will require our focus for at least several decades into the future. Industrial, agricultural, and municipal waste gas emissions have to be reduced, and production processes have to be more sustainable through energy and resource-efficient technologies. Biological gas treatment processes already meet the more sustainable requirements to contribute to these efforts but show limitations in various areas that need to be overcome to expand their applicability.

Biological gas treatment can be defined as the transformation of gaseous compounds to less harmful or more valuable products through the action of microorganisms before utilization or cleaning before atmospheric release (Kennes and Veiga, 2013). Biological gas purification processes are widely diverse as microorganisms, like most life forms, possess unique biological and biochemical features. The biotransformation and/or mineralization processes typically take place in the presence of oxygen under aerobic conditions but can also take place under anoxic or anaerobic conditions (e.g., anoxic biogas desulfurization using nitrate, anaerobic degradation of chlorine compounds, gas-phase methanol coupled to thiosulphate reduction to produce valuable volatile fatty acids, or conversion of syngas and biogas into commercial products such as fuels and bio-based chemicals).

The bioconversion of gaseous compounds takes place by either pure strains or mixed microbial communities, primarily bacteria, the catalyst of this process thriving typically in a complex ecosystem. The microorganisms are mostly embedded in a biofilm, a slimy film that adheres to a surface and protects the microorganisms from extreme or changing conditions and enhances communication among them. The mixed microflora living in the biofilm consists of pollutant degraders, competitors and predators, which usually have significantly different properties from free-floating bacteria of the same species, such as for example, an increased resistance to extreme contaminant concentrations. It can be expected that organic and inorganic compounds that form biomass are slowly released and turned over in the biofilm, including materials from dead cells being re-used by growing cells and higher organisms (**Figure 3-1**).

Two processes are occurring simultaneously in typical biological gas treatment systems. The first step is the mass-transfer from the gas phase to the liquid phase containing the microorganisms, which is highly dependent on the gaseous compound solubility in the liquid (which is a function of Henry's law gas constant). Once the gaseous compounds are transferred to the microorganisms, the second step, biological conversion of the compound, can occur. These processes of mass-transfer and biological conversion occur almost instantaneously within a bioreactor treating gaseous compounds.

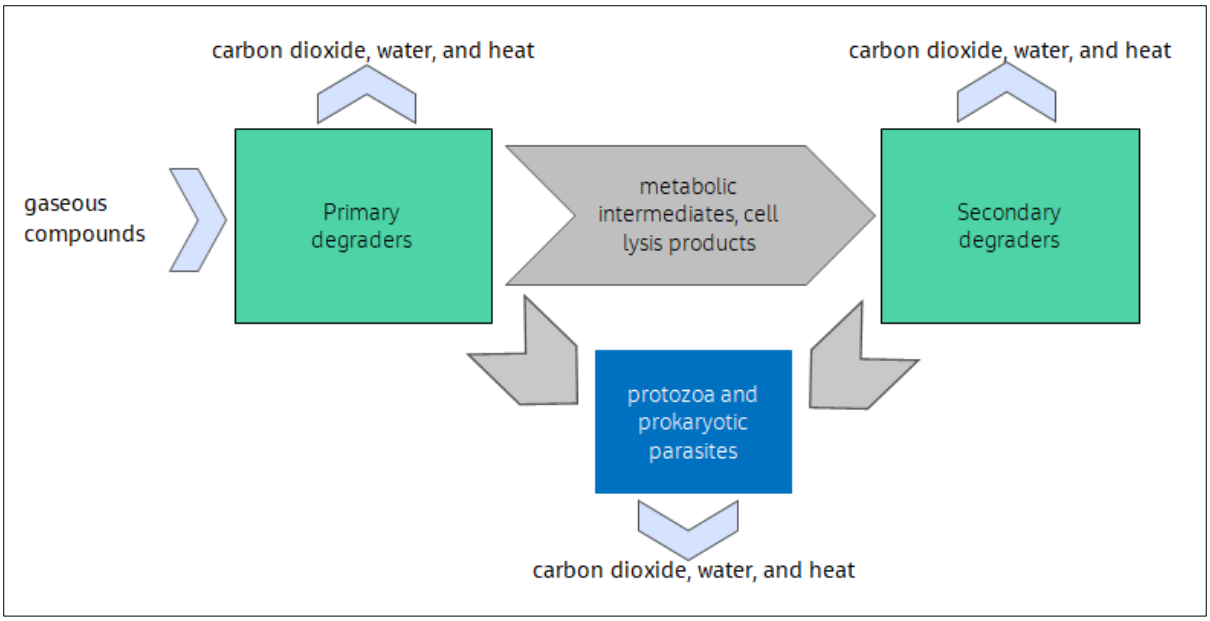


Figure 3-1 Typical bioconversion process in an aerobic biological gaseous treatment system.

Biological Gas Purification Techniques

The treatment of gaseous waste streams or the recovery of gaseous resources using biotechnologies has gained acceptance as a cost effective and sustainable alternative compared to conventional techniques such as chemical scrubbing, incineration, and adsorption. It is considered a 'greener' technology because of its relative low carbon footprint and relatively low operating costs as it operates without the continuous input of resources such as harsh chemicals, adsorbents, or combustion fuel. In addition, biological gas treatment is generally safe as it is operated at ambient pressure and temperatures, does not involve a concentration step with risk of smouldering or fire, and eliminates health and safety risks associated with the storage and handling of chemicals.

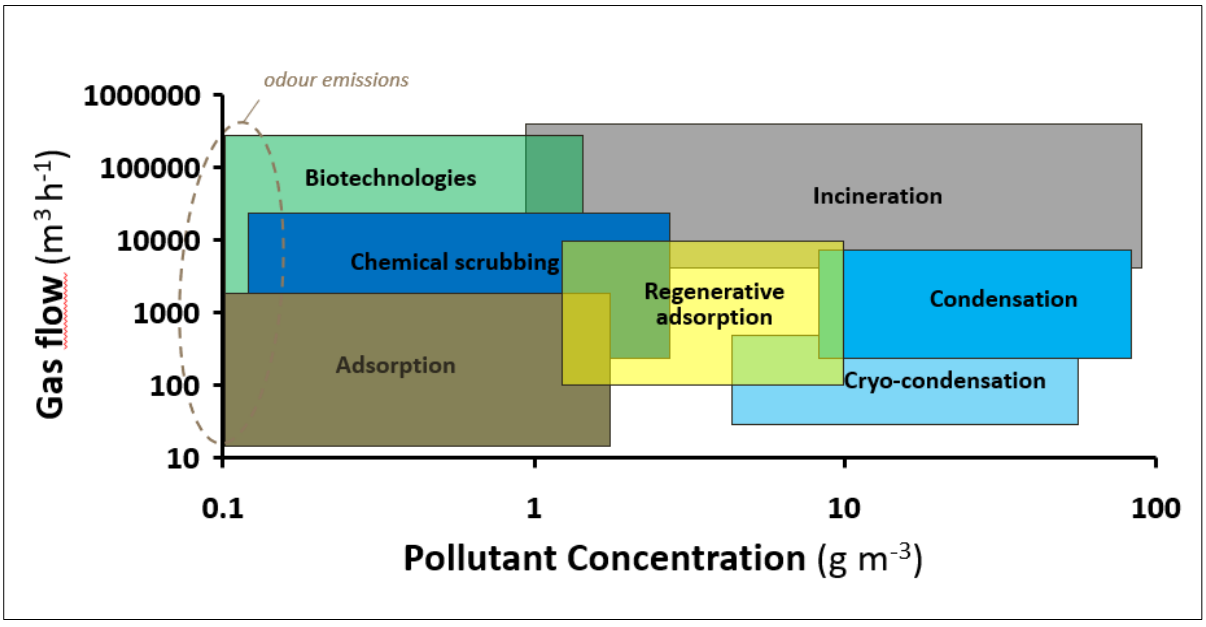


Figure 3-2 Typical application range of gas treatment technologies (adapted from van Groenenstijn en Hesselink, 1999).

Figure 3-2 illustrates the typical application range of gas treatment technologies when gas flow rate and gaseous compound concentration are considered only. Adsorption processes (mainly activated carbon filtration) and thermal oxidative processes (incineration) strongly dominate the field of industrial applications but require typically a constant input of resources (i.e., combustion fuel, adsorbents) making them less sustainable. Moreover, thermal oxidative processes lead to high GHG emissions: carbon dioxide, methane slip and nitrous oxide (which has a considerable greenhouse potential and known to be formed during thermal oxidative processes).

Today, biological processes are available for the treatment of industrial, agricultural, and municipal (waste) gas emissions, and are sometimes combined with non-biological processes. Biological processes have shown to be an economical and more sustainable alternative to conventional gas treatment technologies in many application fields (Soreanu and Dumont, 2020; Dobslaw and Ortlinghaus, 2020; Kraakman et al., 2014; Kennes and Veiga, 2013; van Groenenstijn and Kraakman, 2005; Kraakman and de Waal, 2006; Estrada et al., 2013; Gabriel and Deshusses, 2004). **Figures 3-3** to **3-7** shows some examples of full-scale biological gas treatment systems applied in different industries where the PhD candidate has been involved over the past years. The research and development of innovative bioprocesses for gas treatment and their implementation is ongoing in a broader range of applications. Low-emission gas treatment technologies that are both energy and resource efficient could be mandated in the near future to help meet future needs of upgrading gaseous streams (e.g., biogas) and/or reducing air pollution (e.g., industrial waste gas or dilute methane emissions) and could further stimulate the acceptance and the implementation of bioprocesses for gas treatment.

Figure 3-3 An industrial biotrickling system treating 126,000 m^3 h^{-1} of foul air from a large sewage interceptor system (courtesy of Melbourne Water, Melbourne, Australia).

Figure 3-4 An industrial biological system purifying 51,000 m^3 h^{-1} of waste gas from a viscose processing facility and recycling sulfuric acid back to the facility production process (courtesy of 3M, Elyria, OH, USA).

Figure 3-5 An industrial biological system treating 35,500 m^3 h^{-1} of foul air from stripped groundwater at a food processing facility (courtesy of Budweiser, Jacksonville, FL, USA).

Figure 3-6 A bioscrubber type system to clean biogas and generate a high value gas for energy generation (courtesy of Gippsland Water, Gippsland, Australia)

Figure 3-7 An industrial biotrickling system treating 47,600 m^3 h^{-1} of waste gas from a water resource recovery facility (courtesy of JEA, Jacksonville, FL, USA).

Biological gas treatment techniques are traditionally classified as biofilters, bioscrubbers and biotrickling filters (Kennes and Veiga, 2013). Biofilters are systems where the microorganisms are immobilized on the biofilter media and maintained moist through intermittent irrigation. Bioscrubbers are traditionally defined as two reactor-units with liquid recirculating between them. In the first reactor-unit, contaminants are absorbed from the gas-phase in the liquid phase through mass-transfer. In the second unit, the contaminants are converted by microorganisms suspended in the liquid (water suspended growth biomass). Biotrickling filters are defined as reactor-units with a packing through which water is trickled, and where the absorption of contaminants from the gas-phase to the liquid-phase and degradation of the contaminants take place in the same unit where microorganisms are mostly immobilized on the packing (fixed-film biomass). The mobile liquid phase in bioscrubbers and biotrickling filters provide benefits to better control relevant liquid process conditions such as pH, salt-content, nutrient concentrations, and biofilm moisture as well as prevent accumulation of toxic metabolites and intermediate compounds produced during biodegradation. Moreover, a humid environment can be better maintained as it is a necessity to the growth and reproduction of microorganisms, especially bacteria.

Most traditional biological gas treatment techniques use a structure (packing media) to maximise the gas-liquid contact area. They may be considered laminar gas-liquid contactors because mass transfer takes place mostly through diffusion – the random Brownian motion of individual compounds in a medium. Examples of more recently proposed and partly developed concepts of biological gas treatment are:

- Rotating contactors (Padhi and Gokhale, 2016; Datta and Philip, 2014; Von Rohr and Ruediger, 2001)
- Membrane bioreactors (Wu et al., 2024; Lebrero et al., 2013; Kumar et al., 2008; Kraakman et al., 2007)
- Airlift bioreactors (Guieysse et al., 2011)
- Stirring tank bioreactors (Roche Rios et al., 2009)
- Foam bioreactors (Kan and Deshusses, 2003)

- Two-phase partitioning bioreactors (Munoz et al, 2012)
- Capillary bioreactors (Kreutzer et al., 2005; Rocha Rios et al., 2013; Lopez De Leon et al., 2023)

Combined reactors or reactor stages optimized to maximize the biocatalytic activity of different microorganisms have been developed to treat a potentially broader range of compounds more effectively. This is because contaminated gaseous streams nearly always contain a mixture of many chemical compounds. These many compounds usually have different chemical properties as can be seen from, for example, their water solubility and their biodegradability. Multiple degradation zones are typically required for the simultaneous removal of gaseous mixture of compounds with different chemical groups. A preferential degradation can be expected for certain (often hydrophilic and relatively small) compounds over other (often hydrophobic or more complex) compounds that are less bioavailable (Zehraoui and Sorial, 2015; Myung Cha, 1999). A variety of microorganisms is usually required and different environmental conditions for the microorganisms are preferred. Using different stages or reactors optimized for the different microorganisms, a potentially broader range of compounds can be degraded in the bioreactor system more effectively. For example, a biotrickling filtration process with 'once-through' irrigation establishes different microbial consortia along the height of the packing bed and would be more suitable for treating gaseous mixture of compounds with different chemical groups than a bioscrubbers with continuous recirculation with mainly homogeneous conditions throughout the reactor (Kraakman, 2008).

3.2 Biological Systems for Improving Indoor Air Quality

Biological Processes Relevant to Biological Indoor Air Purification

There is currently no single physical-chemical technology able to remove all indoor air pollutants in a cost-effective way, which might provide opportunities for bioprocesses. The large variability in type and concentration of indoor air pollutants, because of the periodic occurrence of pollution events (cleaning/polishing, use of air fresheners, cooking, painting, smoking, etc.) and the random introduction of new pollution sources such as new electronic devices, furniture, etc., requires treatment using microorganisms with a large functional versatility and robustness. In this context, metabolically versatile large-genome microorganisms should play a key role on biological indoor air treatment. The large genome of these microorganisms includes many accessory genes encoding active substrate transport, environmental sensing, multiple catabolism, stress response and secondary metabolisms, which confers them with the ability to carry out many non-essential activities related to substrate accession and stress response. These properties are critical to colonize and survive in complex and variable environments (Guieysse and Wuertz 2012). The size of the genome is typically a respectable indicator of metabolic adaptability in bacteria, since the genome of prokaryotes holds a low quantity of non-coding genes, and its coding density is rather constant. Bacteria with a genome size > 5 mega-base-pairs (Mbp) are often considered large-genome microorganisms, which correspond typically to aerobic mesophilic bacteria. Large genomes typically host a large and effective portfolio of enzymes capable of sensing, accessing and

simultaneously metabolizing a broad range of pollutants at trace level concentrations (µg L^{-1} - ng L^{-1}), which would be particularly relevant for indoor air treatment.

Biological Based System Design Configurations

Indoor applications are often limited by the size of the indoor air purifier. Plant-based (botanical) biofiltration has received recently increased attention due to its economic, environmental, and social benefits, including psychological impacts of botanical plants in an indoor space. The relatively large air purifier to room volume ratio typically required for current botanical indoor air systems restrains the development and implementation of biological air purification systems (Guieysse et al. 2008). Therefore, the design of compact indoor air purifiers with high effectiveness is a challenge for biological based systems to establish a healthy indoor environment, which requires a more complete treatment of air; that is not only VOCs, but all other pollutants including CO_2, PM, CO, and NO_x. Different bioreactor design configurations or combinations of different biological treatment approaches (**Figure 3-8**) may overcome this constraint, and potentially other challenges such as mass transfer limitations, bioavailability, guaranteed microbial safety, control of indoor air relative humidity, and CO_2-removal, while being simple and robust enough to provide long-term sustainable economic functionality with minimal maintenance.

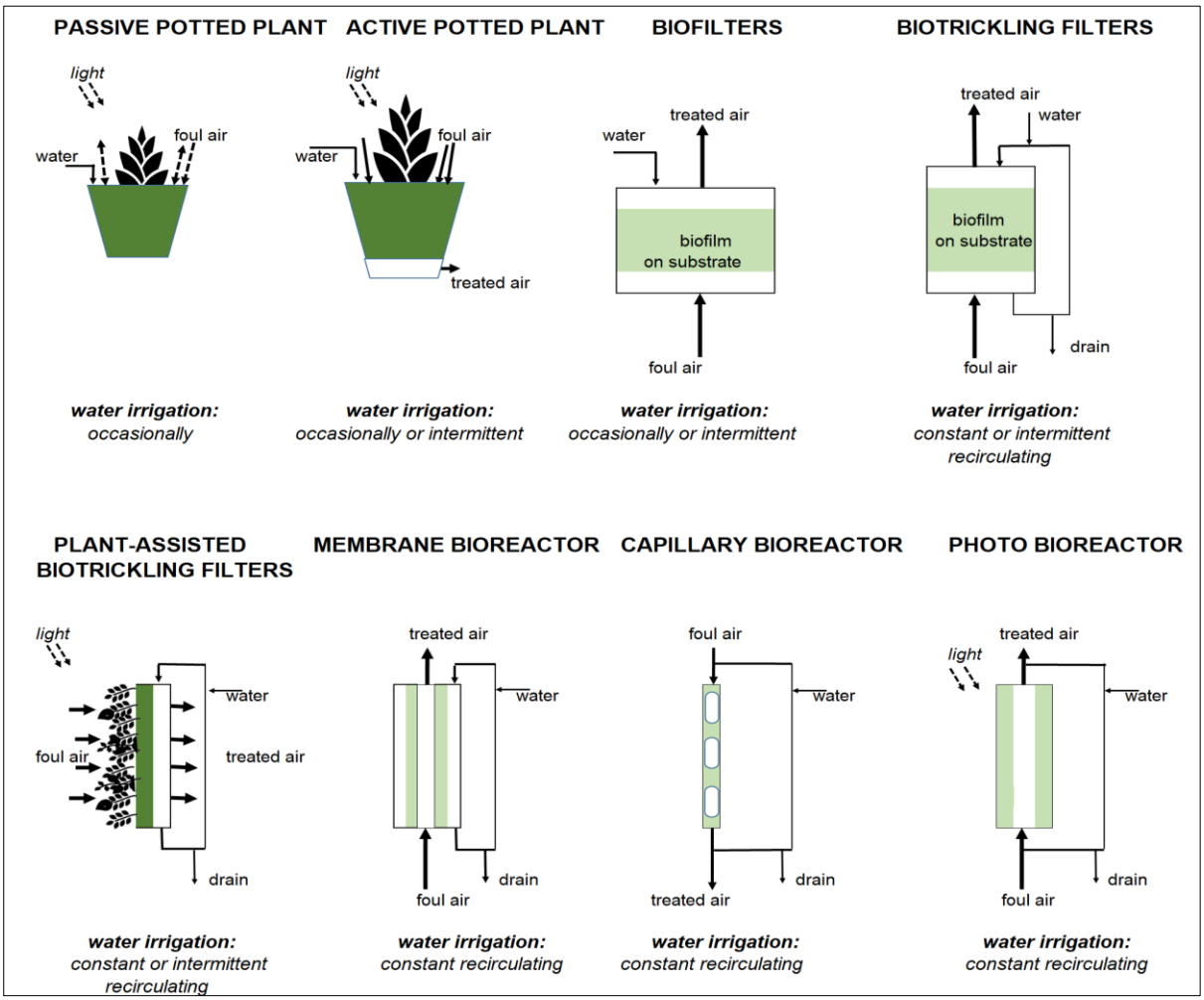


Figure 3-8 Process schematics of typical biological air treatment system design configurations.

An overview of biological system studies for indoor air purification is provided in **Table 3-1**. The treatment of pollutants using plants (phytoremediation) is mature and often applied for remediation of contaminated soil and water polluted with organic pollutants such as hydrocarbons. Biotreatment of indoor air using potted plants has been extensively investigated and all plants tested were shown to be capable of removing VOCs from indoor air (Wolverton 1997; Wood et al. 2006; Liu et al. 2007; Yang et al. 2009; Irga et al. 2013; Pacheco-Torgal et al. 2015). A comprehensive overview of the research on botanical plants related to indoor air quality is provided by Irga et al. (2018). While potted plants are considered passive systems that depend on the diffusion of pollutants (relatively slow for the indoor air pollutant low concentrations, especially in spaces without forced air circulation), active biotreatment systems use active ventilation (fans) to improve the removal capacity. Plant-based biotrickling filters (PBTFs) are active biotreatment systems containing hydroponic plants growing in vertical panels that eliminate maintenance difficulty related to potted plants in soil as further discussed by Soreanu et al. (2013). Although some VOCs present in indoor air can directly be taken up and further metabolised by plants, the VOCs are more extensively removed by microorganism present in the rhizosphere around the roots of the plants (Pacheco-Torgal et al. 2015) and on the plant leaves (James et al., 2024). However, the removal of carbon dioxide, sulfur dioxide, nitrogen dioxide and ozone appear to be partially or solely plant facilitated (Fikiey et al. 1981; Pacheco-Torgal et al. 2015; Oh et al. 2011; Torpy et al. 2014a). These VICs are generally taken up by the plant stomates (gaseous compound exchange pores) during daylight hours (Pacheco-Torgal et al. 2015).

Examples of Bio-based Indoor Air Purification Systems

The market of biological purification systems for improving indoor air quality is rapidly expanding, but only a few commercially available plant-based systems have proven to achieve high and long-term removal efficiency for relevant VOCs such as formaldehyde (Torpy et al. 2014b). Green walls are not necessarily installed to control the indoor air quality but are an illustration of interior landscaping and are popular in office buildings mostly because they enhance the aesthetics and may help align company brands with dedication to sustainability. **Figure 3-9a** shows an example of an aesthetic green wall consisting of moss requiring no extra light or regular watering while adsorbing sound (Ambius 2020). The availability of multiple design concepts using botanical and microbial approaches is clearly promising and deserves to be further investigated. Different system types have been developed, ranging from personal mobile air purifiers (Andrea 2020), as shown in **Figure 3-9b**, to larger building air purifiers fully integrated with the HVAC system of building, as shown in **Figure 3-9c**, where air is circulated through a vertical green wall consisting of plants in a porous rooting material (Nedlaw Living Walls 2020).

Table 3-1 Overview of biological system studies for indoor air purification.

System design	Airflow	Synopsis of results	References
Potted Plant	Passive	VOC removal capacity has successfully been tested for about 200 plant species in about 50 studies. The most popular VOCs investigated were BTEX and formaldehyde, but some studies included acrylonitrile, trichloroethylene, methanol, ethylhexanol, octane and α-pinene. Typically, 10-20% TVOC removal has been recorded within one hour for a plant in a 10 L gastight glass jar.	(Chen et al., 2024; Irga et al. 2018; Wolverton 1997; Wood et al. 2006 ; Yoneyama et al. 2002; Liu et al. 2007; Yang et al. 2009; Irga et al. 2013; Soreanu et al. 2013)
	Passive	Ultrafine particle (PM) reduction is illustrated for nearly all plant species tested. The plant foliage density as well as tree architecture seems most relevant enabling a small (11%), yet statistically significant hydrophobic and hydrophilic PM reduction in homes.	(Stapleton and Ruiz-Rudolph 2018; Weerakkody et al. 2017)
	Passive	VIC removal capacity has been proven for CO_2, SO_x, NO_x, CO, and O_3, although NO_x removal may negatively affect plant health.	(Montaluisa-Mantilla, et al., 2023; Fikiey et al. 1981; Pacheco-Torgal et al. 2015)
	Active	Enhances the flow of pollutants to the root zone compared to passive systems, increasing the VOC and PM removal capacity. Among them ~ 50% removal of $PM_{2.5}$ and $PM_{10.}$	(Lohr and Pearson-Mims 1996; Liu et al. 2007; Wang and Zhang 2011; Irga et al. 2017a; Treesubsuntorn and Thiravetyan 2018)
Plant-assisted Biotrickling Filter	Active	VOC removal (10 – 75% in a single-pass configuration) proven for BTEX, methylethylketone, formaldehyde, acetone, octane, α-pinene, decane, ethylacetate and ethylhexanol.	(Darlington and Dixon 1999; Darlington et al. 2001; Llewellyn et al. 2002; Llewellyn and Dixon 2011; Mikkonen et al. 2018; Irga et al. 2019)
Biofilter	Active	The removal of multiple typical indoor air pollutants such as toluene and formaldehyde was shown to be > 90% in a single-pass configuration. A mixture of 71 VOCs was tested in a biofilter inoculated with yeasts with most compounds removed.	(Ondarts et al. 2012; Prenafeta-Boldú et al. 2019)
Biotrickling Filter	Active	Formaldehyde and BTEX effectively reduced (respectively, 100% and 65-93%) in a single-pass configuration.	(Lu et al. 2010)
Membrane Bioreactor	Active	Experiments performed with both microporous and dense-phase membranes provided a proof of concept for different VOCs and odorous compounds.	Van Ras 2005; Lebrero et al. 2013)
Capillary Bioreactor	Active	High removal rates (13 or 17 times greater than those tested biotrickling filters) of methanol and toluene were obtained. Mass transfer capacity was investigated with methane as model compound showing removal > 100 g m^{-3} capillary channel h^{-1}.	(López De León et al. 2019; Rocha-Rios et al. 2013)
Photo-Bioreactor	Active	CO_2 reduction up to 95% was proven alongside with the significant removal of VOCs, NO_x and NH_3.	(Soreanu and Dumont 2020)

Maintaining optimal moisture control is critical and automated moistening when a fan pulls air through the plant root zone would be important as incorporated by Phytofilter in their active potted plant air purifier system (Phytofilter 2020). Remote monitoring using sensors

and management performing plant care including providing water, light and ventilation may be used to facilitate the management of active green walls in its specific building environment. These basic functions may be combined with a series of critical conditions such as temperature and relative humidity (RH), as well as carbon dioxide and certain VOCs as proposed and tested by Liu and colleagues (2018). Biological air purification is considered a 'green' technology that can boost the eco-efficiency of smart-buildings and bring extra advantages to aesthetics and Indoor Environmental Quality (IEQ). However, hybrid systems still need to be developed for a completer and more compact biotreatment of indoor air; and that is not only VOCs, but all other pollutants including CO_2, PM, CO, and NO_x, while maintaining microbial safety and eliminating elevated indoor air relative humidity, so that it can fully contribute to a better indoor air quality.

Figure 3-9 Examples of commercially available plant-based systems for indoor environments: (a) an aesthetic passive moss wall (courtesy of Ambius), (b) an active potted plant (courtesy of Andrea) and (c) a vertical active green wall integrated with the building HVAC system (courtesy of Nedlaw Living Walls).

3.3 Biological System for the Abatement of Dilute Methane

Methanotrophic Microorganisms Relevant to Dilute Methane Treatment

Older studies on methane biofiltration have tended to concentrate on abiotic factors such as packing material, temperature, inlet loading rate, pH, nutrient loading rates (Melse and van der Werf, 2005; Nikiema et al., 2009). However, more recently, research on methane biofiltration has increasingly considered the microbial communities in these biofilters (Lopez et al., 2013; Pratt and Tate, 2018; Ahmadi et al., 2024). This is because it has been noted that the biofilter performance and stability is linked to the microbial community structure (Kim et al., 2014a; Syed et al., 2017).

Methanotrophs are Proteobacteria, which are a major (about a third of all bacteria) diverse group of gram-negative bacteria. Gram negative bacteria have a relatively thin cell wall (containing peptidoglycan) and a second outer membrane (containing lipopolysaccharides) surrounding the cell. Proteobacteria have the unique biochemical characteristic of possessing an extreme diversity of energy-generating mechanisms.

Methanotrophs are found in diverse environments and different species are adapted to widely different ranges of temperature, pH, salinity, and nutrient status. Aerobic methanotrophs are often found at the oxic/anoxic boundaries of environments where organic material is biodegraded anaerobically into methane. Methanotrophs are able to metabolize methane as their only source of carbon and energy. They can grow aerobically or anaerobically and require single-carbon compounds to survive. Under aerobic conditions, they combine oxygen and methane to form methanol using the mono-oxygenase enzymatic reaction and using a methanol dehydrogenase enzymatic reaction to form formaldehyde, which is then incorporated into organic compounds. For a systematic and comprehensive overview of basic aspects of Methanotrophs see *Microbiology Monographs Volume 32 Methanotroph: Microbiological Fundamentals and Biotechnological Application* (Microbiology Monographs Volume 32, 2019).

All methanotrophs have the enzyme methane monooxygenase (MMO), which catalyses methane oxidation to methanol that starts a series of biochemical oxidation reactions that ultimately produces CO_2 and H_2O. The methane degradation pathway to carbon dioxide is similar for all methanotrophs. Firstly, MMO catalyses the reaction between a single oxygen atom from oxygen and methane to form methanol. Secondly, methanol is oxidized to formaldehyde by methanol dehydrogenase, which is further oxidized to formate through various intermediates. Finally, formate is oxidised to carbon dioxide by formate dehydrogenase. MMO exists in soluble and particulate forms with most methanotrophs able to express pMMO, while sMMO is expressed only by a limited number of strains and in the strict absence of copper (Dalton, 1991). The particulate or membrane bound methane monooxygenase (pMMO) can be produced by all methanotrophs and has shown to exhibit significantly higher affinities (higher reaction rates at lower methane concentrations, as expressed by its lower half-saturation constant (K_s), and higher conversion rate (as expressed by the pseudo-first order-rate constant values V_{max} and K_s) (Yoon and Semrau, 2008; Yoon, 2009). pMMO contains copper and has shown to be very sensitive to oxygen (Nguyen et al., 1998).

Methanotrophs are classified into three types (I, II and X) with the main difference in the pathway used for formaldehyde assimilation: Type I use the ribulose monophosphate

pathway, Type II use the serine pathway and Type X primarily use the ribulose monophosphate pathway but also can also use the serine pathway (Hanson and Hanson, 1996). Type I methanotrophs dominate in methane-poor/oxygen-rich environments, whereas Type II methanotrophs typically dominate in methane-rich/oxygen poor environments. No specific methanotroph type has shown notably higher methane oxidation capability among all methanotroph types (Strong et al., 2015). The growth of both type I methanotrophs (*Methylomonas* and *Methylobacter*) and type II methanotrophs (*Methylocystis* and *Methylosinus*) have been identified in traditional biofilter treating methane. It is now known that type I and type X are gamma-proteobacteria and type II are alphaproteobacteria (Semrau et al., 2011). Methane-oxidizing microorganisms are typically obligate methanotrophs, able to use only C1 compounds (like methane, methanol, formaldehyde). However, some examples of type II methanotrophs are able to grow on a selection of compounds with C – C bonds and are therefore called facultative (Semrau et al., 2011).

Inhibition of methanotrophic bacteria by the intermediates of the oxidation of methane (methanol, formaldehyde, and formate) has been observed at relatively low methane concentrations (Hanson and Hanson, 1996). The sensitivity of methanotrophs to product toxicity can be a limitation. Ammonium has also shown to be able to significantly reduce the methane oxidation rate although the sensitivity toward ammonium varies extensively among methanotrophs. This inhibition can be either the result of competitive inhibition of MMO by ammonium (during methane biofiltration, methanotrophic activity is diverted towards the nitrification of ammonium) or the result of inhibition by the products of ammonium oxidation (hydroxylamine and nitrite) (Nyerges and Stein 2009; Veillette et al. 2011). Methanotrophic inhibition could also be caused by acidification by nitrifying bacteria (Hernandez et al., 2015). However, nitrogen is an important macronutrient because it makes up about 10 to 14 % (w/w) of a dry cell basis, and increasing nitrogen concentrations as sodium nitrate has shown to stimulate the methane oxidizing biofilter performances (Girard et al., 2011).

Temperature has been demonstrated as an important parameter affecting methane oxidation rate. Methanotrophs are in general mesophilic, with 25 to 35 °C as their optimal temperature, although thermophiles and psychrophiles have also been discovered (Dunfield, 2009; Hernandez et al., 2015). They require a neutral pH ~ 7 (Heyer et al., 2005), while too high salinity (> 6 mS/cm) has been shown to be detrimental to methane oxidation (La et al., 2018). Methanotrophs have shown to have a wide range in substrate affinity with the apparent half-saturation constants (K_s) values to methane ranging from about 0.01 to 100 µM, which means they can consume a broad range of methane concentrations down to trace levels of atmospheric concentrations of < 1.8 ppm_v (La et al., 2018).

Examples Bio-based Methane Treatment Systems

The most applied example of a bio-based system treating methane is a bio-cover (BC) applied as landfill cover. It is a passively aerated system to control low-volume point-source methane emissions at landfills. There is an increased research focus on the development of low-cost technologies that limit landfill methane containing gas release from sites where gas collection systems have not been implemented because they are not economically feasible.

Compost based bio-cover systems offer an excellent methane oxidation potential of 100%, but only ~ 35 to 60% removal is typically measured in field systems (Dever et al., 2011, Chanton et al., 2011, Fjelsted et al., 2020). The passively aerated bio-covers are typically

unable to use the full potential of the active layer of the cover because it requires oxygen to penetrate through the top surface into the bio-cover layer creating zones of low or depleted oxygen levels.

Sustaining the microbial methane oxidation in landfill covers is vital and mainly depends on diffusive ingress of atmospheric oxygen into the bio-cover as well as moisture and texture levels (Huber-Humer et al, 2011). Its longevity and effectiveness can be enhanced with more engineered bio-covers, especially to enhance oxygen availability, maintain proper moisture content and preserve structural integrity of the active layer. Biological filtration used for methane mitigation from landfills has been applied frequently, but development is still ongoing to improve long-term operation (Fjelsted et al., 2020).

Unlike bio-covers at landfills where gas is emitted over an area of land, confined sources can be actively ventilated, and the gas treated in more advanced engineered biofilters for better process control. Several organic and inorganic media types have been used for methane biofiltration including compost, peat, soil, composted pine bark. Inorganic filter beds have been gradually investigated in different reactor designs over the last 15 years as summarized in **Table 3-2** as they do not deteriorate with time, while higher elimination capacity can be obtained. **Table 3-2** also shows some of the recent innovation tested such as new media, additives such as a second liquid phase, hydrophobic microorganisms, and methods to alleviate accumulation of intermediates or to identify microbial stress. However, all studies require large gas contact times of several minute, which shows that mass transfer of the methane from the gas phase to the microbes still hampers the bioprocess of methane abatement.

Table 3-2 Overview of biological system studies performed within the last 15 years on the abatement of dilute methane (< 5% v/v = ~31,000 mg m^{-3}) illustrating typical removal efficiency (RE), elimination capacity (EC) at empty bed gas resident time (EBRT).

System design[1)]	Concentration (mg m^{-3})	EBRT (min)	Synopsis of Results	References
BF	800 – 6,000	3.2 – 17.5	Gravel material used as media showed RE between 35-95% RE and **EC between 5-60 g m^{-3} h^{-1}**. An increase in the CH_4 concentration has less effect on the RE than an increase in the gas contact time. This study established that the gas flow rate must preferably be low for good removal efficiencies (i.e., >90%), corresponding to EBRT >8.7 min, for a CH_4 concentration ≤ 1.1% v/v, and in the presence of sufficient quantities of nutrients (e.g., [N] = 0.75 g L^{-1} and [P] = 1.5 g L^{-1}).	Nikiema and Heitz, 2009
	500 - 6,300	4.1	Rock materials (particle sizes: 2 and 5 mm) and one porous clay particles (7 mm) with the 2 mm rock performing best. The RE up to ~56% RE and the **EC up to ~50 g m^{-3} h^{-1}**. Increasing the gas face velocity from 0.40 cm per second by 30% did not increase RE. Non-irrigation of biofilter causes the performance to decrease significantly (e.g., 45% decrease in 1 week) even with the pre-humidification of the gas phase. Average percentage of CH_4 converted into CO_2 was ~ 70%.	Nikiema and Heitz, 2010
	160 – 2,800	4.1	Gravel material (8 mm) used as media. A synthetic nutrient solution was sprayed at the top of the biofilter daily. The RE up to 38% and the **EC up to ~15 g m^{-3} h^{-1}**. The RE was stable for [NO_3^-] from 0.1 to 0.5 g N L^{-1}, but decreased significantly when was adjusted to 0.01 g N L^{-1}. Carbon and nitrogen mass balances suggested that the carbon accumulated within the biofilter was used for the production of exopolymeric substances or intracellular compounds.	Girard et al., 2011
	1,250 – 3,100	4.0 - 6.5	Two types of media compared (organic: wood pine bark chips, perlite, compost and inert: polyurethane foam cubes operated for 250 days. The RE up to 30% and the **EC up to ~10 g m^{-3} h^{-1}**. An environmental assessment was performed and showed that nutrient concentration and nutrient source are important.	Gomes-Cuervo et al., 2017
	31,000	20.0	Perlite as media / The medium was circulated four times per day and was replaced every week. The methanotrophic proportion of total biomass gradually increased to 41 %. Type I methanotrophs became predominant at the end of the 108 days.	Kim et al., 2014
	6,200	1.6 – 19.5	Bituminous coal used as packing (2-3 cm) to test as a simple means to treat coal mine ventilation air (MVA) using a heap of coal typically readily available at coal mine sites. Nutrient medium was added once every three days. The RE up to ~20% and the **EC up to ~27 g m^{-3} h^{-1}**. Additional inoculation with a culture of *Methylosinus sporium* only enhanced methane EC during the initial 12 weeks.	Limbre et al., 2014
	11,700 – 22,200	4.4	A clear increase of the soluble microbial products (SMPs) in the liquid phase, especially in the protein fraction (during N limitation) but also the polysaccharide fraction (during acidification), was observed during instable operations, and was proposed as a potential indicator of microbial stress. The biofilter (wood pine bark, perlite, and compost as media) showed a RE up 62% and an **EC up to 11 g m^{-3} h^{-1}**.	Hernandez et al. 2015
	600 – 8,000	6.0	Rock media was evaluated on the responses of nutrient starvation as well as both of absence of methane and nutrient solution. In the case of transient state, the biofilter was quite flexible in both types of shock loads (sudden variations of inlet concentration or gas flow rate) and responded quickly. The RE ranged from 52 to 87% and the **EC up to ~45 g m^{-3} h^{-1}**.	Ferdowsi et al. 2016

System design[1)]	Concentration (mg m^{-3})	EBRT (min)	Synopsis of Results	References
	40	0.25	Autoclaved Aerated Concrete used as media (a lightweight building material exhibiting porosity up to 80%). The filter was installed at an enclosed space with one cow. The RE accounted for ~17% and the **EC for ~3 g m^{-3} h^{-1}**. Carbon dioxide was removed in the biofilter by the likely carbonation reaction with the binder material of AAC (tobermorite) and thereby complete carbon sequestration from the converted methane was obtained.	Ganendra et al., 2015
	1,050 – 22,500	7.4 – 42.8	The expanded vermiculite as media outperformed other media (organic, sponge-based and blast furnace material). An overall high CH_4 conversion efficiency (>90%) at EBRT as low as 29.5 min. The RE reached up to ~95% and the **EC up to ~13 g m^{-3} h^{-1}**.	Brandt et al. 2016
	5,580	70	Different media tested (two sizes of volcanic rock, polyurethane sponge and activated carbon produced from digested sludge) with sponge performing best/ The RE up to ~35% and the **EC up to ~2 g m^{-3} h^{-1}**.	Sun et al., 2018
	430 – 1,370	6.0	Inorganic media and operated over four years. RE reached 80% after seven weeks when operated at CH_4 inlet concentrations ~ 700 to 800 ppm_v and an EBRT of 6 min. The biofilter often recorded REs higher than 65% for inlet methane of 1900–2200 ppm_v and an EBRT of 6 min. The rate and interval of the nutrient supply showed to be important in maintaining high performance. At the end of the experiment, the RE deteriorated due to a long shutdown of 12 weeks and the extended operation.	Ferdowsi et al., 2023
BC	31,000 – 62,000	72 - 2200	Columns with compost as active cover representing a landfill biocover. The highest methane oxidation rate was obtained at the lowest gas contact time (1.2 hours = 72 minutes) at which the removal efficiency was 99%, indicating that the maximum oxidation capacity of the column had not been reached.	Thomasen at al., 2019
	27,000 – 57,000	24 - 186	A field pilot using an open-bed compost filter actively loaded with a mixture of landfill gas and ambient air. The highest methane oxidation rate was obtained at the lowest gas contact time (0.4 hours = 24 minutes), at which the removal efficiency was 58%. The RE up to ~80% and the **EC up to ~9 g m^{-3} h^{-1}**. Preferential airflow was observed along the edges of the 1.2-meter media bed.	Fjedsted et al., 2020
	31,000	N/A	Daily covers (a biocomplex textile) for the simultaneous mitigation of greenhouse gases (GHGs) and odours for operational landfills were made by inserting inorganic biocarriers (perlite and tobermolite) between nonwoven fabrics. The maximum RE for CH_4 and DMS of the bio-complex textile were 90.9% and 100%, respectively. A recovery of 2-3 days was required after a 17-day starvation period.	Choi et al., 2018
BTF	15,300	4.0	Internal gas recirculation to increase gas face velocity from 0.3 to 6.6 cm s^{-1}. Nitrogen was identified as the key limiting factor to be maintained above 100 mg N L^{-1}. Dissolved organic carbon concentration (TOC) identified as inhibiting when > 100 mg L^{-1}. Mineral medium was daily added with a dilution rate between 0.05 d^{-1} and 0.27 d^{-1}. Mass transfer limitations from liquid phase to biofilm with additional mass transfer limitation due to biomass accumulation in the packed bed. The RE up to ~10-15% and the **EC up to ~25-30 g m^{-3} h^{-1}**.	Estrada et al., 2014.
	14,300	4.0	BTFs with polyurethane foam operated with two liquid phases (water + 25% v/v silicone oil) was evaluated using two different inocula. Despite the low similarity, the analogous operating conditions resulted in a similar bacterial population at the end. The RE was up to 40% with an **EC up to 60 g m^{-3} h^{-1}**. The silicone oil reduced the metabolites concentration in the aqueous phase.	Lebrero et al., 2015

System design[1)]	Concentration (mg m^{-3})	EBRT (min)	Synopsis of Results	References
	11,100	4.8	**EC increased from 22 to 51 g m^{-3} h^{-1}** when 10% silicone oil was added resulting in a RE of 40%. Mineral medium was continuously added with a dilution rate of 0.1 d^{-1}. Specific methane elimination capacities obtained were between 0.08 and 0.015 g methane per gram biomass per hour, and were superior to most of values reported in literature which are in the order of 10^{-6} to 10^{-2} g g^{-1} h^{-1}.	Rocha-Rios et al., 2009
BF +	4,800	4.2	The effect of six non-ionic surfactants was analysed in two BFs with stones as media. Addition of Brij increased RE from 35% to 38-46%, and the addition of Tweens between 43-48%. The RE reached up to 48% and the **EC up to 45 g m^{-3} h^{-1}**.	Ramirez et al., 2012
	13,600	20	A pure strain of *Graphium sp*. was used to inoculate to a compost biofilter. A low pH nutrient solution containing the antibiotic chloramphenicol was used to promote fungal growth over possible competing bacterial strains. A high RE of 90% was obtained at an EC of 37 g m^{-3} h^{-1}. Despite the pH and antibiotic, a high bacterial diversity was found. A batch assay revealed that *Graphium sp.* was not able to sustain the oxidation of CH_4 unless methanol was supplemented	Lebrero et al., 2016
STR	15,900	4.8	Operated at a stirring rate of 800 rpm / **EC increased from 75 to 106 g m^{-3} h^{-1}** when 10% silicone oil was added resulting in a RE of 57%. Mineral medium was continuously added with a dilution rate of 0.1 d^{-1}. Specific methane elimination capacities obtained ranged between 0.015 and 0.025 g methane per gram biomass per hour, which were superior to most of values reported in literature which are in the order of 10^{-6} to 10^{-2} g^{-1} h^{-1}.	Rocha-Rios et al., 2009
HFBR	9.900	45-55	The effect of nitrogen was investigated in Phase 1 showing that a low concentration of ammonia (25 mg L^{-1}) would enhance methane removal performance. In Phase 2, silicone oil was added and supported a performance increase between 31% and 79%. In Phase 3, a non-ionic surfactant (Brij 35) was added, which entailed an increase in removal rates by 105-171% compared to Phase 1.	Kennelly et al., 2012
CBR	25,000	< 1	**EC of up to 77 g m^{-3} capillary channel h^{-1}** was obtained in the reactor in which the gas phase was internally recirculated. A biomass pulse doubled the biomass concentration showed system was still mass transfer limited. The suspended biomass concentration varied between 0.3 and 0.8 g L^{-1} through the experiment with a specific methane EC of 0.015 g methane g DS^{-1} h^{-1}. A minimum of 70% of the carbon present in CH_4 was oxidized to CO_2. Abiotic measurements showed that the organic phase (10% v/v 200 cSt silicone oil) decreased the mass transfer in the capillary, likely due to an increased liquid viscosity.	Rocha-Rios et al., 2013

[1)] BF = Biofilter, BC = Bio-cover, BTF = Biotrickling filter, BF+ is Biofilter with an additive, STR = Stirred Tank Reactor, HFBR = Horizontal flow bioreactor, CBR = Capillary Bioreactor.

3.4 Limitations of Biological Gas Treatment Processes

Bioavailability and Mass transfer Limitations

Biological purification of air and process gaseous streams is typically hindered by mass transfer limitations when contaminants are hydrophobic and/or are present at low concentrations. Bioavailability is an expression of the fraction of the pollutant mass present at a specific time in a compartment that has the potential of being assimilated by an organism (Vallero 2011). Contaminants with high solubility in water such as alcohols and aldehydes are readily removed from the air by biological air filtration, while other contaminants such as long-chain hydrocarbons or methane, with low aqueous solubility, would benefit from an enhancement of mass transfer. In addition, the low concentrations (e.g., indoor air contaminants or dilute methane) typically cause increased mass transfer limitations and thus a reduced bioavailability for effective removal during a biological gas purification process.

For example, a biological indoor air cleaning system would require a large value of the biological purifier volume to room ratio, which is typically not feasible due to the high footprint cost of buildings. For instance, an indoor air biological purifier for a room with dimensions 8 m × 5 m × 2.5 m (L × W × H) would require a relatively large volume of about 1,100 – 3,300 litres, assuming the typical gas residence time of 20 - 30 seconds of industrial applications for a 95% removal efficiency and an room air exchange rate of 4 volumes per hour, which equals a purifier volume of 1 – 3% of the total room volume (Guieysse et al. 2008). This would be challenging for biological based systems to obtain effective indoor air cleaning performances in reasonably compact sizes.

The mass-transfer is dependent on the gaseous compound, the bioreactor system, as well as different operating conditions (Kim and Deshusses, 2008; Dorado et al, 2009; Kraakman et al, 2011) as discussed further in the next chapter (Chapter 4). Poor-water soluble compounds that have a Henry coefficient higher than 1 are typically considered not suitable and/or economical viable for biological gas treatment purification.

Other Biological Gas Treatment Limitations

At low carbon and nutrient loading rates the biomass would reach a stationary phase in which carbon and nutrient compounds are only used for the maintenance of the microbial cells and dead cells are replaced by new cells while target to secondary degraders (see **Figure 2-1**). This stationary situation may continue for years as can be observed in biofilters treating low-concentration odorous compounds (van Groenestijn and Hesselink, 1993). Increased volumetric carbon loading rates accelerates the overall biomass production considerably, with the risk of biomass-induced clogging and additional operational costs. Only limited small-scale studies at high VOC concentrations have been able to prevent biomass-induced clogging in biological waste gas treatment systems (Dobslaw and Ortlinghaus, 2020; van Groenestijn et al., 2001). Multiple methods have been investigated to prevent biomass clogging, including mechanical (i.e., back flushing, submerging, agitating, squeezing), chemical (i.e., pH shift, addition of oxidizing agents or detergents), and biological (i.e., predation, starvation, nutrient limitation, thermophilic), but only few methods have been tested and applied on industrial scale (Dobslaw et al., 2018).

In addition, very important for biological gas treatment process applications is reliability, which is the combination of robustness and resilience. The process robustness reflects the capacity of a treatment system to maintain functionality with certain changes such as inlet fluctuations and operational upsets. The resilience is the rate at which a treatment system returns to its original state after being disturbed. Biological systems may be impacted by sudden or longer-term changes in parameters such as inlet concentrations, pH, water content, temperature, and nutrients. Reliability (*R*), the combination of robustness and resilience, may be quantified as the sum of multiple risks for upsets:

$$R = \Sigma (p \times E) \qquad \text{(Equation 3-1)}$$

with *p* the probability of occurrence of an upset and *E* the negative effect of an upset. The probability of occurrence of an upset or an equipment failure (*p*) may be expressed as the expected number of occurrences per year (number/year) or as the percentage of operating time during which it is likely to occur (e.g., a critical pump failure or a water supply failure). The negative effect of the upset (*E*) may be expressed as the loss of the removal efficiency (%) or the impact on the people living near the treatment system (Kraakman et al., 2014; Cabrol et al., 2012).

For the interested reader that would like to learn more about biological gas treatment processes, the following two excellent books that share experiences from researchers and practitioners from all over the world are recommended: The first is *From Biofiltration to Promising Options in Gaseous Fluxes Biotreatment Recent Developments, New Trends, Advances, and Opportunities* (Soreanu and Dumont, 2020) and the second is *Air Pollution Prevention and Control: Bioreactors and Bioenergy* (Kennes and Veiga, 2013). In addition, the review of Dobslaw and Ortlinghaus (2020) provides additional technical and economical details and present limitations and corresponding proposed solutions to help overcoming some of the challenges of biological air and gas treatment methods.

4. GAS-LIQUID MASS TRANSFER CONSIDERATIONS

Chapter overview

This section reviews the mass transfer aspects of biotechnology for gas treatment in general terms, with an emphasis on the underlying principles. Hydrophobic gaseous compounds, as well as compounds with very high vapor pressures, are poorly water soluble, and therefore only present at low concentrations in the liquid phase or biofilm. They exhibit a low bioavailability because biodegradation typically follows first order reaction kinetics.

The first section *Gas-liquid Mass transfer Phenomena* contains the following subsections*: Mass Transfer or Kinetically Limited, Defining Mass Transfer, Determining Mass Transfer Rates, Factors Influencing Mass Transfer.* The second section discusses *Opportunities and Challenges to Improve Gas-Liquid Mass Transfer*. The third section *Capillary Reactors* explains and discusses critical parameters of capillary reactors, which are investigated in this study to determine feasibility to overcome bioavailability in biological gas treatment processes.

This chapter may be considered an update to the previous publication: Kraakman, N.J.R., Roche Rios, J., van Loosdrecht, M.C.M. (2011). **Review of Mass Transfer Aspects for Biological Gas Treatment**. *Appl. Microbiol. Biotechnol.* 91: 873-886.

4.1 Gas-liquid Mass transfer Phenomena

Mass Transfer or Kinetically Limited

Understanding the rate-limiting steps in a system generates opportunities to optimize the design and operations of the system for a specific application. Typically, the reaction in a bioreactor is operating under either mass-transfer or kinetically limited conditions.

In biological gas treatment systems, such as biotrickling filters, bioscrubbers, airlift bioreactors and stirred-tank bioreactors with a mobile water phase that contains biomass, increasing the biomass concentration in the liquid phase would be a relatively simple way to determine whether the reactor is operating under mass-transfer or kinetically limited conditions. When a change in the amount of contaminant removed per reactor volume (removal capacity) is seen at a sudden increased biomass concentration, the operation of the system is kinetically limited.

When biomass is not available or not properly adapted to operating conditions of the bioreactor being tested, then a sudden increase of the inlet contaminant concentration applied while monitoring EC can identify biology or mass transfer as potential rate-limiting step (Estrada et al., 2014). This method has been used in the study herein when investigating the methane treatment in a capillary bioreactor (see **Chapter 8**). In addition, when in different experiments, the EBRT is changed at constant substrate loadings, rate-limiting step discrimination could be created, especially when individual reactors sections are monitored as shown for example by Paca et al. (2009).

Another way to determine whether the reactor is operating under mass-transfer or kinetically limited conditions is to change the operating temperature significantly and measure the efficiency at different gas velocities as shown by Barton et al. (1999). A large change in removal efficiency at a different temperature indicates kinetic limitation as the mass-transfer parameters diffusion (increases with temperature) and Henry's constant (decreases with temperature) are somewhat temperature sensitive, but in general not as significant as the biodegradation parameters.

Mathematical expressions, in particular the sensitivity analyses of dimensionless numbers (e.g., Damkohler number, Thiele Modulus, Peclet number) can be effective to clarify at least the interplay of mass transfer and biodegradation kinetics (Cowger et al.,1992). The Damkohler number is defined as the ratio of the reaction rate to the mass transfer rate (the sum of advection and diffusion rates). The Thiele number is defined as a ratio of the reaction rate to the diffusion rate. The Peclet number is the ratio of the rate of advection to the rate of diffusion of compounds in a gas or liquid. Sensitivity analyses of dimensionless numbers in biological gas treatment models have been used by different authors (Goncalves and Gonvind, 2009; Aroca et al., 2009) to demonstrate successfully whether the operation of the reactor was likely to be mass-transfer or kinetically limited. Bosma et al. (1996) defined the bioavailability as the inverse of the Damkohler number for the case of dissolution-controlled biodegradation and proved that the bioavailability number (B*n*) can be a useful tool to predict threshold concentrations below which no biotransformation is possible in soils slurries and percolation columns.

Oxygen is often used to characterize mass transfer in bioreactors because it's important for aerobic microbial processes and presents the gas-to-liquid oxygen mass transfer coefficient as a convenient metric to compare mass transfer performance. Standard guidelines for measuring oxygen mass transfer coefficients have been established for completely mixed suspended growth bioreactors, such as aeration basins at wastewater treatment plants. This involves the depletion of the oxygen pure water by sparging nitrogen gas followed by air or oxygen supplied to the system while monitoring the dissolved oxygen concentration over time until saturation (the so-called Outgassing method). Alternatively, the Oxygen Transfer Rate (OTR) method can be used, in which sulphite is added to the liquid and sulphite oxidation (using a rapid Co^{2+}-catalysed reaction of oxygen with sulphite at the gas-liquid interphase) is monitored over time by measuring sulphite concentration. This method mimics the microbial uptake of oxygen in biotic configurations and is considered more accurate than the Outgassing method (Munoz et al., 2018). The OTR method has also been used in this study to measure gas-liquid mass transfer under different operating conditions (see **Chapter 5**).

It is important to note that in most situations a reactor is not either mass transfer or kinetically limited but is a complex combination of both. It could very well be possible that the removal is substrate (mass-transfer) limited deep in the biofilm, but kinetically limited near the aqueous/biomass phase. In addition, as mass-transfer and kinetic rates change along the height of reactor, the rate-limiting step might differ along the height of the bioreactor when considered as being not completely mixed. Finally, as the biomass grows and could accumulate over time on fixed film bioreactors, the pore volume of the media can be reduced, reducing the interfacial area between the gas phase and the biofilm. In that case mass-transfer limitation can be induced after a long time of operation as adeptly illustrated by Popat and Deshusses (2010).

In summary, although limited tools exist to properly determine what the rate limiting step is in a biological gas treatment system, different authors have demonstrated that they can be used successfully to compare and optimise bioreactor systems.

Defining Mass Transfer

Mass transfer of the target compounds (contaminant and oxygen) from a gas phase into the liquid phase in biological gas treatment systems is typically described using the two-film theory from Lewis and Whitman (1924). This model uses two phases (e.g., gas and liquid or liquid and biofilm) that have different concentrations and are not in equilibrium according to Henry's law. Only at the gas-liquid interface such equilibrium exists, and the target compounds move from or to this interphase with a certain velocity, which is dependent on the type of compound and the properties of the two phases. These velocities are defined in mass transfer rate coefficients. The overall mass transfer coefficient ($k_{overall}$) is a combination of the different partial intrinsic mass transfer coefficients, often reduced to a mass transfer rate coefficient for the gas phase (k_G), a mass transfer rate coefficient for the liquid phase (k_L) and a mass transfer rate coefficient for the biofilm (k_B) as shown in Eq. (4-1).

$$1/k_{overall} = 1/k_G + 1/k_L + 1/k_B \qquad \text{(Equation 4-1)}$$

The mass transfer coefficients are a function of the contaminant physical-chemical properties, the medium properties, the internal reactor characteristics as well as the operating conditions of the reactor system. In suspended reactors (bubble columns, airlift and stirred tanks), Equation 4-1 continues being valid considering k_B as the resistance due to the water film around the cell or flocks of cells. If the resistance to the mass transfer in the gas and the biofilm is negligible (as might be expected for most bioreactors, especially at low contaminant concentrations), the overall volumetric mass transfer rate R (g m^{-3} s^{-1}) from the gas phase to the aqueous phase (where microorganisms are suspended or growing as a biofilm) takes place at a rate that is described (Koch, 1990) in Eq. (4-2).

$$R = k_L a\ (C_G/H - C_L) = (D_{AL}/\delta_{film})\ a\ (C_G/H - C_L) \qquad \text{(Equation 4-2)}$$

where D_{AL} (m^2 s^{-1}), H (dimensionless) and δ_{film} (m) are the gaseous contaminant diffusivity in the liquid, the Henry coefficient, and the liquid film thickness, respectively. C_G and C_L are the contaminant concentrations (g m^{-3}) in gas and liquid, respectively.

The term $k_L a$ (s^{-1}) is a volumetric mass transfer coefficient and consists of all concentration independent factors that determine the mass transfer rate, where k_L is the mass transfer coefficient (m s^{-1}) and a is the specific interfacial area (m^2 m^{-3}) between the gas and liquid phase. k_L and a are often difficult to obtain separate experimentally. However, $k_L a$ can be obtained from macroscopic measurements (see also next section). Although $k_L a$ is not a direct measure of performance, because it is sensitive to biomass concentration and reactor liquid medium properties, it can be used to evaluate different mass transfer approaches including different reactor configurations and/or operations.

The gaseous contaminant diffusivity of low-molecular weight compounds in gas is in generally in the range of 1 x 10^{-5} m^2 s^{-1} (Warneck,1988) and in water in the range of 1 x 10^{-9} m^2 s^{-1} (Harms and Bosma, 1997). From Eq. (3-2) it can be deduced that R can be increased in different ways, for example (a) by reducing the liquid film thickness via reduction of the water flow (biotrickling filters) or by increasing turbulence (stirred tank bioreactor), (b) by increasing the gas-liquid contact area through a support (liquid or solid) or by increasing turbulence, and finally, (c) by reducing the Henry-coefficient, which increases the gradient of concentrations (driven force for the mass transfer). The latter can be conducted by increasing the affinity between the contaminant and liquid phase, for example by modifying the liquid phase composition (see also **Chapter 8**).

Figure 4-1 shows a schematic representation of mass transfer in a bioreactor for gas treatment applications in which the biofilm can be a fixed film on a packing or biomass suspended in the liquid phase.

As observed in **Figure 4-1**, in a packed or laminar reactor as a biotrickling filter, the contaminant or oxygen can be transferred from the gas stream (G) to the cells through two water films or interfaces, one adhered to the package forming a biofilm, and other with the free water flowing through the packing (L). In both interfaces, the contaminant (or oxygen) will be partitioned according to the thermodynamic equilibrium (Henry's law). However, as the equilibrium exists only in the interface (Lewis and Whitman, 1924), a concentration's gradient between the interface and the liquid bulk leads to a net mass transfer flux (N). As the interface has no volume, the mass transfer accumulation is not possible, and equality of fluxes can be

established ($N_g = N_l = N_B$). **Figure 4-1** continues being valid to represent the mass transfer from the gas to liquid in a slurry or suspended bioreactor considering the biofilm on the liquid side as a single cell or flocks of cells dispersed, and the biofilm on the gas side as a single cell or flocks of cells in direct contact with a bubble.

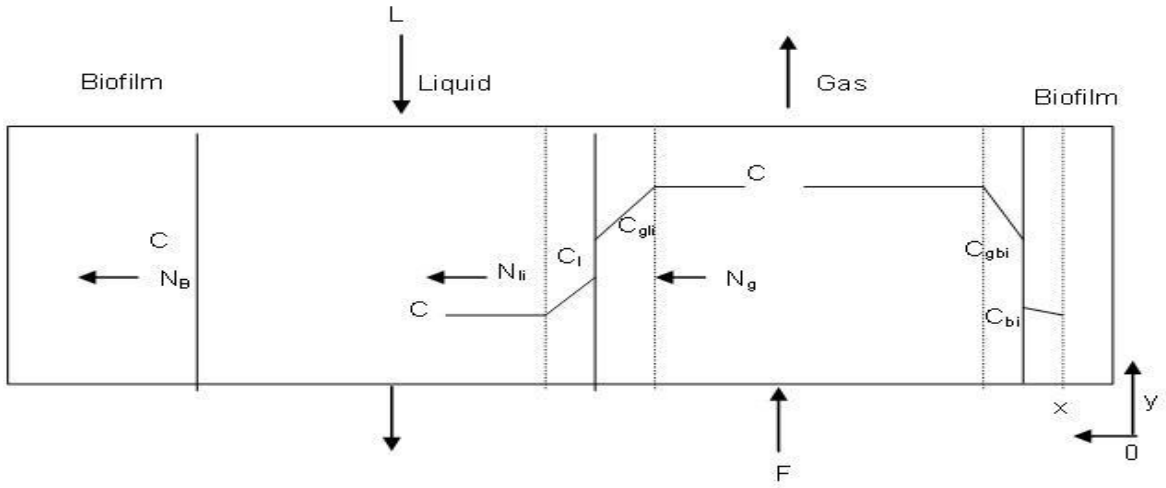


Figure 4-1 Illustration of mass transfer typical for biological gas treatment processes (Kraakman et al., 2011).

Mass transfer takes place through both diffusion – the random Brownian motion of individual compounds in a medium – and by advection, in which compounds are transported by the larger-scale motion of currents in the medium. Convection is used to refer to the sum of advective and diffusive transfer.

Bioavailability is nevertheless often limited to certain air contaminants because the gas-liquid partitioning (Henry-coefficient) of the contaminant is limiting mass transfer to the microorganisms. Its high hydrophobicity and/or its low concentration, and sometimes its limited biodegradability, results in poor removal rates in traditional biological gas purification systems. Contaminants with a dimensionless Henry-coefficient > 0.1 can be considered hydrophobic and its availability for microbial processes in the liquid phase or biofilms is in generally mass transfer limited.

Factors influencing Mass Transfer

The intrinsic mass transfer coefficient is a function of the contaminant physical-chemical properties, the medium properties (e.g., viscosity, salt, and organic content), the internal reactor characteristics (e.g., gas and liquid flow behaviour, surface area and wet-ability of the packing material) as well as the operating conditions (e.g., gas velocity, liquid velocity, pH, and temperature). Some of these parameters and their relevance to biological gas treatment systems are discussed below.

The overall volumetric mass transfer coefficient k_La (s^{-1}) is directly related to the effective interfacial area ($m^2\ m^{-3}$) when considering conventional biological gas treatment systems such as biofilters and biotrickling filters. The effective interfacial area is often different from the specific surface area (a) of packing material, as part of the packing surface might not be wetted or could be in a dead zone not being effective for mass transfer. Water droplets and

swirls on the other hand could increase the effective interfacial area. Recently developed plastic packings for wet scrubbers uses this methodology of drip points to create a myriad of small droplets, multiplying the surface area for gas-liquid contact with minimal resistance to gas flow. The effective interfacial area depends on the operation conditions of the system. To determine the interfacial area physical methods such as electro-resistivity, light transmission and reflection techniques can be used, but usually the effective interfacial area is determined by mass-transfer measurements in the presence of a fast chemical reaction as proposed by Joosten and Danckwerts (1973). This method uses the absorption of relatively low concentrations (< 1% v/v) carbon dioxide-enriched air in 1M NaOH solution. Rejl et al. (2009) showed that this method can only be used when the gas velocity is > 0.5 m s^{-1}, otherwise the gas phase resistance becomes too large. Although the required gas velocity is in the range (0.3 – 3 m s^{-1}) typically found in packed columns used for absorption (e.g., wet chemical scrubbers) or distillation and evaporation, it is too high for most conventional biological gas treatment systems, which normally operate in the range 0.02 – 0.4 m s^{-1}. Therefore, this standard method might be less suitable to determine the exact effective interfacial area in a biological gas treatment system. The K_La could be quantified using the sulphite method, which measures the oxygen transfer rate (OTR), discussed above. This methodology determines the maximum rate of oxidation of sodium sulphite resulting from the oxygen transfer from the gas phase to the liquid in which there is no dissolved oxygen.

Packing materials have specific surface areas and not all parts of the surface may contribute to mass transfer as, for example, not all parts are always wetted. The wetted specific surface area is a percentage of the total specific surface area of the packing material, also sometimes expressed as wettability factor, and is dependent on factors such as gas and liquid flow. This wettability is critical for the overall performance for packed columns used for absorption (e.g., wet chemical scrubbers) or distillation and evaporation, which might not necessarily be true for all biological gas treatment systems. The catalytic reaction in a chemical scrubber normally takes place in the liquid phase, while the catalytic reaction in most commonly used biological gas treatment systems (biofilter and biotrickling filter) takes place not so much in the liquid phase but for the majority in the biofilm, even in biotrickling filters with continuous recirculation (Cox et al., 2000). In addition, due to biological growth on the packing material the surface becomes hydrophilic and therefore wettability is much higher than the bare surface properties.

Direct gas-biofilm mass transfer is preferred when the catalytic reaction takes place in the biofilm. In a biological system, the liquid is required to prevent drying out of the biomass and is a transport medium for the supply of nutrients and sometimes the removal of degradation products (e.g., sulphuric acid as the result of hydrogen sulphide oxidation). Transport of water over the biofilm is necessary to maintain a high-water activity but can form an extra barrier for mass transfer as illustrated by Popat and Deshusses (2010) among others, where the EC in their biotrickling filter experiment was the highest when recirculation of the liquid was temporarily stopped.

Another important factor is the air distribution, which is, most of the time, not taken into consideration when modelling biofiltration. Most models presume that air flow within the reactor is plug flow (Devinney and Ramesh, 2005), which might be a too simplified assumption.

Prenafeta-Boldu et al. (2008) showed the importance of the presence of stagnant air zones in different packing materials and demonstrated that increasing airflows reduces stagnant air zones and can consequently reduce potential diffusion limitations.

Many biological gas treatment models are based on the equilibrium according to Henry's law at the gas-liquid interface. However, the presence of biomass can have a substantial effect on this equilibrium as illustrated by Davison et al. (2000) and Barton et al. (2003), and further discussed by Barton et al. (2008). High biomass or organic levels of more than 15 g dry weight per litre can be found in biofilms present in biological gas treatment systems. The overall mass transfer is directly related to the Henry-coefficient and measurements of Henry-coefficients and maximum solubility in aqua-biomass mixtures are necessary to compensate for the additional organic constituents. The Henry-coefficient of, for example, toluene decreased by a factor of 30 compared to pure water when the biomass content was 30 g dry weight per litre and its maximum solubility increased by a factor 4 compared to pure water when biomass content was 0.25 g dry weight per mL. At 100 g biomass per litre, the Henry's value for trichloroethene was only about 2% of that in pure water and even at relatively low biomass levels, such as 10 g per litre, the partitioning constant was less than 10% of that in pure water. In the absence of these experimental data, Barton et al (2008) recommended use of octanol-water partitioning constants rather than the gas-water partitioning constants. Although the authors showed that the use of octanol-water partitioning constants is not a reliable predictor, they illustrated that the effect of biomass on the Henry-coefficient (trend and order of magnitude) is described correctly. This is consistent with Deshusses and Johnson (2000), who reported that the removal of VOCs in conventional biofilters was affected by both the Henry-coefficient and to a lesser extent also by the octanol/water partition constant of the VOCs.

4.2 Opportunities and Challenges to Improve Gas-Liquid Mass Transfer

General concepts

Improvements in design and/or operation of biological gas treatment systems are needed to overcome current limitations in mass transfer that cause a limited bioavailability. Different concepts have been proposed to overcome mass-transfer limitations of gaseous contaminants in biological gas treatment systems. **Figure 4-2** and **Table 4-1** summarise these concepts and provides a high-level qualitative evaluation that considers economic, environmental, and social aspects such as impacts on capital and operation costs, operating & maintenance complexity, footprint, resources such as energy & materials, resilience & reliability, sustainability (carbon footprint, disposal), side streams impacts, and health & safety aspects.

Although some strategies showed promising results in terms of improved performance, newer strategies are still needed to make biofiltration more applicable and cost-effective, especially for the treatment of highly hydrophobic contaminants (e.g., dilute methane which is poorly soluble in water, highly volatile, and has high chemical stability) or low concentrations (e.g., Indoor Air Quality applications requiring minimum space/footprint).

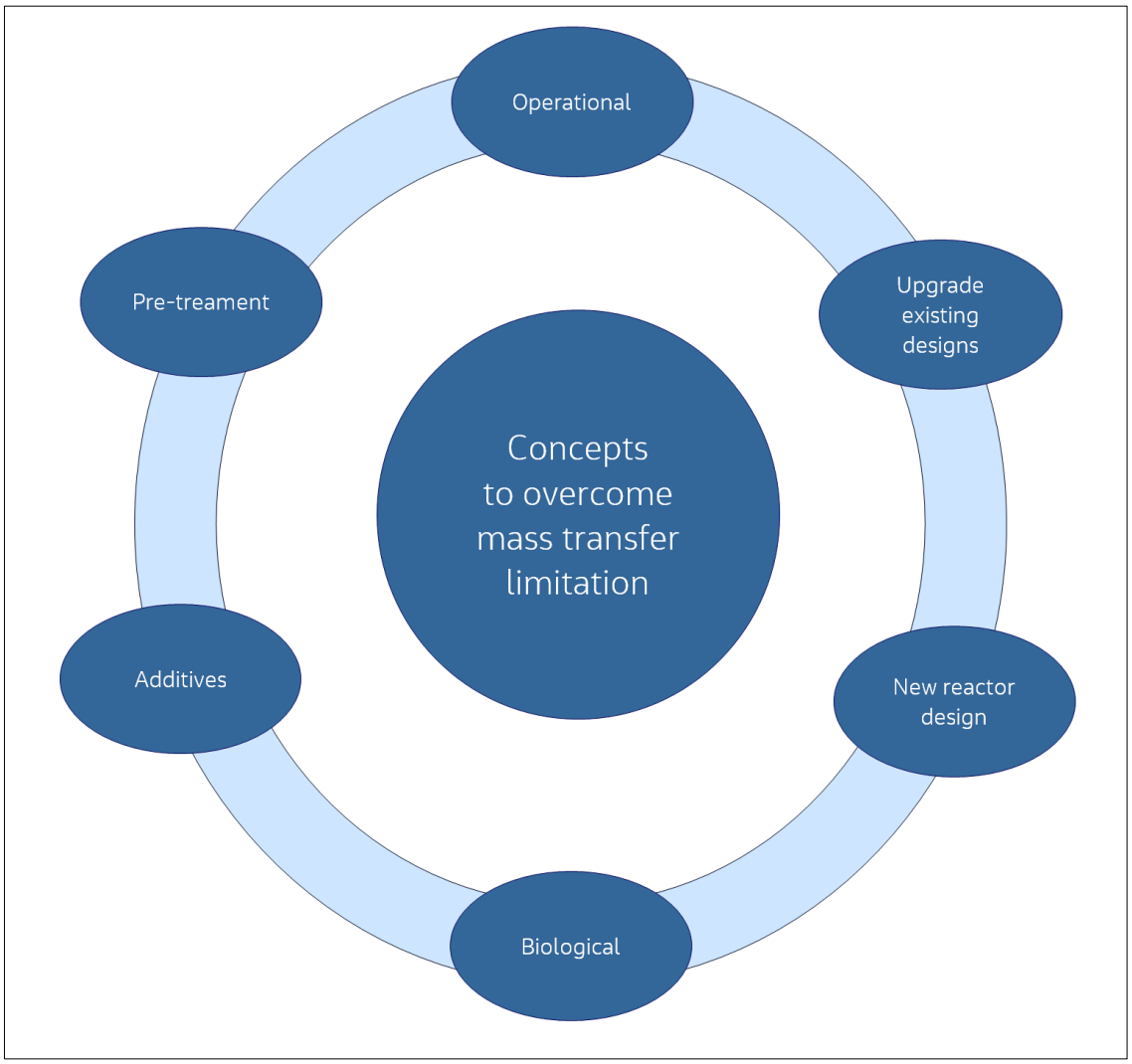


Figure 4-2 Concepts to overcome mass-transfer limitations in biological gas treatment processes.

Table 4-1 Examples to overcome mass-transfer limitations in biological gas treatment processes.

Concept	Advantages	Disadvantages	Examples
Operational			
Increase air velocity	Can use existing reactor designs.	Requires more open stackable media. Requires more energy (increased pressure losses).	Dorado et al., 2009
Intermittent irrigation (in BTF systems)	Can use existing reactor designs.	Minimal improvements (still laminar reactor).	Yu et al., 2022; Kraakman et al., 2021; San-Valero et al., 2017
Apply internal gas recirculation	Can use existing reactor designs (with some adjustments).	More energy required (increased pressure losses). More complex reactor.	Estrada et al., 2014
Upgrade existing Reactor Design			
Improve packing media	Can use existing reactor designs.	Minimal improvements (still laminar reactor).	Sun et al., 2018; Gomes-Cuervo et al., 2017; Brandt et al. 2016; Limbre et al., 2014
Apply static magnetic field	Can use existing reactor designs.	More energy required.	Quan et al., 2018
Pre-treatment			
Non-plasma	Can use existing reactor designs. Contaminant hydrophilized by partial oxidation.	Requires additional reactor. Requires more energy. Risk of undesired by-product (CO, NOx and O_3). Risk of fouling.	Dobslaw et al., 2020 Dobslaw et al., 2017; Schiavon et al., 2017; Karatum et al., 2016; Wei et al., 2013
Ultra-violet	Can use existing reactor designs.	Requires additional reactor. Requires more energy. Risk of fouling of UV-bulbs.	Dobslaw et al., 2020; Saucedo-Lucero et al., 2015; Zhu et al., 2015
Biological			
Apply hydrophobic microbes (e.g., fungi)	Can use existing reactor designs.	Risk of increased pressure losses (fungi mycelium). Risk of excessive deterioration of EC.	Marycz et al., 2022; Lebrero et al, 2016; Van Groenestijn et al., 2001
Predation of thick biofilms	Can use existing reactor designs.	Requires an effective secondary degrader.	Won et al., 2004; Woertz et al., 2002a,2002b; Cox and Deshusses, 1999
Co-metabolism (hydrophilic VOCs)	Can use existing reactor designs.	Addition of VOCs.	Lamprea Pineda, et al., 2021
Quorum sensing (QS)	Can use existing reactor designs.	Addition of QS molecules or quorum quenching enzymes.	Chen et al., 2019
Additives			
Addition of a non-aqueous phases	Can use existing reactor designs.	Requires ongoing addition of a non-aqueous phase.	Leberero et al., 2019; Munoz et al., 2012; Ramirez et al., 2012a, 2012b
Addition of surfactants	Can use existing reactor designs.	Requires ongoing addition of a surfactant.	Lamprea Pineda, et al., 2021, 2024 Wu et al., 2022
Addition of electrolytes	Can use existing reactor designs.	Requires ongoing addition of electrolyte.	Stone et al., 2017
Addition of nanoparticles	Can use existing reactor designs.	Requires ongoing addition of nanoparticles.	Stone et al., 2017
New Bioreactor Designs			
Foam Reactors	Requires less energy. Improved control.	More complex reactor. Limited airflow.	Kan and Deshusses, 2003
Tubular Reactors	Requires less energy.	More complex reactor.	Chen et al., 2012
Horizontal Reactors	Requires less energy.	More complex reactor.	Kennelly et al., 2012
Membrane Reactors	Requires less energy. Improved control.	More complex reactor.	Wu et al., 2024; Lebrero et al., 2013
Capillary Reactors (see Section 4.3)	Requires less energy. Improved control.	More complex reactor.	Lopez De Leon et al., 2023; Roche Rios et al., 2013; Kreutzer et al., 2005

4.3 Capillary Reactors

Introduction

The most investigated and most applied biological gas treatment methods (biofilters and biotrickling filters) can be called laminar contactors. Laminar flow occurs when a gas or liquid flows in parallel layers, with minimal disruption between the layers. Laminar flow is a flow regime characterized by high diffusion and low advection (i.e., the transport by the larger-scale motion of currents in a medium, for example through mixing) and is the opposite of turbulent flow. The mass transfer rate of a target contaminant through a water film by diffusion is relatively slow when compared to diffusion through gas (in general by a factor of approximately 10,000). Therefore, improved convection by advection (e.g., through mixing) will improve mass transfer through a water film.

Mixing is typically applied in liquid reactors to enhance reactions including mass transfer, but mixing requires high energy inputs. Energy input (e.g., mixing speed or pressure drop) is a critical parameter for the design and application of process equipment in general. Research efforts are needed in the search of less energy-intensive reactors to further enhance mass transfer rate. **Capillary reactors can combine good mass transfer with relatively low pressure drop, two important factors affecting cost effectiveness for many industrial applications of biological gas treatment systems and have, for this reason, been investigated herein.**

Capillary gas-liquid contactors may be structures of parallel straight microchannels (small round or square capillary channels) separated by a thin wall. The hydrodynamics of gas-liquid flow in capillary channels have been extensively investigated within the context of chemical reaction engineering (Nijhuis et al., 2001; Kreutzer et al., 2005b; Shao et al., 2010). Examples of study areas and applications including chemical processing where for example no back-mixing is desired, micro devices (e.g., lab-on-a-chip applications) or compact heat exchangers (e.g., printed circuit cooling systems) are discussed in Gupta et al. (2010) and Kreutzer et al. (2005).

Capillary reactors are becoming increasingly significant as multiphase reactors, considering the advantages that they offer, in comparison with conventionally gas-liquid contactor such as wet scrubbers, gas-liquid stirred tank reactors, and airlift reactors for a host of processes (Liu et al., 2005). These advantages, which include low pressure drop, high gas-liquid mass transfer rates, and minimum axial dispersion (plug flow), stem from the uniquely structured multichannel configuration of capillary channels. Some studies have shown that the use of capillary reactors, in lieu of trickle beds, results in higher productivities and a very significant reduction in reactor size for specified chemical processes (Haase et al., 2016). Segmented flow is increasingly being used in numerous industrial processes due to these unique hydrodynamic characteristics.

Capillary gas-liquid contactors provide low pressure losses when flowing through a capillary channel, because capillary forces can become dominant over gravity forces when the channel diameter is small enough while at the same time energy is not required to maintain small gas bubble sizes. As the channel diameter decreases, capillary forces which have no influence in large diameter channels can become dominant. Capillary action is the process of a liquid flowing in a narrow space without the assistance of, or even in opposition to, any external forces like gravity. The effect can be seen in the pulling up of liquids between two

glass plates, in a small tube, in porous materials such as paper and sand. It occurs because of intermolecular forces between the liquid and the surrounding solid surfaces. If the diameter of the tube is sufficiently small, then the combination of surface tension (which is caused by cohesion within the liquid) and adhesive forces between the liquid and container wall act to propel the liquid upwards against gravity. Capillary forces involve viscous tension (~ μ x u / d) and interfacial tension (~ γ / d), with u standing for the velocity (m/s), μ for the viscosity (Pa s), d for the diameter of the channel (m), and γ for the surface tension of the liquid (N/m).

Surface tension is an important factor in the phenomenon of capillarity. Surface tension is the tendency of liquid surfaces to shrink into the minimum surface area possible. Surface tension is what allows objects with a higher density than water (e.g., certain insects and razor blades) to float on a water surface. Because of the relatively high attraction of water molecules to each other through a web of hydrogen bonds, water has a higher surface tension than most other liquids.

Bretherton (1961) showed analytically that a liquid is pulled upwards when the Bond number (*Bo*) is less than 3.368 (Eq. 4-3), which is the value that can be used to define capillary channels.

$$Bo = \rho \times g \times d^2 / \gamma < 3.368 \qquad \text{(Equation 4-3)}$$

The Bond number is a dimensionless number measuring the importance of gravitational forces compared to surface tension forces for the movement of the liquid front, with ρ being the liquid density (kg/m^3), g the gravitational constant (m/s^2), d the diameter of the capillary channel (m) and γ the surface tension (N/m). A lower liquid density, a smaller capillary channel diameter or a higher surface tension increases the upwards liquid velocity. For air-water this means that the capillary channel needs to have a diameter ~ 5 mm or smaller (Kreutzer et al., 2005b). Note that the addition of impurities such as salts or biomass reduces the surface tension and therefore a smaller diameter of the capillary channel would then be required to be able to maintain a capillary force larger than the gravity force.

Capillary channels can be categorized by their diameter and may considered the following classification (Sattari-Najafabadi et al., 2018):

Conventional channels	d > 3 mm
Mini-channels	3 mm > d < 0.2 mm
Micro-channels	0.2 mm > d < 10 um
Nano-channels	d < 10 um

Flow Patterns

Multiple flow patterns can be observed for a combined gas-liquid flow in capillary channels. **Figure 4-4** shows examples of typical gas-liquid flow patterns that can be observed, which are mainly dependent on the gas to liquid fraction and the gas and liquid properties. The gas-liquid flow pattern that arises is not only dependent on the gas and liquid ratio and its properties, but also the velocity, and the channel geometry (Sattari-Najafabadi et al., 2018).

The dominance of surface tension forces results in patterns different in small channels to those found in large scale systems. Stratified gas–liquid flow (liquid flowing in the bottom in the channel with gas above in a headspace in large pipes) is hardly ever observed in small channels and gas bubbles typically appear within the liquid phase. Increasing the gas-to-liquid ratio turns the bubbly flow into a slug flow and a slug flow into an annular flow.

Two distinct regimes can be identified with the first regime being dominated by surface tension creating bubbly and segmented flow/slug and the second regime being dominated by inertia creating a more annular flow as the falling film flow. Inertia is a property of a body of mass (e.g., liquid) that resists changing its state of motion or state of rest (i.e., the dynamic pressure ~ ρu^2). In between these two regimes is a transitional regime with transition/churn flows (see **Figure 4-4** and **Figure 4-5**).

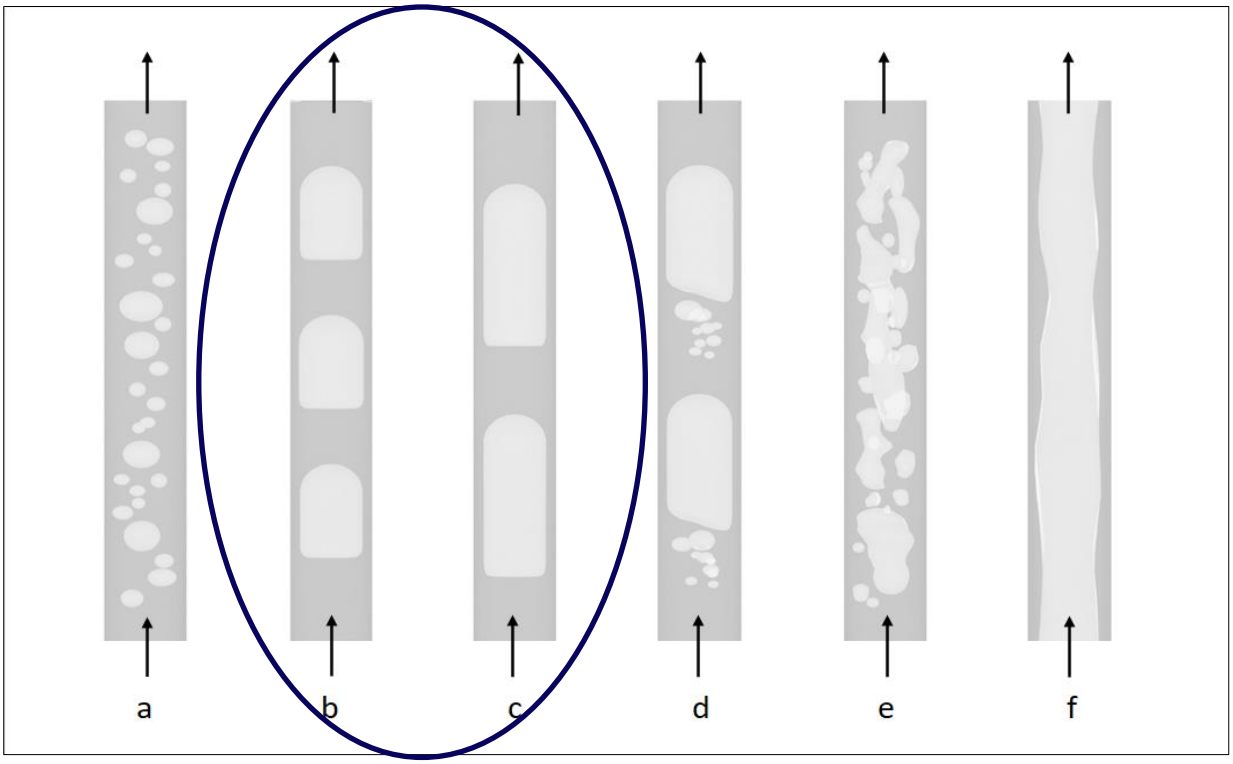


Figure 4-4 Schematic of possible gas-liquid flow patterns in a capillary channel with (a) bubbly flow, (b, c) segmented flow/slug, (d) transition slug/churn flow, (e) churn flow, (f) falling film flow/annular. (adapted from Kreutzer and co-workers, 2005b).

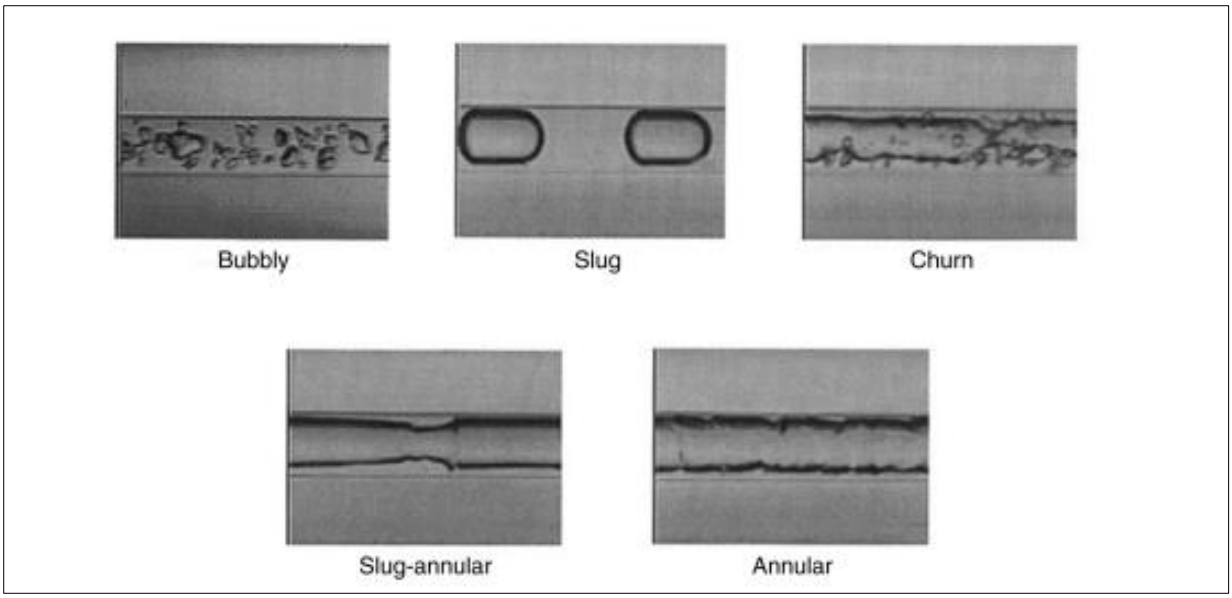


Figure 4-5 Examples of gas-liquid flow patterns in a capillary channel of 1 mm diameter (Triplett et al. 1999).

The boundary between the regimes may be determined by the Weber number, which Rezkallah (1996) based on the gas properties ($We_{Gs} = \rho_G u_{Gs}^2 d/\gamma$). The Weber number is a measure of the relative importance of the fluid's inertia compared to its surface tension, also called the drag force to its cohesion force. Gas density (ρ_G), gas velocity (u_{Gs}), and the diameter of the channel (d) would increase the Weber number, while the surface tension of the liquid (γ) would reduce it. The surface tension dominated regime would occur approximately when $We_{Gs} < 1$ and the inertial regime when $We_{Gs} > 20$. More recently, it was proposed to present flow maps based on the Weber number multiplied by the Ohnesorge number, which considers viscosity (Yagodnitsyna et al., 2016).

The parameters for predicting segmented flow are reasonably well understood in clean liquids, particularly in circular channels (Angeli and Gavriilidis, 2008). However, the presence of impurities such as salts, biomass or second liquid-phase (e.g., silicone oil) and their effect on interfacial tension makes it far more difficult to predict the flow regime.

Mass transfer

The mass transfer is closely related to the flow patterns in the capillary channel. For optimal mass transfer, the preferred flow pattern in capillary channels is segmented flow (also called Taylor flow, intermittent flow, slug flow or bubble train flow), which is a bubble train of alternating liquid slugs and air bubbles with gas and liquid flowing co-currently. Although this flow regime seems to be laminar, the internal liquid circulation increases the mixing of the liquid phase. This recirculating vortex in the liquid slug is the main feature of segmented flow. The mass transfer between the gas and liquid phases is boosted by the internal recirculation within the liquid slug, while mass transfer also benefits from the relatively large interfacial area and small diffusion paths.

Although the first investigations on the gas-liquid mass transfer in glass capillaries under slug flow regime (Irandoust et al., 1992) concluded based on their findings that flow velocity and slug length had no large influence on mass transfer, Berčič and Pintar, (1997) showed that they do actually have a significant effect when they investigated methane absorption into water.

The rate of transport of the compounds through a medium is characterized by resistance to the medium. Input of energy can overcome resistance, such as, for example, mixing in bubble-tank bioreactor to mix the liquid and thereby reducing the diffusion path or to break up air bubbles and thereby increasing the interfacial surface area of the gas bubble with the liquid. The physical input of energy in a system is always limited by the equipment required for the energy input, which will operate with a specific optimal efficiency dependent on its operating conditions. The specific efficiency for example of a mixer is typically ~ 60-70% when operated under optimal conditions. Increasing energy input beyond the optimal condition results in a diminishing benefit on mass transfer. Increased energy consumption results in increased cost of operation, which should be minimized in industrial applications.

The mass transfer using segmented flow is relatively energy efficient, mainly because no energy is required to maintain the small gas bubble size. **Figure 4-6** shows the mass transfer rate versus energy input for typical biotrickling filtration reactors and capillary reactors (Kraakman et al., 2011).

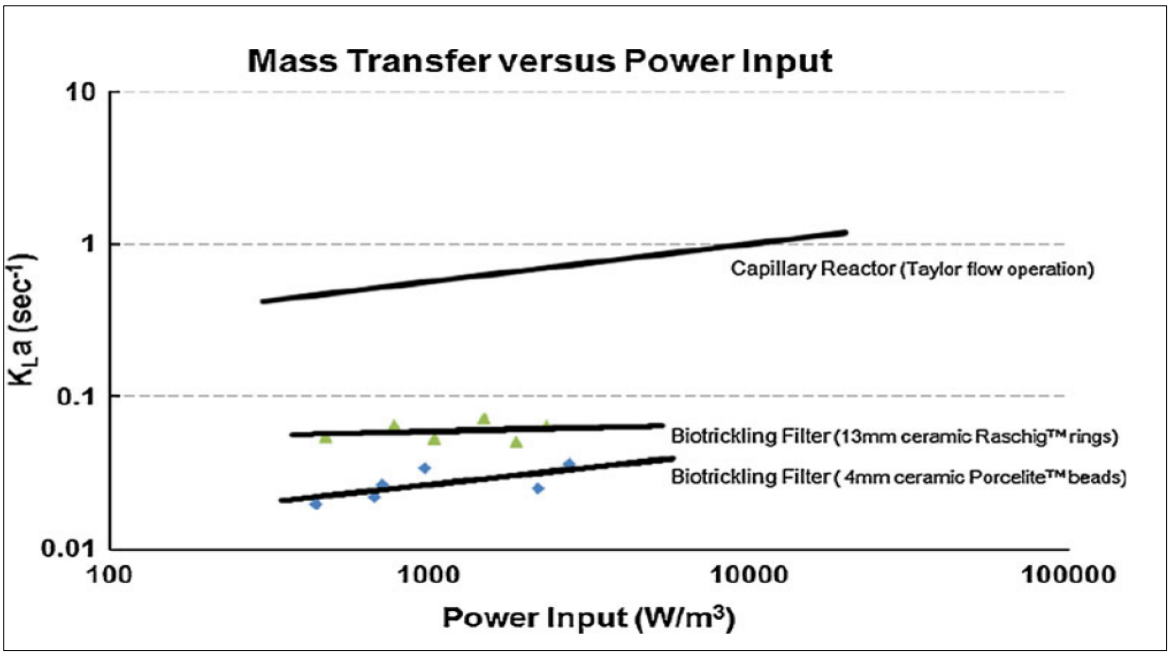


Figure 4-6 Mass transfer and power consumption in capillary reactor operated under segmented flow regime compared to biotrickling filters (Kraakman et al., 2011).

The data for capillary reactors were obtained from Kreutzer et al. (2005a), who illustrated, with an order of magnitude analysis, that the relation between mass transfer rate and the power input per reactor volume for a capillary reactor can be expressed as $k_La \approx 0.1 \times (P/V)^{0.25}$, with P the power input (watt) and V the reactor volume (m^3). The data for the biotrickling filter was obtained from Kim and Deshusses (2008), who were the first to conduct a systematic study to measure mass transfer rates in the most common used biotechnologies for gas treatment (biofiltration and biotrickling filtration).

Good mass transfer is possible in capillary channels because certain gas-liquid flow patterns can create an internal recirculating vortex in the liquid (that is mixing, which enhances the advection in the liquid, something not readily possible in most laminar gas-liquid contactors because the internal structure, i.e. packing, is in the way).

Mass transfer in capillary channels is affected by multiple basic parameters related to the flow pattern, which may include the thickness of the liquid film that surrounds the bubbles

(liquid wall film), the bubble-slug velocity, the bubble, and slug lengths. Mass transfer can occur from the gas bubble to the liquid slug via two routes being (route 1) transfer from the gaseous compounds to the liquid slug at the bubble caps (front and rear) and (route 2) transfer via the liquid film along the gas bubble and the sequential depletion of that liquid film between the wall and the liquid slug as the liquid slug passes by.

Mass transfer - Liquid Wall Film

The thickness of the liquid wall film along the wall of the capillary channel is important for mass transfer when the main mass transfer route is via the liquid wall film (route 2). The liquid wall film thickness is typically only very small compared to the channel diameter. The liquid wall film could be considered stagnant or moving slower than the liquid slug and gas bubble. The liquid wall film and the liquid in the slug do not really mix, and mass transfer between them probably occurs mainly by diffusion rather than convection.

Increased liquid wall film thickness is present when the velocity difference increases between the gas and liquid phase (bubble-slug train velocity and the average liquid phase which includes the liquid wall film and is moving slightly slower).

The film thickness is difficult to measure but can be estimated from the Betherton's correlation as shown in the equation (4-4) below (Betherton, 1961).

$$\delta_F / R = 1.34\, Ca^{2/3} \qquad \text{(Equation 4-4)}$$

Where δ_F is the liquid wall film thickness (m) and R the capillary radius (m) and Ca the capillary number which is defined as $Ca = u \times \mu / \gamma$, where u is velocity (m/s), μ is viscosity (Pa s) and γ the surface tension (N/m). This relationship has shown to be valid for Ca values between about 10^{-3} and 10^{-2}, while at higher Ca values ($Ca > 10^{-2}$) the liquid wall film thickness prediction seems to be improved when using the equation (4-5) below, as discussed by Angeli and Gavriilidis (2008):

$$\delta_F / R = 0.5\, Ca^{1/2} \qquad \text{(Equation 4-5)}$$

At lower Ca values ($Ca < 10^{-3}$) the liquid wall film thickness shows to be substantially thicker than predicted by equation (4-4), most likely due to the presence of surface-active contaminants adsorbed at the gas-liquid interface affecting the liquid wall film thickness. Surfactants at the gas-liquid interface would reduce the liquid wall film thickness due to reduced surface tension.

Mass transfer - Bubble-Slug Velocity and Inertia

The liquid wall film has shown to be also dependant on the inertia when the Ca number is greater than 0.01, which is considered in the Froude number and the Reynold number (Edvinsson and Irandoust, 1996). The Froude number (Fr) is a dimensionless number defined as the ratio of the flow inertia to gravity. The Froude number is based on the speed–length ratio as shown in equation (4-6):

$$Fr = u / (g \times L)^{0.5} \qquad \text{(Equation 4-6)}$$

where u is the local flow velocity (m/s), g is the local external field defined by the gravitational constant (m/s), and L is a characteristic length (m). The Froude number is used to determine the resistance of a partially submerged object moving through water. Fr has an effect at Ca

numbers greater than 0.01 where with increasing *Fr* the film thickness slightly decreases for downward flow, but significantly increases for upward flow in a capillary channel.

The Reynolds number (*Re*) is the dimensional number used to predict fluid flow patterns, such as the transition from laminar to turbulent flow in different situations by calculating the ratio between inertial and viscous forces.

$$Re = \rho \times u \times L / \mu \qquad \text{(Equation 4-7)}$$

where ρ is the density (kg/m^3), u is the liquid velocity (m/s), d is the channel diameter (m) and μ the viscosity (Pa s). *Re* has an increasing effect at higher values for *Re* (De Ryck, 2002) as the liquid wall film thickness continues to increase because of liquid inertia. Inertia is a property that resists changing its state of motion. The effect of liquid inertia was captured by Aussilous and Quere (2000), who after fitting their experimental data resulted in Equation 4-8:

$$\delta_F / R \sim Ca^{2/3} / (1 + Ca^{2/3} - We) \qquad \text{(Equation 4-8)}$$

In summary, several studies have obtained experimental correlations for liquid wall film thickness. Equation (4-4) can be used for condition with low *Ca* values and was shown to be valid for *Ca* values between about 10^{-3} and 10^{-2}, while at higher *Ca* values the liquid wall film thickness prediction seems to be improved when using the equation (4-5). When inertia becomes important equation 4-8 should be used to calculate film thickness (Angeli and Gavriilidis, 2008).

Mass transfer - Bubble Length and Slug Length

The absolute length of the gas bubble (and liquid slug length) will depend on the inlet configuration where the gas and liquid interact. Smaller bubble length may increase mass transfer because the liquid wall film can quickly reach complete saturation each time the gas bubble passes by. A longer gas bubble would in that case not improve mass transfer and mass transfer becomes independent of the gas bubble length.

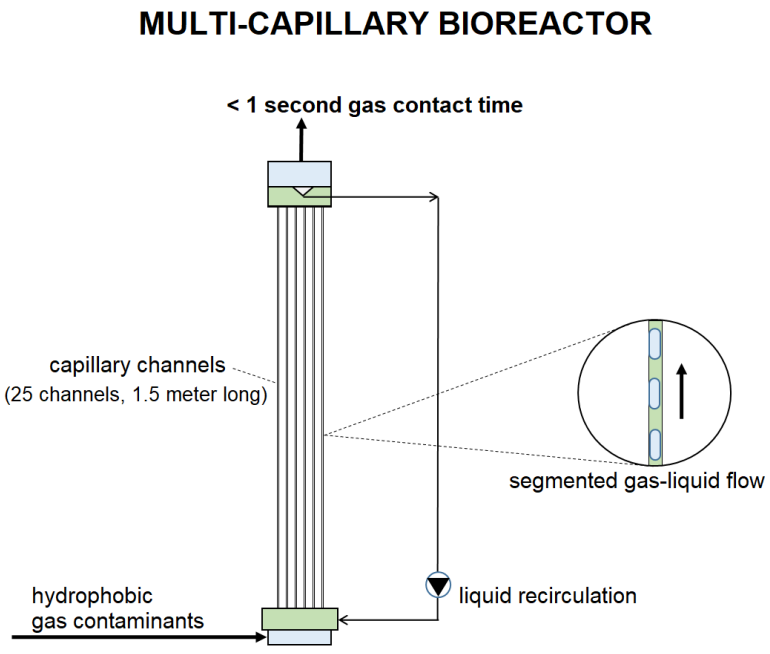
PART II

CAPILLARY CHANNELS AND HYDROPHOBIC CONTAMINANTS

5. HYDROPHOBIC AIR CONTAMINANTS REMOVAL IN A CAPILLARY BIOREACTOR

Chapter overview

Capillary channels were investigated and discussed in this chapter for the continuous mass-transfer of hydrophobic volatile organic compounds under segmented gas-liquid flow pattern (Taylor flow). The work revealed that the overall mass transfer coefficient (K_La) increases most with the gas superficial velocity (UG/L) at each liquid flow evaluated and increased somewhat with gas volume fraction (εG): $K_La = 220\ U_{G/L}^{0.47} / (1 - \varepsilon_G)^{0.18}$. At the highest gas flow evaluated, K_La values above 400 h^{-1} were measured for a wide range of gas to liquid ratios when segmented flow pattern is established. A twenty-five capillary channels bioreactor was designed and built to characterize both mass transfer coefficients and the removal of hydrophobic air contaminants under segmented gas-liquid flow pattern. The removal efficiency of hexane, toluene and α-pinene vapors reached values up to about 75%, 99% and 75%, respectively, at a gas contact time of less than 1 second, which is at least one, but closer to two orders of magnitude shorter than conventional biological gas purification systems. An active contaminant-degrading culture could be sustained in the system and no accumulation of biofilm inside the capillary channels was observed. The bioreactor system showed stable operation during the experiment of 100-days and was robust against three common upset scenarios, possibly facilitated by the highly diverse bacterial community that was observed.



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5.1 Introduction

Biological processes for gas treatment typically operate under mass transfer limited conditions when treating hydrophobic contaminants. Mass-transfer rates may be enhanced by increasing the specific gas-liquid-biofilm contact area in laminar contactors (e.g., biofilters or biotrickling filters) or by increased mixing in turbulent contactors (e.g., stirred tank bioreactors or airlift bioreactors), all requiring an increase in power consumption due to increased pressure losses or increased mixing intensity, respectively (Kreutzer at al., 2005a). Laminar flow refers to a flow regime where gas or liquid flows in parallel layers with minimum disturbance, and where mass transfer is dominated by diffusion. Because diffusion through liquid is relatively slow compared to diffusion through gas, mass transfer enhancement in liquid can be obtained through the motion of the fluid also called advection (e.g., mixing). Capillary reactors with a specific gas-liquid flow pattern (segmented flow pattern) can create internal liquid circulation that has shown to enhance the mass transfer between the gas and liquid phases. Moreover, in a capillary reactor the capillary forces are dominant over other forces as such gravity and viscosity facilitating a low pressure drop over the channels resulting in minimum energy requirements (Peng et al., 2022; Kreutzer et al., 2011; Liu et al., 2005; Kapteijn et al., 1999). In recent years, there has been increasing interest in capillary microreactor technology for process intensification, in multiple applications from emulsion production, synthesis of fine chemicals, and more recently in environmental remediation (Peng et al., 2022). Capillary gas-liquid bioreactors are promising for environmental applications as was shown in earlier studies (Kreutzer et al., 2005a; Lopez De Leon et al., 2020 and 2023; Hoschek et al., 2019; Roche Rios et al., 2013 Ebrahimi et al., 2005; Deaton et al., 2022). However, these studies on capillary gas-liquid bioreactors are limited, mostly dealing with short single capillary channels, limitation test duration or limited in operating conditions or not focused on treating hydrophobic gaseous compounds.

In this study, the fundamental understanding of (1) a multi-capillary channel gas-liquid bioreactor and (2) the removal mechanisms of three model hydrophobic gaseous contaminants were investigated in a capillary bioreactor at extremely low gas contact times. Abiotic and biotic experiments were performed to map the gas-liquid flow patterns at different gas and liquid velocities, followed by the determination of the mass transfer coefficient (K_La) under multi-channel segmented flow conditions. Finally, the performance of a multi-channel capillary bioreactor was investigated for the continuous elimination of three model hydrophobic air contaminants and assessed for operational stability over a 100-day period, while the dynamics of microbial population structure was monitored.

5.2 Material and Methods

Pressure Loss

Prior to selecting the internal diameter of the capillary channel for the capillary bioreactor, the pressure needed for passing ambient air through different capillary channels was determined at different gas velocities. Three glass channels diameters (AFORA; T64, T65 and T67) were used with an internal diameter of 2.4, 3.4 and 5.0 mm, respectively, all 1.5 m in length. The

airflow was measured using a rotameter and the pressure drop was determined using a U-shaped water gauge. The measured pressure losses were converted into Pascal per meter of capillary channel.

Capillary Reactor Set-up

The capillary bioreactor was built of 25 glass capillary tubes with an internal diameter of 2.4 mm, 1 mm wall thickness, and a length of 1.5 m. The liquid phase was recirculated using a pump (0.25 kW ESPA Tecno-05-2M) and measured with a rotameter (Fisher&Porter 10A1197A). The total liquid volume in the bioreactor was 8.4 liter (L). Ambient air from a compressor (ABAC LT50) was introduced in the bottom reservoir via a 3 mm thick perforated PDMS membrane containing about 400 needle holes with a diameter of 0.4 mm. The airflow and the pressure were measured with a rotameter (Aalborg, S/N 51588-2) and a pressure sensor (IFM PN7097), respectively. A schematic representation of the set-up is shown in **Figure 5-1**.

Liquid-Gas Flow Mapping

Different liquid-gas flow patterns can be obtained in a capillary channel (**Figure 5-2**). The gas-liquid flow pattern for optimal mass-transfer is the segmented flow pattern, also called bubble train flow or Taylor flow, characterized by alternating gas bubbles and liquid slugs with lengths greater than the capillary diameter (Liu et al., 2005; Kreutzer et al., 2005b). In this flow regime, the internal liquid circulation increases the gas-liquid mass transfer through local mixing without affecting the axial dispersion (Liu et al., 2005). The establishment of the segmented flow regime was determined visually by varying the gas to liquid flowrate ratio (G/L ratio) and the gas-liquid superficial velocities ($U_{G/L}$), with the gas and liquid flows varied between 1.4 and 23.5 L min^{-1} and 1 to 14 L min^{-1}, respectively. Successful segmented flow was considered when the flow pattern could be established along the entire capillary channel length and in all 25 channels. The gas and liquid consisted of ambient air and demineralized water containing 0.3 M Na_2SO_4, while the segmented flow was also mapped with liquid containing biomass (0.25, 0.5 or 1.0 g dry weight L^{-1}).

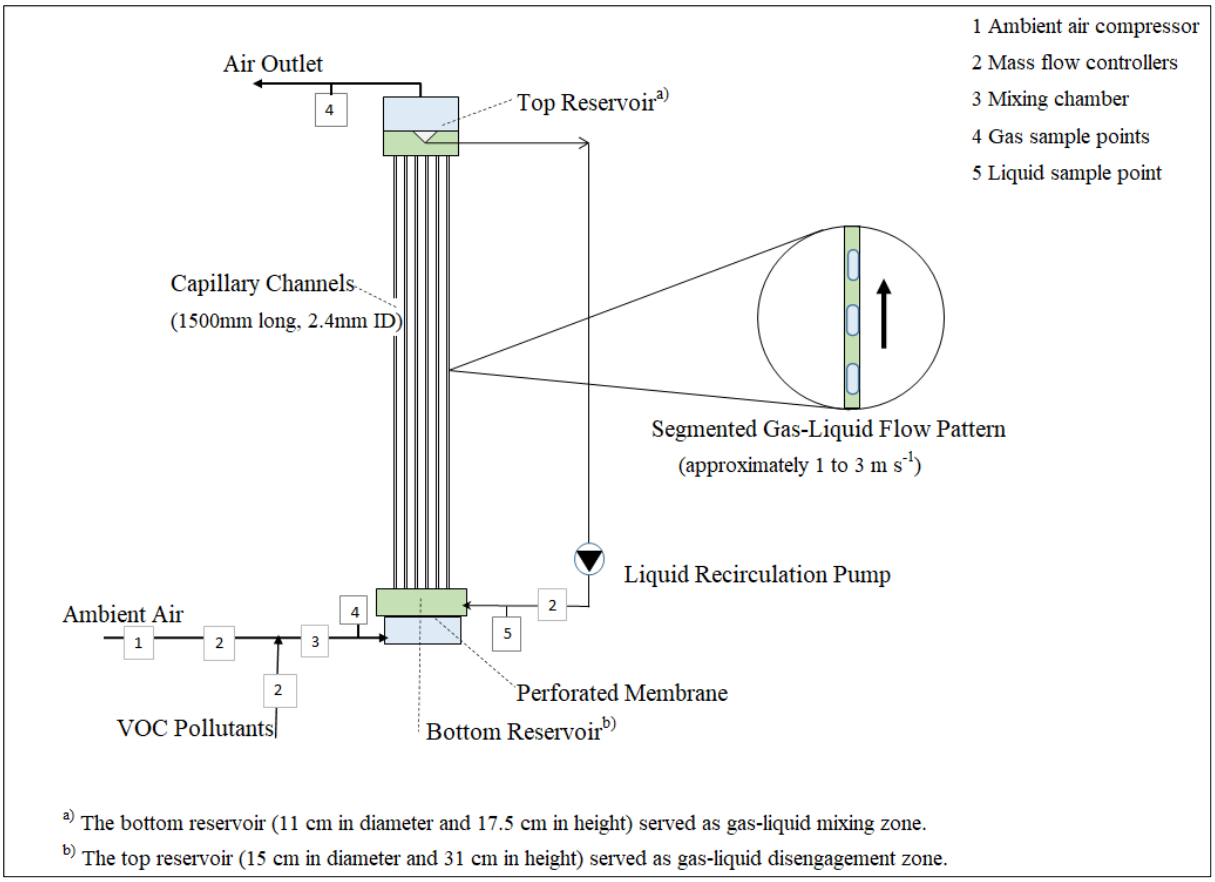


Figure 5-1 Schematic representation of the experimental set-up of the capillary bioreactor.

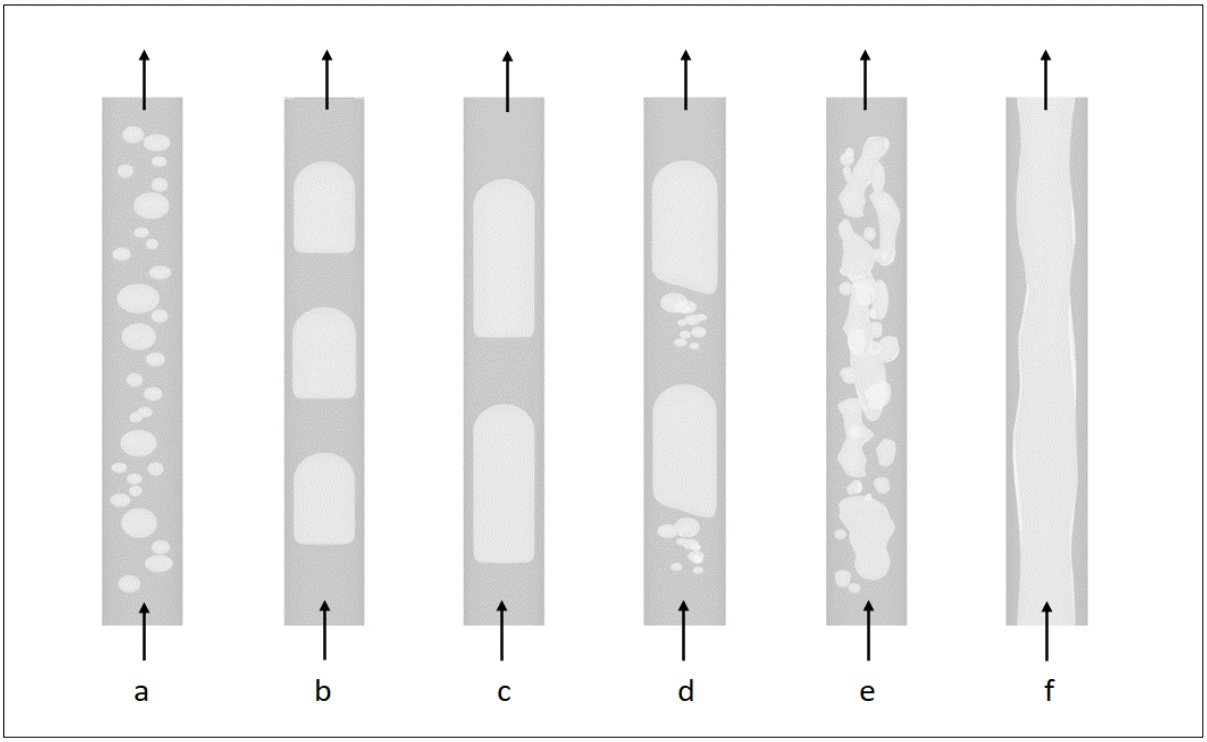


Figure 5-2 Schematic of possible gas-liquid flow patterns in a capillary channel with (a) bubbly flow, (b, c) segmented flow, (d) transition slug/churn flow, (e) churn flow, (f) falling film flow. (adapted from Kreutzer and co-workers, 2005).

Mass Transfer Coefficients

The mass transfer rate for oxygen from the gas phase to the liquid phase (K_La) was determined in the capillary reactor for several segmented flow conditions (liquid flowrates of 2.0, 6.0 and 10.0 L min^{-1} and gas flowrates of 5.8, 9.0 and 12.4 L min^{-1}). The K_La was quantified by the sulfite method, which measures the oxygen transfer rate (OTR) using a rapid Co^{2+}-catalysed reaction of oxygen with sulfite at the gas-liquid interphase, as evaluated by Munoz and co-workers (Munoz et al., 2018). It measures the maximum rate of oxidation of sodium sulfite to sodium sulfate resulting from the oxygen transfer from the gas phase to the liquid in which there is no dissolved oxygen. The K_La experiments were performed in duplicate, and the results are given as the average value ± standard deviation from the duplicate assays.

Hydrophobic Compound Removal

The capillary bioreactor was inoculated on day one (t=0) with an equal amount of biomass from a chemostat bubble column fed with hexane, toluene, trichloroethylene and alpha-pinene, and fresh activated sludge from Valladolid wastewater treatment plant, to obtain an initial biomass concentration of 0.2 g dry weight L^{-1}. A mixture of volatile organic compounds (VOCs) was continuously injected to the inlet airstream using a syringe pump (Fisherbrand Model 100). The VOC mixture contained hexane, toluene and α-pinene as model compounds representing air contaminants different in hydrophobicity and biodegradability.

The system was continuously operated at room temperature (20 ºC) at a gas and liquid flow of 13.9 L min^{-1} and 8 L min^{-1}, respectively. This resulted in an average gas contact time in the capillary channels of 0.5 second, where the average gas contact time is calculated as follows (Eq. 5-1):

$$(V_c \times n_c) / (Q_L + Q_g) \qquad \text{(Equation 5-1)}$$

where V_c the internal volume of the capillary channels (L), n_c the number of capillary channels (-), Q_L is the measured liquid flow rate (L/s), and Q_g the measured gas flow rate (L/s). The liquid was recirculated in a closed loop and demineralized water was added to compensate evaporative water losses. The inlet concentration of the individual VOCs was maintained for 25 days between 5 and 10 mg m^{-3} (Stage I) and between 2 and 5 mg m^{-3} from day 25 to 100 thereafter (Stage II). Liquid samples were taken periodically downstream of the recirculation pump to determine the biomass concentration, the bacterial population structure, pH and conductivity.

Reliability Tests

The reliability of the capillary bioreactor for the abatement of VOCs was investigated after 6 weeks of steady state operation. Process performance (robustness) was evaluated after three upsets scenarios commonly found in industrial gas treatment systems and known to often affect the performance of biological gas treatment systems. Upsets were initiated on days 40, 47 and 61, and consisted of (A) 48 hours of liquid recirculation interruption (pump stopped simulating a pump failure), (B) 48 hours of inlet air interruption (inlet air supply disconnected simulating a fan failure), and (C) 48 hours of both liquid recirculation and inlet air interruption (pump stopped and inlet air supply disconnected, simulating a power supply failure). Upset

scenario A does not stop the VOCs supply but eliminates mass transfer of the VOCs to the liquid containing the microbes. Scenario B and C involves discontinuing the VOC supply which results in starvation of the microbial community. VOC removal in the capillary bioreactor after each simulated upset was measured every 1.5 hours on the first day after restoring normal operating conditions and once per day any day after.

Analytical Methods

VOC concentrations in the inlet and outlet airstreams were measured daily with a GC-FID using Solid Phase Microextraction (SPME) as a preconcentration step (10 minutes SPME-fibre exposure to the air in a 250 mL glass cylinder installed upstream and downstream of the reactor). The GC-FID (BRUKER-3900) was equipped with an Agilent HP-5MSI capillary column (30 m×0.25 mm×0.25 µm). The temperatures in the injector and detector were maintained at 150 and 200 ºC, respectively. The oven temperature was set at 40 ºC for 1.5 min, then increased at 10 ºC min^{-1} to 50 ºC, then after 1 minute increased at 40 ºC min^{-1} to 250 ºC. Nitrogen at 2.5 mL min^{-1} was used as carrier gas and as make-up gas (25 mL min^{-1}). Hydrogen and air flowrates were set at 30 and 300 mL min^{-1}. The SPME-fibres (CAR/PDMS 85µm, Supelco) were initially conditioned at 300 ºC for 1 hour prior to calibration, and a cleaning run was performed before sampling with the above-described GC-FID method. Standards of the hexane, toluene and α-pinene, prepared in 250 mL glass bulbs, were used for quantification using the above-mentioned pre-concentration conditions.

Biomass concentration in the liquid phase was quantified according to Standard Method 2540 D, as well as pH (Crison BASIC-20+) and conductivity (Crison BASIC-30) (APHA et al., 2017). The population structure of the mixed inoculum and biomass present in the capillary bioreactor was determined at the end of Stage I (day 38) and at the end of Stage II (day 100). Genomic DNA was extracted using the MagNA Pure LC DNA Isolation Kit III. Library preparation and Illumina sequencing were performed at the University of Valencia (FISABIO). In brief, library preparation consisted in the generation of 16S rDNA gene amplicons following the 16S rDNA gene Metagenomic Sequencing Library Preparation Illumina protocol (Cod. 15044223 Rev.A). The V3–V4 region of the 16S rRNA gene was amplified using the primers 341F (50-CCTACGGGNGGCWGCAG-30) and 785R (50-GACTACHVGGGTATCTAATCC-30) (Klindworth et al., 2013). Index and sequencing adaptors were added to the gene-specific sequences. The amplicons obtained were quantified on a Bioanalyzer DNA-1000 (expected size ~550 bp). After size verification, the libraries were sequenced using a 2x300pb paired-end run (MiSeq Reagent kit-v3 (MS-102-3001)) on a MiSeq Sequencer (Illumina). R packages used for data analysis included Knitr (Xie, 2014), Knitcitations (Boettiger, 2014), Markdown (Allaire, et al., 2014), Biostrings (Pagès et al., 2020) and Vegan: community ecology package (Oksanen, et al., 2017).

Chemicals

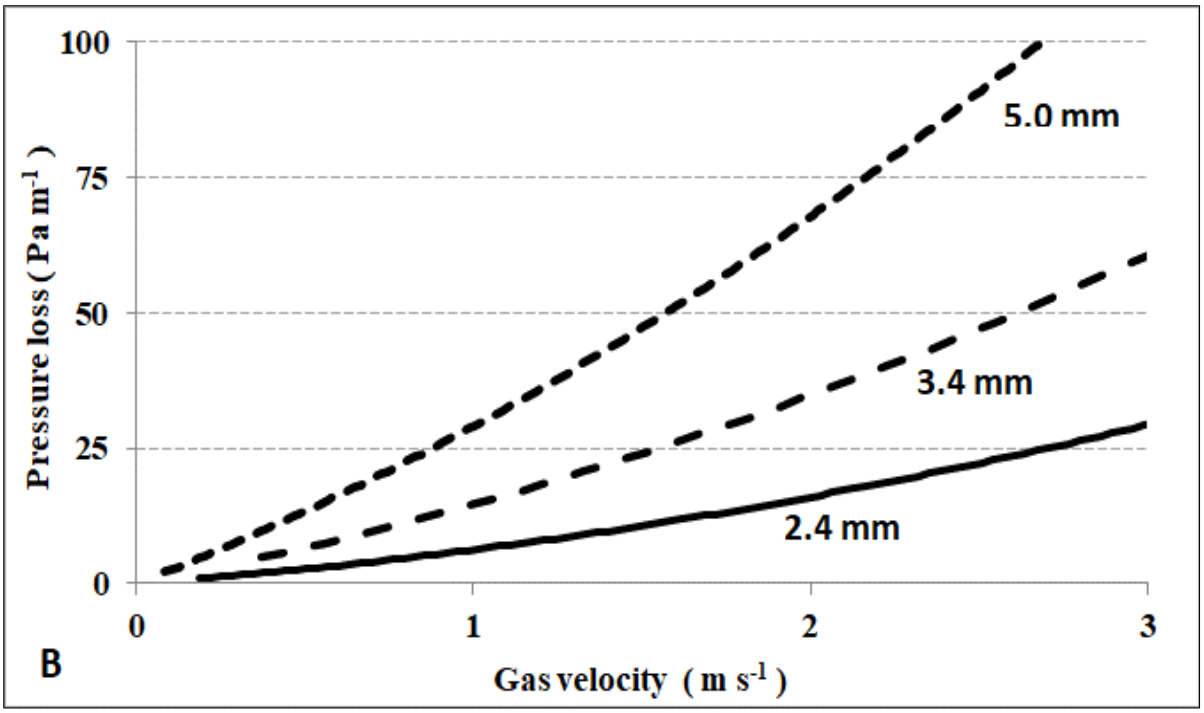
The liquid in the capillary bioreactor consisted of a mineral salt medium containing KH_2PO_4 (0.7 g L^{-1}), $K_2HPO_4{\cdot}3\ H_2O$ (0.920 g L^{-1}), KNO_3 (3 g L^{-1}), NaCl (0.2 g L^{-1}), $MgSO_4{\cdot}7\ H_2O$ (0.35 g L^{-1}), $CaCl_2{\cdot}2\ H_2O$ (0.026 g L^{-1}) and 2 ml L^{-1} trace minerals solution containing EDTA (0.5 g L^{-1}), $FeSO_4{\cdot}7\ H_2O$ (0.2 g L^{-1}), $ZnSO_4{\cdot}7\ H_2O$ (0.01 g L^{-1}), $MnCl_2{\cdot}4\ H_2O$ (0.003 g L^{-1}), H_3BO_3 (0.003 g

L^{-1}), $CoCl_2 \cdot 6\ H2O$ (0.02 g L^{-1}), $CuCl_2 \cdot 2\ H_2O$ (0.001 g L^{-1}), $NiCl_2 \cdot 6\ H_2O$ (0.002 g L^{-1}) and $NaMoO_4 \cdot 2\ H_2O$ (0.003 g L^{-1}). The chemicals used for mineral salt medium preparation (PANREAC, Barcelona, Spain) had a purity of at least 99.0%, while the VOCs hexane (Sigma-Aldrich, Madrid, Spain), toluene (Panreac, Barcelona, Spain) and alpha-Pinene (Sigma-Aldrich, Madrid, Spain) had a purity of 95%, 99.5% and 98%, respectively.

5.3 Results and Discussion

Pressure Loss

Selection of the capillary channel diameter for the capillary reactor considered mass-transfer in the capillary channel (a better mass transfer leads to smaller reactor size) as well as the pressure losses over the capillary channel (an increased pressure loss results in increased energy requirements, typically the main cost for operating a gas treating bioreactor). The overall pressure drop of a capillary reactor is the sum of the pressure losses caused by the liquid slugs and the air bubbles. The required pressure for passing air through a capillary channel was here experimentally determined for three glass capillary channels (internal diameters 2.4, 3.4 and 5.0 mm) at different gas velocities while the required pressure for passing liquid through a capillary channel was calculated.



Figures 5-3 The pressure loss per meter of glass channel of ambient air flowing through glass channels with an internal diameter of 2.4, 3.4 and 5.0 mm as a function of the superficial gas velocity.

The measured pressure losses were lower than 100 Pa m^{-1} for air velocities between 0.1 and 2 m s^{-1}, which are typical gas-liquid superficial velocities required to obtain segmented flow pattern and consistent with those measured by Liu and co-workers (Liu et al., 2005; Kreutzer et al., 2005b). The results of the measured pressure losses show that the pressure loss for conveying a certain amount of gas at identical gas velocity is lower when the diameter

of the capillary channel is reduced (**Figure 5-3**), this may be explained by the air velocity being more laminar in the smaller diameter channels. The measured pressure drops in glass channels used in this study were in similar range to those measured in silicone tubing as reported elsewhere (Kraakman et al., 2008). Hence, while a smaller diameter capillary channel requires more channels to convey a certain amount of air, the overall pressure loss per meter of channels is lower in smaller diameter channels when conveying gas only.

The total pressure loss per length unit in a capillary channel with air-water segmented flow is caused by several frictions. The most significant pressure loss for small capillary channels is caused by the wall friction of the liquid slug and, in case of vertical channel configurations, by the static head especially at larger diameter channels. The liquid wall friction can be estimated using the Hagen-Poiseuille equation (Eq. 5-2), while the static head can be calculated using the volume and density of the liquid slugs.

$$dP_{LWF} / L = 32 \mu U_L / d^2 \qquad \text{(Equation 5-2)}$$

where dP_{LWF} stands for the pressure loss in a capillary caused by liquid wall friction (Pa), L the length of the capillary channel (m), μ the viscosity (Pa s), U_L the superficial velocity of the liquid slug (m s^{-1}), and d the diameter of the capillary channel (m).

Based on the measured pressure loss by the gas (air bubble) and the calculated pressure loss by the liquid (liquid slug), it can be estimated that the total pressure loss per meter capillary channel will range between a few hundred to about thousand Pascal assuming a gas-liquid superficial velocity range of 1 to 2 m s^{-1}, a G/L ratio of 4, and a channel internal diameter between 2.4 and 5.0 mm. This pressure loss is in the similar range of conventional gas treatment technologies. The 2.4 mm internal diameter glass channel was therefore selected for the construction of the multi-capillary reactor since the pressure losses would be still relatively low, while maintaining proper capillarity.

Liquid-Gas Flow Mapping

The establishment of the segmented flow regime was determined visually in the capillary reactor containing a bundle of twenty-five 2.4 mm diameter channels. **Figure 5-4** shows a map of the liquid and gas flow conditions supporting segmented flow. The liquid slug lengths in the capillary channels of the tested capillary reactor system varied between two and about ten times the channel diameter (0.5 to 3 cm), with no significant redistribution inside the channels, i.e., the slug size was unchanged along the height in the reactor. The segmented flow pattern could be observed easily, although at high gas and liquid velocities, it became difficult to distinguish it from churn flow where small groups of bubbles appear at the rear of the liquid slug (see also **Figure 5-2**). The conditions for which segmented flow could be maintained were broad, although more limited when compared to other studies such as Rocha-Rios and co-workers (2013), Kapteijn and co-workers (1999) and Bercic and Pintar (1997), all measured in a single capillary channel at lower gas and liquid superficial velocities. The difference with our study can be explained by our gas-liquid distributor, which required a minimum gas flow and liquid flow to provide sufficient gas-liquid mixing in the inlet reservoir of the capillary reactor to provide segmented flow consistently in all channels.

Pertinent to obtaining segmented flow is the surface tension which must be dominant over other forces such as gravity. The Bond number (Bo) is the ratio of the gravitational force to the surface tension force (Eq. 5-3), where a low value of the Bond number indicates that the surface tension dominates in a system.

$$Bo = \rho g d^2 / \gamma \qquad \text{(Equation 5-3)}$$

where ρ is the liquid density (kg m^{-3}), g the gravitational constant (m s^{-2}), d the inner diameter of the capillary channel (m), and γ the surface tension (N m^{-1}). Kreutzer and co-workers (2005b) proposed that a Bo number lower than 3.3 is required to obtain a segmented air-water flow pattern in a single channel. This threshold would be achieved for a capillary channel with an internal diameter of less than about 5 mm while using water and ambient air at room temperature. However, our results showed that additional conditions are required in a multi-channel reactor such as sufficiently high superficial gas-liquid velocities so that adequate gas-liquid mixing and distribution can be achieved in the bottom gas-liquid mixing reservoir.

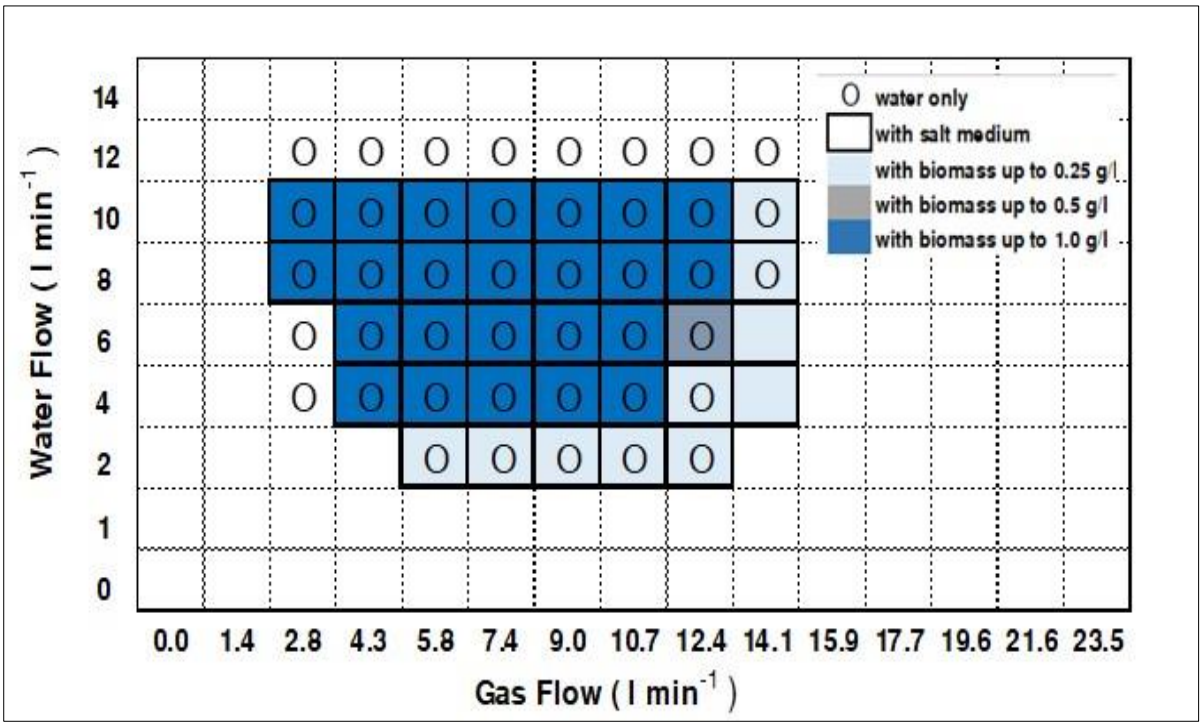


Figure 5-4 Occurrence of segmented flow in the capillary reactor in all the twenty-five channels under the different gas flowrate and liquid flowrate conditions using water only, salt medium and biomass additions to the mineral salt medium.

The impact of the salt media and biomass (compared to demineralized water) on the gas-liquid flow pattern is shown in **Figure 5-4**. The presence of salt as well as biomass reduced in general the range of gas-liquid conditions for which segmented flow could be established, mostly at the lower end of the liquid flow rate and at the higher end of the gas flow rate.

Mass Transfer Coefficients

The results of the measurements for gas-liquid mass transfer coefficient (K_La) for oxygen transfer in the capillary reactor under nine different gas and liquid flow conditions are shown

in **Table 5-1**. The highest K_La value of 462 h^{-1} was recorded at a gas flow rate of 9 L min^{-1} and a G/L ratio of 1.5, which corresponds to an average superficial gas and liquid slug velocity in the capillary channel of 3.2 m s^{-1}, assuming that the liquid wall film thickness is negligible. Values above 400 h^{-1} were all measured at the relatively high gas flow of 12.4 L min^{-1} for all G/L ratios tested ranging from 1.2 to 6.2, corresponding to an average gas contact time in the channel of ~ 0.5 s to ~ 0.7 second, respectively.

Table 5-1 Influence of the gas and liquid flowrate on the oxygen mass-transfer in the capillary reactor. Values presented as the steady-state average with the corresponding standard deviation (± SD, n = 2).

Liquid Flow (L min^{-1})	Gas Flow (L min^{-1})	G/L Ratio (-)	ε_G (-)	$U_{G/L}$ (m s^{-1})	RT_G (s)	K_La (h^{-1})
2.0	5.8	**2.9**	0.75	1.2	**1.3**	**294 ± 16**
2.0	9.0	**4.5**	0.82	1.6	**0.9**	**328 ± 16**
2.0	12.4	**6.2**	0.86	2.1	**0.7**	**436 ± 16**
6.0	5.8	**1.0**	0.49	1.7	**0.9**	**349 ± 2**
6.0	9.0	**1.5**	0.60	2.2	**0.7**	**462 ± 12**
6.0	12.4	**2.1**	0.67	2.7	**0.6**	**446 ± 7**
10.0	5.8	**0.6**	0.37	2.3	**0.6**	**356 ± 4**
10.0	9.0	**0.9**	0.47	2.8	**0.5**	**369 ± 11**
10.0	12.4	**1.2**	0.55	3.3	**0.5**	**415 ± 12**

Correlating the mass transfer data obtained for the capillary reactor operated under the conditions tested using a continuous stirred tank reactor (CSTR) model similarly to that proposed by Bercic and Pintar (1997), results in the following equation (Eq. 5-4):

$$K_La = 220\ U_{G/L}^{\ 0.47} / (1 - \varepsilon_G)^{\ 0.18} \qquad \text{(Equation 5-4)}$$

where K_La is the overall mass transfer coefficient (h^{-1}), $U_{G/L}$ the gas bubble-liquid slug superficial velocity (m s^{-1}) and ε_G the average gas volume fraction (-) in the channels of the capillary reactor (**Figure 5-5**).

The unit length (i.e., gas bubble length + liquid slug length) was non-homogeneous among the twenty-five capillary channels as can be expected, with the average unit length estimated to be about 3 cm and did not change notably with the conditions evaluated. The K_La was found to be mostly related by the gas bubble-liquid slug superficial velocity ($U_{G/L}$) and less by the gas-liquid ratio (i.e., the average gas volume fraction ε_G), which is consistent with the observations made by Bercic and Pintar (1997), but here defined for a multi-channel reactor under higher flow rates and with liquid containing the salt media. The gas-liquid distribution using a perforated membrane in the capillary reactor in our study made it possible to use multiple capillary channels bundled in one reactor. However, it did not allow to control the gas bubble and liquid slug lengths independently, and thus the impact of these individual lengths could not be analyzed.

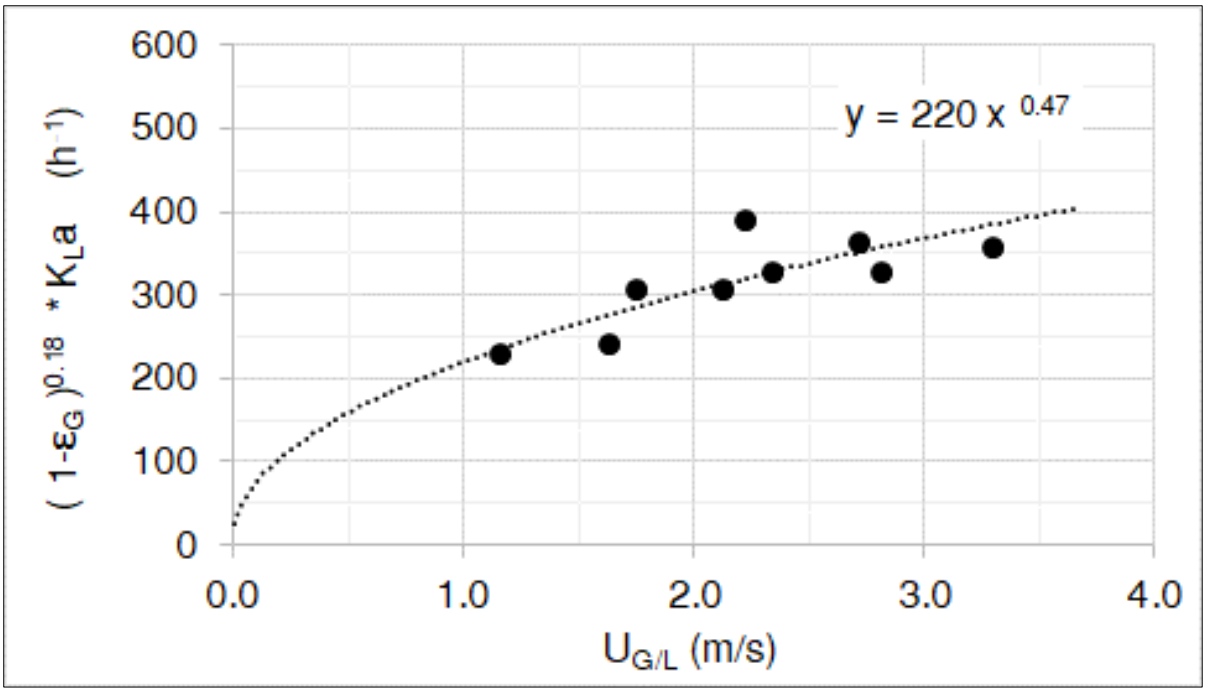


Figure 5-5 Correlation of the mass transfer data to the gas bubble-liquid slug superficial velocity ($U_{G/L}$) and the average gas volume fraction (ε_G) of the gas bubble-liquid slug.

The overall mass transfer coefficients measured in this study (> 400 h^{-1}) were superior, especially when taking into account the extremely short gas contact time, compared to those reported for conventional biological gas treatment systems, with K_La values ranging typically between 20 and 250 h^{-1}, as measured for biotrickling filters or conventional bubble column bioreactors and typically requiring longer gas contact times (Kim and Deshusses, 2007; Dorado et al., 2009; Lebrero et al., 2012 a; San-Valero et al., 2014; Petersen and Arvin, 1995).

Hydrophobic Compound Removal

Continuous treatment of the hydrophobic contaminants was established in the capillary bioreactor at an air flow and liquid flow of 13.9 L min^{-1} and 8 L min^{-1}, respectively, which corresponds to a gas contact time of 0.5 seconds in the capillary channel. Operation and performance were stable without replenishing the liquid in the reactor; the pH of the recirculating liquid remained at 7.6 during the entire experiment (100 days), which suggested that no acidic or alkaline (potentially toxic) metabolite accumulated.

A significant removal of the three VOCs was observed after inoculating the capillary bioreactor (**Figure 5-6**), with a gradually increasing toluene removal during the first two days indicating growth or acclimation. The removal efficiencies of hexane, toluene and α-pinene averaged 58 ± 10%, 90 ± 5% and 30 ±12%, respectively, during Stage I. The lowering of the inlet VOC concentration (day 25) did not significantly change the removal efficiency of hexane or toluene, which were on average 57 ± 6% for hexane and 92 ± 8% for toluene during Stage II. In contrast, the average removal of α-pinene increased from 30 ± 12% during Stage I to 46 ± 15% during Stage II, while, in general, a less consistent removal was observed for α-pinene.

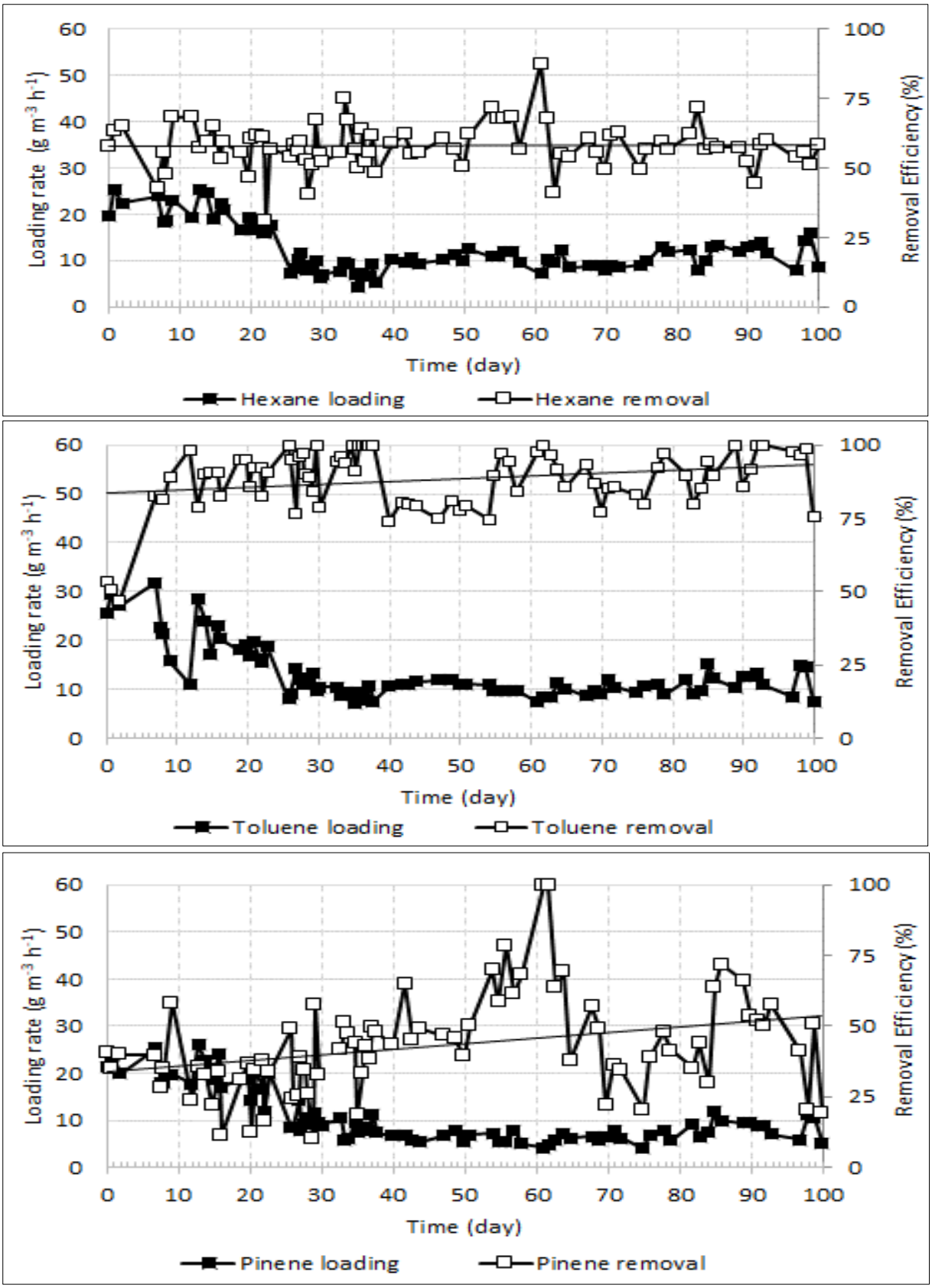


Figure 5-6 Time course of the loadings rate (■) and removal efficiencies (□) of hexane (upper), toluene (middle) and α-pinene (lower) in the capillary bioreactor during Phase 1 (day 0 – 25) and Phase 2 (day 25 – 100). The straight line shows the overarching trend of the removal efficiency during the 100-day testing period.

The VOC removal efficiencies observed were high considering that the gas contact time in the capillary channels was only 0.5 second, and that the inlet VOC concentrations were low, which reduced the driving force for mass transfer from the gas to the liquid as illustrated by Eq. 6-5:

$$R = K_L a \, (C_G/K_H - C_L) \qquad \text{(Equation 5-5)}$$

where R is the mass transfer rate (g m^{-3} h^{-1}), $K_L a$ the overall mass transfer coefficient for each VOC (h^{-1}), C_G the contaminant concentrations in gas (g m^{-3}), K_H Henry-coefficient (dimensionless) and C_L the contaminant concentrations in the liquid phase (g m^{-3}) (Koch, 1990).

Of the three model VOCs evaluated, toluene has the lowest dimensionless Henry-coefficient (K_H = 0.5) and was removed consistently better than hexane and α-pinene, confirming that K_H is a determining factor for mass transfer. However, α-pinene has a lower dimensionless Henry-coefficient (K_H) than hexane (5 versus 71), meaning gas α-pinene is significantly better absorbed in water and thus more bioavailable than hexane at equal gas concentration. Moreover, α-pinene has a higher octanol-water partitioning coefficient ($K_{o/w}$) than hexane (4.5 vs. 3.1). The octanol-water partition coefficient is commonly used to classify the hydrophobicity of a compound and has been recognized as an indication of the uptake of a contaminant into biological membranes. In addition, presence of biomass in the liquid can influence the Henry-coefficient as discussed by Barton and co-workers (2008) and they recommended the use of $K_{o/w}$ rather than the K_H to calculate mass-transfer from gas to water – biomass mixtures. Although the authors showed that the use of $K_{o/w}$ does not always predicts the correct mass-transfer value, they observed that the effect of biomass on the Henry coefficient (trend and order of magnitude) is described correctly. In our study, both K_H and $K_{o/w}$ do not explain why hexane was better removed than α-pinene and may suggest that α-pinene removal was hampered by biokinetic limitations.

The biodegradation of α-pinene may be more complex due to its larger molecular weight and its different (cyclic) structure than hexane. The biodegradation of α-pinene may involve its partial enzymatic conversion outside the bacterial cell into smaller compounds that can then be taken up more readily by the bacterial cells, according to the mechanism proposed by Miller and Allen (2000).

The capillary reactor set-up contained an inlet reservoir (gas-liquid mixing zone) and the outlet reservoir (gas-liquid disengagement zone), and it can be assumed that most of the biodegradation takes place within the reservoirs (as they hold most of the liquid containing the biomass). It can also be assumed that nearly all the gas-liquid mass-transfer takes place inside the capillary channels as the air bubbles are relatively large (estimated about 0.6 cm in diameter on average). However, the experimental setup was chosen for practical reasons and scaling-up the capillary bioreactor system would require a more optimized configuration of the reservoirs (with a reduced liquid height) to minimize the hydrostatic pressure losses across the liquid phases.

Bioreactor Reliability Tests

Reliability is the combination of robustness and resilience, where robustness reflects the capacity of a system to maintain its functionality when subjected to changes. The resilience is the rate at which a system returns to its original state after being perturbed. Both the robustness and resilience were evaluated for three common upset scenarios likely to occur in actual biological gas treatment systems: water pump failure, air fan failure and power supply failure. The results showed that both upset test A (the 48-hour interruption of the liquid recirculation) and upset test B (the 48-hour interruption of the air supply) impacted the removal of toluene only: removal of toluene dropped from steady state values >95% to about 80% immediately after restoring liquid recirculation. Two weeks were needed for the capillary bioreactor system to fully recover preceding toluene removal capacity. It is interesting to note that the third upset test two weeks later (upset test C: stopping both the liquid recirculation and the air supply) did not impact the removal of toluene. This indicates an increased robustness of the biomass community towards liquid recirculation and air supply interruptions after being exposed a few weeks before to upset A and B. None of the upset tests did negatively affect the removal of hexane and α-pinene. Upset test C resulted in a temporary increase of the removal of α-pinene from 65% to about 100% the first day after restoring the normal operation conditions and may be explained by a transient sorption effect.

Relevant to long-term stability of the process is the observation that segmented flow in the capillary bioreactor could be maintained throughout the 100-day study. Overall, these results show that stable operation and performance of the capillary bioreactor could be maintained over extended periods of time and was not significantly affected by the tested upsets.

Microbial Characterization

The biomass content was on average 0.25 ± 0.06 g dry weight L^{-1} and increased during 100-days of operation of the bioreactor from 0.20 g L^{-1} (day 1) to 0.29 g L^{-1} (day 100). This indicates that biomass can be sustained in a capillary bioreactor even at the relatively low inlet VOCs concentrations tested in this study. The successful application of capillary bioreactor systems for air pollution control also requires absence of clogging of the individual capillary channels with biomass over time. No signs of biomass accumulation in any of the capillary channels were observed during the 100-days operation with the biomass in the bioreactor a suspended cell culture. This observation is consistent with the findings of Lopez de Leon and co-workers (2020) who also did not observe biofilm formation inside capillaries when operated at higher VOC concentrations favorable to biomass growth. This is also consistent with Studer (2003) showed that biofilm accumulation could easily be controlled with relatively low shear forces. Thus, it is likely that the high recirculating liquid velocity inside the capillaries caused sufficient shear to prevent biomass accumulation.

Biological characterization of the cultures involved revealed that high-quality filtered reads were obtained after sequencing of the V3–V4 region of the 16S rRNA gene in the different biomass samples of the inocula and bioreactor culture broth. The rarefaction curves reached the plateau, indicating that the sequence depth was sufficient to represent the diversity of the bacterial community in the samples (**Figure 5-7A**). The diversity of the bacteria

in the capillary reactor on day 38 and day 100 was ~ 300 Operational Taxonomic Units (OTUs), with an OTU the operational definition commonly used to classify groups of closely related species.

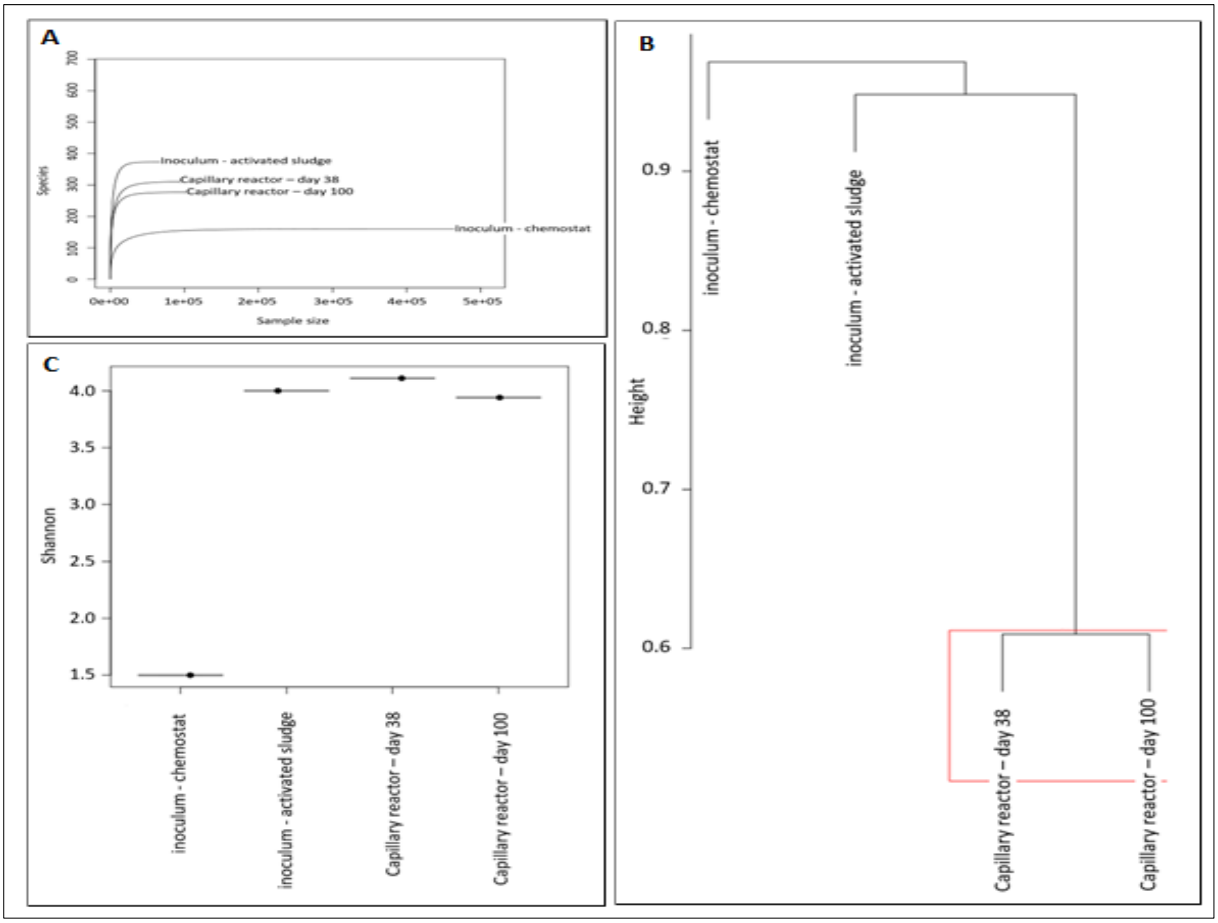


Figure 5-7 The biological characterization of the cultures involved illustrating the rarefaction curves of OTUs (A), the hierarchical cluster dendrogram of bacterial communities; the height axis displays the distance between observations and/or clusters; the horizontal bars indicate the point at which two clusters/observations are merged (B), the Shannon diversity index values (C).

Cluster analysis showed a clear separation of the structure of microbial communities between the inoculum samples and the samples collected from the capillary bioreactor (**Figure 5-7B**). Interestingly, the observed bacterial diversity of the samples based on Shannon index values was markedly high in the capillary bioreactor samples (**Figure 5-7C**). Despite the high diversity of the Inoculum-Activated Sludge sample, the composition of the bacterial community drastically changed in the capillary bioreactor (**Figure 5-8**), most probably because of the different substrates used for bacterial growth resulting in different selective pressure. The high diversity may also be key to support the resilience of the microbial communities towards perturbations, which may explain the high robustness of the capillary bioreactor against the upset scenarios applied (Girvan et al., 2005; Saikaly et al., 2011; Rodriguez et al., 2017).

Overall, Proteobacteria and Bacteroidota represented the dominant phyla in both capillary bioreactor samples, followed by Actinobacteria, Planctomycetota, Verrucomicrobia,

Chloroflexi and other less represented phyla (**Figure 5-8**). The relative abundance of members of Actinobacteria, Bacteroidota and Chloroflexi increased after the reliability tests applications, suggesting their ability to better cope with the tested upsets.

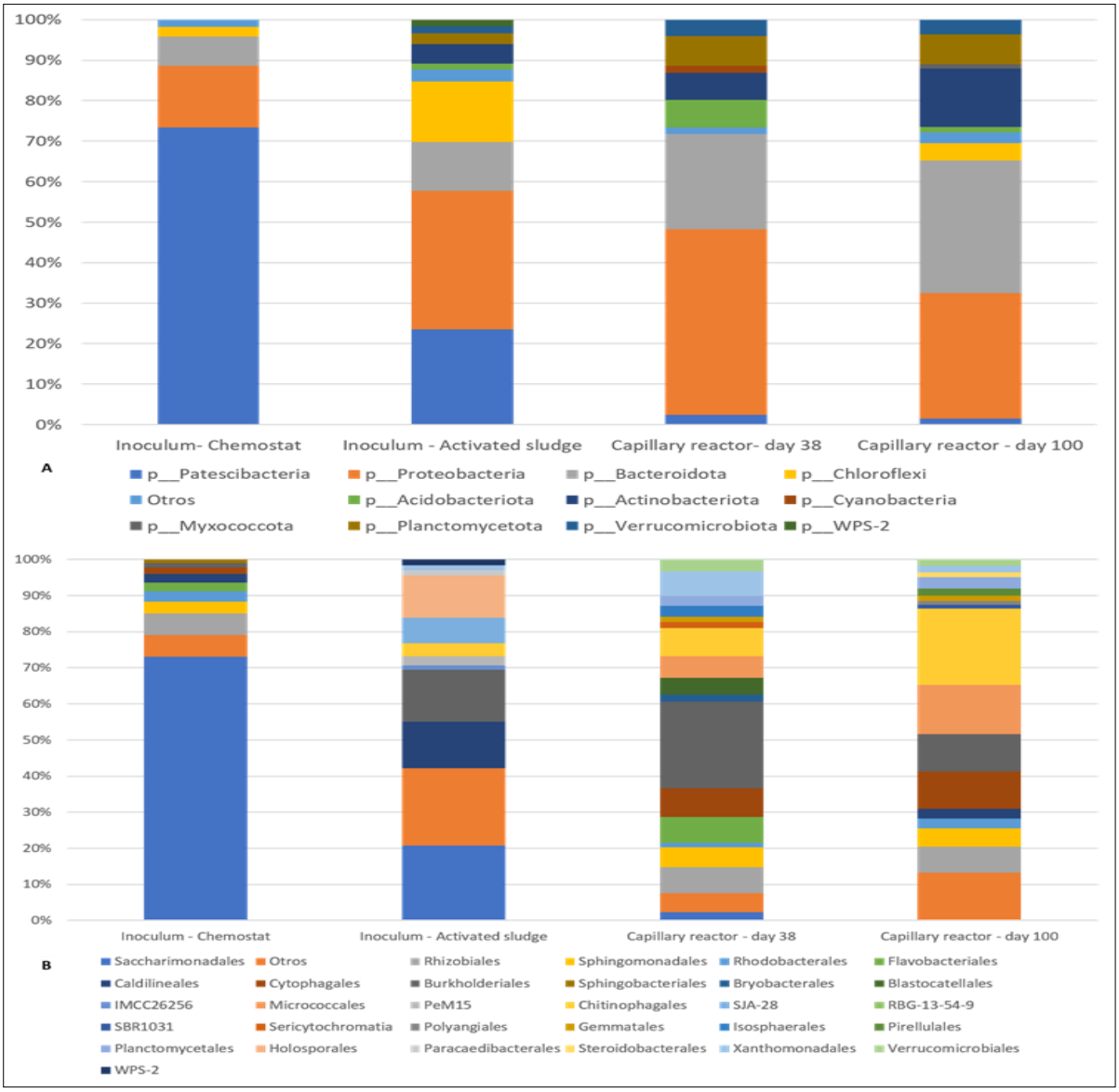


Figure 5-8 The composition of the microbial community of the inoculum and multi-channel bioreactor samples obtained by sequencing the V3–V4 of 16S rRNA gene using the MiSeq. Illumina instrument. Relative abundance (%) at the Phylum (A) and Order (B) taxonomic levels is shown. Groups with relative abundances smaller than 1% are not shown.

5.4 Conclusions

A multi-channel capillary bioreactor was investigated for the continuous treatment of hydrophobic VOCs. This work revealed that the overall mass transfer coefficient typically increased most with the gas superficial velocity ($U_{G/L}$) at each liquid flow evaluated and increased somewhat with gas volume fraction (ε_G). At the highest gas flow evaluated, K_La values above 400 h^{-1} were measured for a wide range of gas to liquid ratios. At only 0.5 second

of gas contact in the channels, the removal efficiency of the model air contaminants hexane, toluene and α-pinene was on average 58%, 90% and 44%, and up to about 75%, 99% and 75%, respectively. This extreme low gas contact time is at least one but closer to two orders of magnitude less than conventional biological air treatment systems even if the wall thickness of the capillary channels would be considered. An active contaminant-degrading culture could be sustained in the system and no accumulation of biofilm inside the capillary channels was observed. The bioreactor system showed stable operation for 100-days and was robust against three common upset scenarios, possibly facilitated by the highly diverse bacterial community that was observed. Overall, this work opens new opportunities for expanding the application field of biological processes to control emissions of air contaminants.

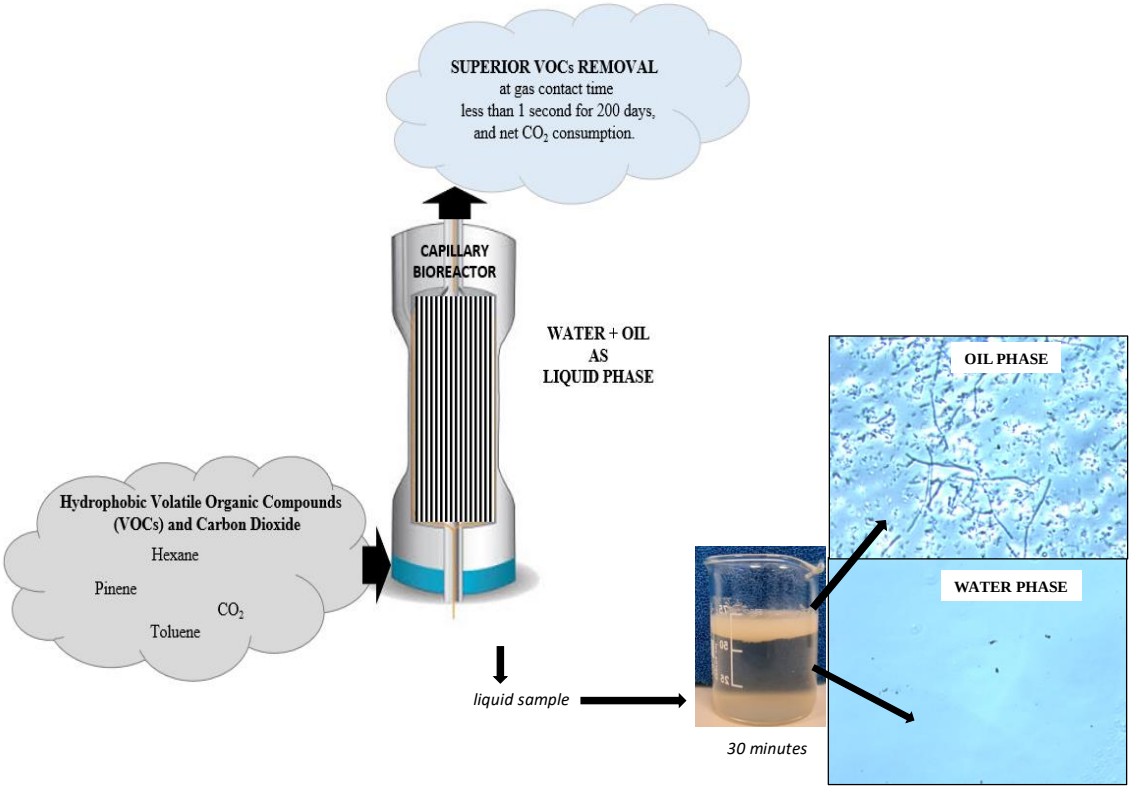
PART III

PROCESS INTENSIFICATION

6. PROCESS INTENSIFICATION THROUGH SILICONE OIL ADDITION

Chapter overview

A multi-channel capillary bioreactor devoted to the continuous abatement of hydrophobic volatile organic compounds (VOCs) by a bacterial and bacterial/microalgae consortium was investigated for 200 days. Toluene, α-pinene and hexane removal in the capillary bioreactor was up to 99%, 98%, and 55%, respectively, which is remarkably high considering the low gas contact time of less than 1 second. Addition of silicone oil increased the removal efficiency (RE) of α-pinene within two days from 45 ± 6% to 98 ± 2%, probably through alleviation of biokinetic inhibition provided by the oil acting as buffer for the α-pinene and/or its metabolites. The RE of toluene increased after silicone oil addition over a period of about eight weeks from 81 ± 3% to 99 ± 1%, most likely via microbial adaptation. On the contrary, the removal of hexane did not increase following silicone oil addition, potentially due to the inhibition of hexane or its metabolites as the bioreactor was deliberately operated without replenishing the recirculation liquid. Interestingly, biomass adhered to the silicone oil phase rather than residing in the water phase. The bacterial diversity was substantially enhanced, and probably contributed to the observed stable performance of the capillary bioreactor.



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6.1 Introduction

Traditionally, physical-chemical technologies have been used to abate gaseous pollutants because of their relatively small size (low gas contact times), rapid start-up (which allows for intermittent operation), and extensive experience in both design and use. Yet, biological processes are now generally recognized as a reliable and economical alternative for the abatement of waste gases containing mostly hydrophilic pollutants and low concentrations (Soreaunu and Dumont, 2020; Kennes and Veiga, 2013; Estrada et al., 2012; van Groenestijn en Kraakman, 2005). Moreover, the growing emphasis on sustainability and process safety is often an important driver for the application of biological air purification processes as they are operated at ambient temperatures/pressures with minimum environmental impact.

Nonetheless, biological gas treatment processes are inherently constrained by the mass transfer of hydrophobic gaseous pollutants. Pollutants with a large dimensionless Henry's law coefficient (HG/W) (>0.10 at 25 ^{o}C) are normally limited in terms of mass transfer as their poor solubility in water, especially at low concentrations, decreases their availability in the biofilm phase or the aqueous phase containing cells. Indeed, the high hydrophobicity of VOCs requires long gas contact times that demand large reactor footprints and limit their cost-effective abatement in biological processes (Kennes and Veiga, 2013; Estrada et al., 2012).

Enhancing mass-transfer from the gas phase to a liquid containing microorganisms typically entails an increase in power consumption (e.g., to enhance mixing), while power consumption is a key parameter for economically sustainable applications. Capillary reactors operated at an explicit gas-liquid flow pattern can create in small (capillary) channels an internal liquid circulation that enhances mass transfer by the short-distance transport mechanism. This segmented gas-liquid flow pattern, also known as Taylor flow or bubble-train flow, consists of alternating liquid slugs and gas bubbles, which enhances mass-transfer and has been reported to yield superior heat and mass transfer rates (Yao et al., 2020; Peng et al., 2022). Moreover, capillary forces are dominant in the capillary channel over other forces as such gravity and viscosity, which result in minimum pressure drop requiring minimum energy to move the air and liquid through the channels (Kreutzer et al., 2005; Liu et al., 2005). Capillary reactors have gained interest for process intensification due to both their enhanced mass-transfer and improved reaction kinetics (Peng et al., 2022; Kreutzer et al., 2005; Haase et al., 2016). In the last decade, thanks to the rapid progress in the integration of microfluidic devices and miniaturization technology, the application of capillary channel microreactors to intensify chemical and biocatalytic processes has increased significantly (Yao et al., 2020; Peng et al., 2022; Yao et al., 2005; Karande et al., 2006). Unfortunately, studies on capillary gas-liquid reactors that involve biological conversions to abate gaseous pollutants are scarce Kraakman et al., 2023; Lopez de Leon et al., 2020) and primarily deal with single channels.

Furthermore, microbial inhibition due to load surges or sudden changes in operating conditions can also hinder the performance of bioprocesses. Water-immiscible liquids known as non-aqueous phase liquids (NAPLs) were initially used in the production process of products of commercial significance to promote microbial bioconversions of inhibiting or hydrophobic substrates. Biological gas treatment processes using a NAPL added to the aqueous medium have emerged over the last decade as a platform to overcome microbial inhibition by

interfering substrates or metabolites (Lebrero et al., 2019; Monoz et al., 2012; Zamir et al., 2023). A NAPL may also be used as a buffer against load surges or sudden changing operating conditions or against periods of starvation by serving as a reservoir (Hernandez et al., 2011). In addition, a NAPL may enhance the mass transfer pathway for hydrophobic pollutants in a biological gas treatment reactor constrained by the mass transfer that would demand high gas contact times and associated large reactor volumes and footprints (Lebrero et al., 2019; Munoz et al., 2012). Different studies proved that the addition of a NAPL can increase the removal efficiency of hydrophobic VOCs in bioreactors (Li et al, 2023; Lhuissier et al., 2022; Lin et al., 2023; Pascual et al., 2020). The objective of this study was to investigate the effect of silicone oil as a NAPL on the overall performance and continuous operation of a multi-channel capillary bioreactor treating hydrophobic air pollutants. Toluene, α-pinene, and hexane were used as model compounds, representing indoor air pollutants different in hydrophobicity and biodegradability. Low VOC concentrations (< 5 mg m^{-3}) were applied as lower concentrations limit mass transfer rates, which would be applicable to the treatment of hydrophobic indoor air pollutants.

The focus was here on indoor air pollutants, as an example, but the approach to treat a mixture of hydrophobic contaminants using capillary bioreactors could also be applied to other scenarios, such as industrial emissions, gas upgrading, gas fermentation processes, or dilute-methane greenhouses gas (GHG) emissions as discussed elsewhere (Lopez de Leon et al., 2020; Bordel et al., 2024; Kraakman et al., 2021; Rocha-Rios et al., 2013; Lebrero et al., 2016).

Indoor air quality (IAQ) is lacking the same focus as outdoor air pollution, while the health risks related to long-term poor IAQ have become more apparent (Royal College of Physicians, 2018). The indoor air pollutants concentration is most of the time higher than the outdoor air pollutants concentration, especially in urban areas. Moreover, buildings are progressively being sealed against outdoor weather conditions to obtain heating and cooling energy cost savings (EPA, 2020; EEA, 2022; Coster et al., 2023). Modern buildings increasingly rely on mechanical ventilation with reduced outdoor fresh air intake, leading to higher indoor air pollutant concentrations (Broderick et al., 2017). With humans spending about 90% of their time indoors, effective simple indoor air purification methods are needed to obtain IAQ standards in addition to energy efficiency savings (Broderick et al, 2017). The types of indoor air pollutants and their current treatment methods are discussed elsewhere Broderick et al., 2017; Gonzalez-Martin et al., 2021), as well as recent advances in biological methods for improving IAQ (Kraakman et al., 2021.

6.2 Materials and Methods

Chemicals

The liquid medium used in the capillary bioreactor experiments consisted of a Brunner mineral salt solution prepared as described elsewhere (Kraakman et al., 2023). The silicone oil (polydimethylsiloxanes) that was used as second liquid phase exhibited a viscosity of 20 cSt (Sigma-Aldrich, Madrid, Spain). Silicone oil was chosen here because this NAPL fulfils critical selection criteria and is therefore commonly used as additional liquid phase in studies and applications that involves two-liquid phase bioreactors (Lebrero et al., 2019; Munoz et al., 2012). Criteria for the selection of a NAPL includes high affinity and high diffusivity for the target pollutants, high stability, and non-biodegradability (to avoid NAPL losses), low vapor pressure (to avoid NAPL losses due to evaporation), biocompatibility (non-toxic), non-hazardous nature (for operators and environment), and availability in bulk and at low cost. Silicone oil with a low viscosity was used in this study as the liquid viscosity can have an adverse effect on segmented flow regime in a capillary channel. This optimal flow regime for mass-transfer requires that the surface tension forces dominate over viscous forces (Kreutzer et al, 2005), and because oil is more viscous than water and reduces the surface tension of water, it therefore tempers the capillarity of a liquid.

Liquid-Gas Flow Pattern Mapping

The different flow patterns of gas and liquid possible of flowing through a capillary channel are illustrated in Figure 1. The occurrence of the optimal liquid-gas flow pattern for mass-transfer in a capillary channel was mapped at various gas-to-liquid flowrate ratios (G/L ratio), at various gas-liquid superficial velocities ($U_{G/L}$), and with and without the presence of a second liquid-phase (i.e., silicone oil). The parameters for predicting segmented flow in a single channel are well understood in clean liquids (Shao et al., 2009). However, the presence of impurities such as a non-aqueous liquid-phase (e.g., silicone oil), and their effect on interfacial tension to maintain segmented flow are not well defined. The visual presence of the segmented flow regime was mapped in 1.5-meter-long capillary channels with different internal diameters ranging from 2.4 mm to 5.0 mm. The liquid flow and gas flow varied between 0 and 1.0 L min^{-1}. The gas consisted of ambient air and the liquid consisted of demineralized water or demineralized water containing 20% (v/v) silicone oil (20 cSt). This abiotic experiment was undertaken with high silicone oil concentrations in a multi-channel configuration to better define experimental conditions in the multi-channel capillary bioreactor.

Capillary Bioreactor Set-up

The main part of the capillary bioreactor consisted of 25 glass capillary conduits (internal diameter of 2.4 mm and external diameter 4.4 mm) with a length of 1.5 m each. Figure 2 shows a schematic representation of the multi-channel capillary bioreactor. A pump (0.25 kW ESPA, Tecno-05-2M) was used to recirculate the liquid (8.4 L) and a rotameter (Fisher & Porter, 10A1197A) was used to measure the liquid recirculation flow rate. A compressor (ABAC LT50) was used to introduce ambient air in the bottom reservoir via a perforated EPDM membrane.

Inlet airflow and the air pressure at the inlet and outlet of the bioreactor were monitored by means of a rotameter (Aalborg, S/N 51588-2) and a pressure sensor (IFM, PN7097). **Table 6-1** provides an overview of the main operating parameters during the 200 days of operation of the capillary bioreactor at an extremely low gas contact time of less than 1 second.

Table 6-1 Key Operating Conditions in the Multi-Channel Capillary Bioreactor.

Stage	Gas Treatment	Days	Silicone Oil Addition (% v/v)	Recirculating Liquid Flow Rate (L min^{-1})	Inlet Gas Flow Rate (L min^{-1})	Empty Channel Gas Residence Time (s)
I	VOCs	0-32	0	8	13.9	0.7
		33-95	5	8	13.9	0.7
		95-122	10	8	13.9	0.7
		122-150	10	6	13.9	0.7
II Note 1)	VOCs + CO_2	150-200	10	6	13.9	0.7

Note 1) See Chapter 7

Impact of Silicone Oil on Hydrophobic VOC Removal in Capillary Bioreactor

The capillary bioreactor was inoculated with biomass (initial concentration ≈ 0.5 g dry weight L^{-1}), which originally consisted of biomass from a chemostat fed with hexane, toluene, trichloroethylene and α-pinene, and fresh activated sludge from Valladolid (Spain) wastewater treatment plant. The biomass was taken from a previous study where its population structure was characterized by extracting and analysing the genomic DNA (Kraakman et al., 2023). A VOC mixture was continuously injected to the inlet ambient air airstream using a syringe pump (Fisherbrand, Model 100). The VOC mixture contained α-pinene, hexane, and toluene as model compounds representing air pollutants, different in hydrophobicity and biodegradability.

The system was continuously operated at room temperature (controlled at 20 ºC) while the liquid was recirculated in a closed loop and demineralized water was occasionally added to compensate for evaporative water losses or liquid losses due to liquid analyses. The applied gas and liquid flow rates of 13.9 L min^{-1} and 8 L min^{-1}, respectively, resulted in an average empty channel gas residence time in the capillary channels of 0.7 s, where the empty channel gas residence time (ECRT) was defined as follows (Eq. 6-1):

$$ECRT = (V_c \times n_c) / (Q_g) \qquad \text{(Equation 6-1)}$$

where V_c is the internal volume of a capillary channel (L), n_c the number of capillary channels in the capillary bioreactor (-), Q_g the gas flow rate (L s^{-1}). The *ECRT* is similar to the empty bed residence time which is commonly used as a design parameter for gas treatment systems but

does not represent the real contact time of the gas inside the capillary channel. The real contact time of the gas in the capillary channels would be ~ 0.5 s as that would consider the liquid flow rate (Q_L) and the liquid film along the wall of the capillary channel, which can be expected to be in this study about 150 µm (van Baten and Krishna, 2004).

The recirculation liquid was not replaced by fresh medium during the entire experiment of 200 days. The following changes were performed for the first 150 days (Stage I): adding 5% (v/v) silicone oil (with a viscosity of 20 cSt) on day 33 with a further increase to 10% (v/v) on day 95; and a reduction of the liquid flow rate from 8 L min^{-1} to 6 L min^{-1} on day 122, while keeping the gas flow constant (see also Table 1). The biomass concentration, pH, and conductivity of the recirculation liquid were periodically determined. The inlet concentration of each VOC was similar, and all maintained between 2 and 5 mg m^{-3} throughout the entire experiment (Stage I and Stage II), which are representative for highly concentrated indoor environments and some diluted industrial emissions.

Combined VOCs and Carbon Dioxide Removal in Capillary Bioreactor

The heterotrophic–phototrophic synergism between microalgae and bacteria in the capillary photobioreactor was investigated from day 150 onwards to elucidate whether it could be a sustainable platform for the biological removal of both CO_2 and VOCs in a single bioreactor. The capillary bioreactor was inoculated with a mixed microalgae consortium on day 150 (start of Stage II). During the final period of Stage I, the operating parameters remained unchanged to explore the potential of VOCs and CO_2 co-abatement. The microalgae biomass (300 ml with a concentration of 2.6 g dry weight L^{-1} containing the main species *Pseudoanabaena sp*. (98%) and *Chlorella vulgaris* (2%) was obtained from a high-rate algal pond operated at the Institute of Sustainable Processes (University of Valladolid, Spain) increasing the overall biomass concentration in the capillary bioreactor by about 0.1 g dry weight L^{-1}. Additional illumination was provided with two cool white light emitting diodes (LEDs) strips (Mean Well, model LPV-100-12, 12 Volt, 8.5 Amp), which were wrapped around the bottom and top reservoirs, and the capillary channels. Aluminium foil was installed externally to direct the light towards the reactor surface. The average photosynthetic active radiation at the reactor wall was 100-150 µE m^{-2} s^{-1}. The inlet ambient airstream contained an average CO_2 concentration of 412 ± 51 ppm_v, to which CO_2 produced from the mineralized VOCs in the bioreactor was added. The biomass concentration, pH, conductivity of the recirculation liquid, and the inlet/outlet CO_2 and VOC concentrations were also periodically measured during the Stage II duration of 50 days. The CO_2 removal during Stage II was defined as the difference in CO_2 concentration between the inlet and outlet airflow of the capillary reactor and considered the formation of CO_2 from the mineralized VOCs inside the reactor.

Analytical Procedures

The VOC concentrations in the inlet and outlet airstreams were measured once every weekday using Solid Phase Microextraction with an adsorption time of 10 minutes (SPME-fibre: CAR/PDMS 85 µm, Supelco) and a GC-FID (BRUKER-3900) according to the method described elsewhere (Kraakman et al., 2023). The biomass concentration was determined according to Standard Method 2540 D. Samples for measuring CO_2 concentrations were drawn from the

inlet and outlet of the capillary bioreactor during the illuminated period (Stage II) and analysed using a 430 GC-TCD (Bruker, Palo Alto, USA) equipped with a CP-Molsieve 5 Å (15 m × 0.53 mm × 15 μm) and a CP-PoraBOND Q (25 m × 0.53 mm × 10 μm) columns. The oven, injector and detector temperatures were maintained at 45, 150, and 200 °C, respectively. Helium was employed as the carrier gas at 13.7 mL min^{-1}.

6.3 Results and Discussion

Liquid-Gas Flow Pattern Mapping

This study established the optimal flow pattern to enhance the mass-transfer from the gas to the liquid phase (segmented flow with alternating liquid slugs and gas bubbles) as shown in **Figure 6-1**, which is consistent with the observations from other capillary studies (Liu et al., 2005; Rocha-Rios et al., 2013). The presence of impurities such as a second liquid-phase (e.g., silicone oil), and their effect on interfacial tension, makes more difficult to predict the flow regime in a capillary channel. The addition of 20% (v/v) silicone oil into water was here investigated to determine if segmented flow could be maintained at different gas and liquid flow rates. The addition of silicone oil poses a risk of disrupting proper segmented flow, as the oil reduces the surface tension of water, and, consequently, tempers the capillarity of a liquid. When oil is added to water, it disrupts surface tension because the strong hydrogen bonds between water molecules cannot be properly formed in the presence of oil. On the other hand, viscosity of a liquid slightly increases the capillarity of a liquid as per Eq. 2, when silicone oil is dispersed in the water as second liquid phase. Our results showed that the addition of silicone oil supported segmented flow at increased liquid velocities but not at increased gas velocities. **Figure 6-1** shows a map of the liquid flow and gas flow conditions supporting segmented flow with and without silicone oil in two channels different in diameter, which helped to define the experimental conditions in the multi-channel capillary bioreactor.

Kreutzer and co-workers (2005) showed that a channel can have an internal diameter up to about 5 mm when using ambient air and water at room temperature to provide capillarity, meaning the dominance of surface tension forces over other external forces like gravity. Indeed, the occurrence of segmented flow could be obtained in our study in all capillaries up to 5 mm and was observed at gas velocities up to 0.5 L min^{-1} and liquid velocities up to 0.5 L min^{-1}. At higher gas and liquid flow rate combinations, the segmented flow pattern could not be maintained in all capillary channels. This can be explained by the increase in the viscous drag forces relative to the surface tension forces, which compromises capillarity. The Capillary number (*Ca*) represents this relation between viscous drag forces and capillary forces (Equation 6-2):

$$Ca = \mu \times v / \gamma \qquad \text{(Equation 6-2)}$$

where μ is the viscosity (Pa s^{-1}), v the liquid velocity (m s^{-1}), γ the surface tension of the liquid in the gas phase (N m^{-1}). Higher liquid velocities will result in a higher capillary number, which becomes less dominated by capillary forces such as surface tension and explains why segmented flow can only be obtained up to a certain liquid velocity.

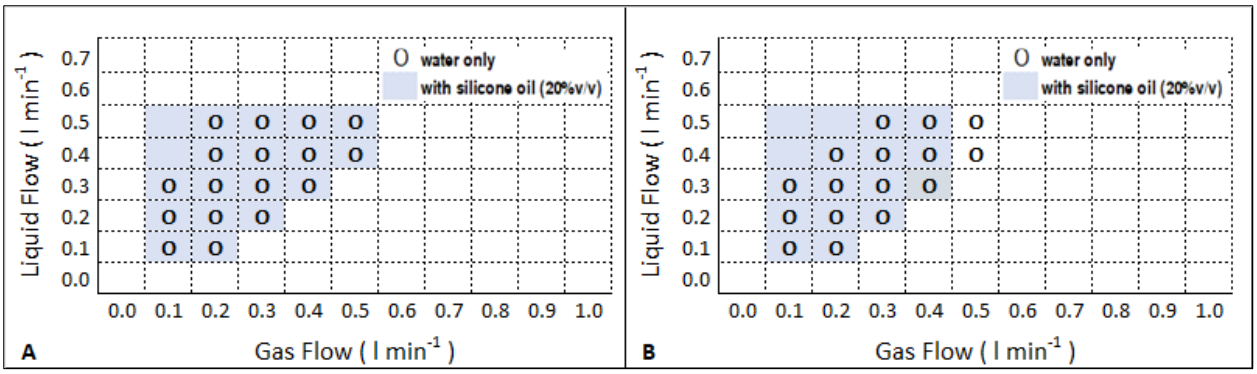

Figure 6-1 Occurrence of segmented flow in capillary channels with internal diameter of 3.4 mm (A) and 5.0 mm (B) under the different gas flowrate and liquid flowrate conditions using water only and water with silicone oil.

Impact of Silicone Oil on Hydrophobic VOC Removal in a Capillary Bioreactor

The removal of the hydrophobic VOCs was investigated in the capillary bioreactor with and without silicone oil as non-aqueous phase liquid under the segmented flow pattern conditions. The VOC removal after the initial start-up period (15 days) in the capillary bioreactor without any silicone oil addition was on average 45 ± 6% for α-pinene, 44 ± 10% for hexane and 81 ± 3% for toluene (**Figure 6-2**), which is consistent with a previous study undertaken in a similar bioreactor configuration as shown in **Chapter 5**.

The addition of 5% (v/v) silicone oil on day 33 did significantly increase the removal efficiency (RE) of α-pinene from 45 ± 6% to 95 ± 3%. An instant peak in α-pinene RE was observed directly after the addition of the oil, due to the initial absorption in the silicone oil, then increasing to remain stable after two days. An increase to 10% (v/v) silicone oil on day 95 further enhanced the RE of α-pinene to 98 ± 2%. This is remarkable since the addition of silicone oil did not have any significant effect on the removal of hexane regardless of the concentration (5 or 10 % v/v). Both α-pinene and hexane have a high affinity for silicone oil as reflected by the gas-oil partitioning coefficient ($H_{G/Silicone\ Oil}$) when compared to the gas-water partitioning coefficient ($H_{G/Water}$) as illustrated in **Table 6-2**.

The addition of 5% (v/v) silicone oil (on day 33) did not initially increase the RE of toluene but resulted in a steady increase of toluene removal from about 80% (81 ± 3%) to just above 90% (93 ± 2%) by day 40, which likely indicated microbial adaptation to the new condition with the dispersed second liquid phase. A further increase to 10% (v/v) silicone oil on day 95 did not show any further enhancement of the toluene removal, and in fact, slightly reduced the RE of toluene to 86 ± 2%. Of the VOCs evaluated, toluene has the lowest dimensionless Henry-coefficient ($H_{g/Water}$=0.3; **Table 6-2**) and was removed better than hexane

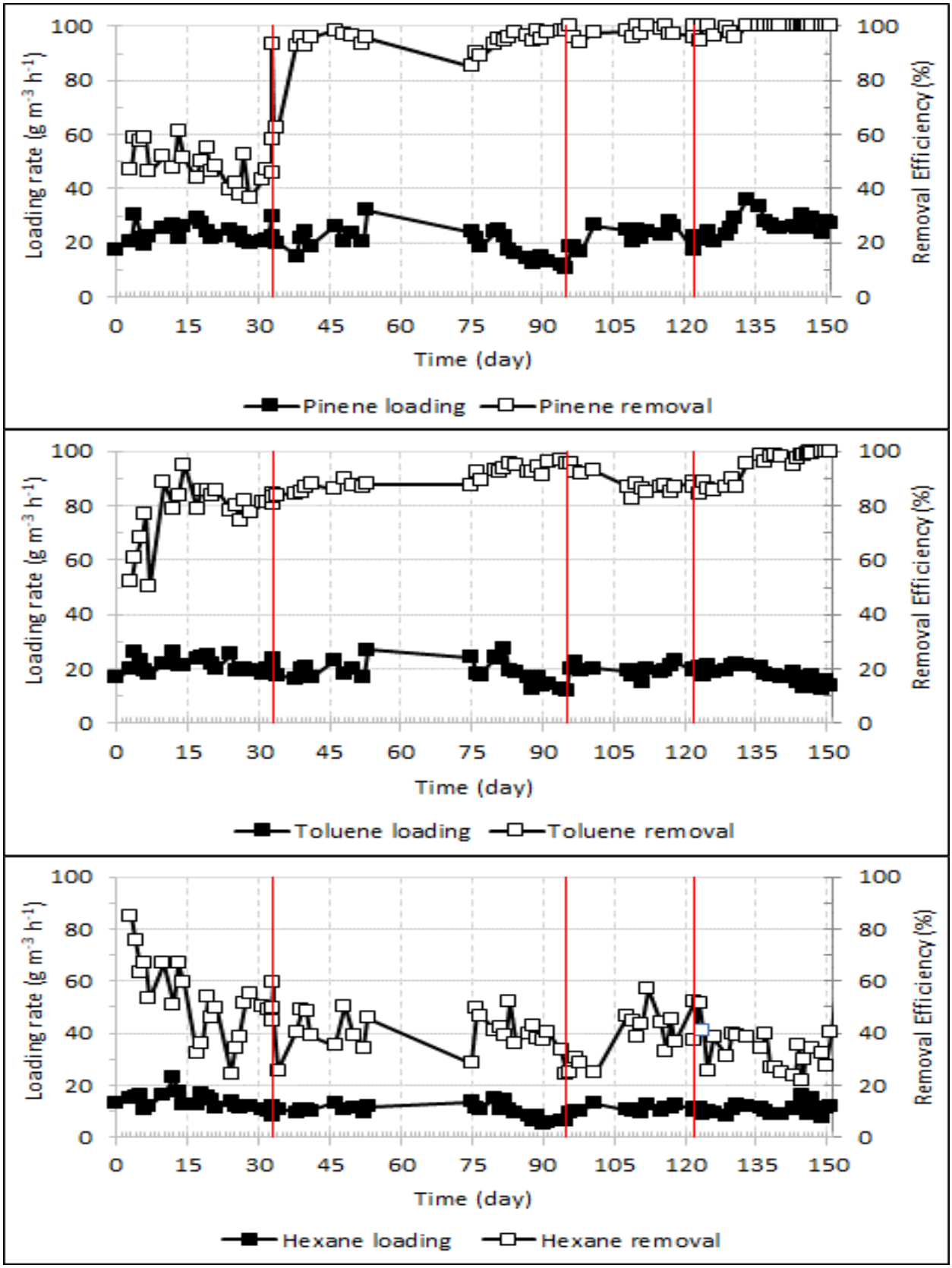

Figure 6-2 Time course of the loadings rate (■) and removal efficiencies (□) of α-pinene (upper), toluene (middle) and hexane (lower) in the capillary bioreactor, with the vertical lines the days at which key operating changes were introduced: addition of 5% (v/v/) silicone oil (day 33), increased to 10 % (v/v) silicone oil (day 95), and increase gas-to-liquid ratio (day 122).

and α-pinene during the initial period without silicone oil, confirming that $H_{g/Water}$ is a key factor for gas-liquid mass transfer and associated RE in a capillary bioreactor.

The initial α-pinene RE was slightly lower compared to that of hexane (**Figure 6-2**) and is unlikely to be the result of mass-transfer limitations. This is because hexane has a much higher dimensionless Henry-coefficient ($H_{G/Water}$) than pinene (71 *vs* 8 as illustrated in **Table 6-2**), meaning α-pinene is significantly better absorbed from the gas phase into the water phase at equal gas concentration. The pinene gas concentration was also on average slightly higher than the hexane concentration during the entire experiment (4.7 mg m^{-3} vs 2.2 mg m^{-3}), and a higher concentration benefits mass transfer. Moreover, α-pinene has a higher octanol-water partitioning coefficient (log $K_{o/w}$ = 4.83) compared to hexane (log $K_{o/w}$ = 3.90). The octanol-water partition coefficient (log $K_{o/w}$) is typically used to quantify the hydrophobicity of a pollutant and may be used to predict the uptake of a compound into biological membranes. $K_{o/w}$ is the most common way to express lipophilicity of a compound and has been shown to influence the removal efficiency of VOCs in conventional biological gas treatment systems (Deshusses and Johnson, 2000).

Table 6-2 Water Solubility and Partitioning Coefficients of Target Gaseous Compounds[1].

Compound	Molar Mass[2]	Water Solubility[3]	$H_{Gas/Water}$	log $K_{Octanol/Water}$	$H_{Gas/Silicone\ Oil}$[4]
α-Pinene ($C_{10}H_{16}$)	136.2	2.5	8	4.83	0.00018
Hexane (C_6H_{14})	86.2	9.3	71	3.90	0.0058/0.0044
Toluene (C_7H_8)	92.1	526	0.3	2.73	0.00064/0.00089
Carbon dioxide (CO_2)	44.0	2900	1.2	0.83	0.15
Oxygen (O_2)	32.0	39	32	0.65	3.6

[1] at 25 °C (National Center for Biotechnology Information, National Library of Medicine, 2024; Patel et al., 2017; Munoz et al, 2012).
[2] g mol^{-1}
[3] mg L^{-1}
[4] 20 cSt silicone oil

The findings in this study suggest that the initial α-pinene removal was limited by biokinetics as the α-pinene may be more difficult to degrade due to its higher molecular weight and its different (bicyclic) structure. The biodegradation of α-pinene could require partial enzymatic conversion into smaller molecules in the liquid phase before they can be taken up by the bacterial cells more readily (Miller and Allen, 2005). The addition of silicone oil may have provided a buffer for the α-pinene and/or its metabolites, thus mitigating previous biokinetic inhibition. The steep improvement of α-pinene RE after silicone oil addition in the capillary bioreactor from 45 ± 6% to 95 ± 3% is consistent with observations in a study that involved a conventional biotrickling filter where the α-pinene RE improved from 50 to 98% after the addition of 5% (v/v) silicone oil (Montes et al., 2010). However, an important difference between both experimental studies is the empty bed gas contact time, which is more

than one order-of-magnitude shorter in the capillary bioreactor (0.7 seconds in this study *vs* 14 seconds in the conventional biotrickling filter study), while requiring theoretically the same order-of-magnitude of energy per volume of treated air.

Similarly, the removal of hexane in this study might also have been hampered by biokinetic limitations rather than mass transfer, which was already boosted by the internal recirculation in the segmented flow pattern inside the capillary channels. Hexane RE did not increase with the additions of the NAPL, even though the affinity of silicone oil for hexane is more than 12,000 times higher than for water. Muñoz and co-workers (2013) also observed that the addition of silicone oil did not increase hexane removal in their stirred bioreactor tank study and identified that the formation of metabolites would have been the most likely reason for the inhibition. This would also be consistent with the study by Li and co-workers (2023), who detected the hexane degradation intermediates 2-hexanone, 2-hexanol, 1-butanol, acetic acid, and acetone in the aqueous phase in stirred bioreactors with silicone oils treating hexane. Moreover, Cantera and co-workers (2016), observed improved methane abatement in a stirred bioreactor with silicone oil as NAPL after increasing dilution rate of the aqueous phase. It was therefore concluded that the deliberate absence of replenishment of the recirculation liquid in our study may also have contributed to metabolic inhibition of hexane.

A further increase in α-pinene removal was obtained when the liquid flow was changed from 8 to 6 L min^{-1} on day 122, increasing the Gas-to-Liquid ratio, while keeping the gas flow rate constant. The RE of α-pinene increased from 98 ± 2% to 99.5 ± 1%. Similarly, an increase was observed in the average removal of toluene, which increased from 86 ± 2% before day 122 to 95% ± 5% after day 122, reaching over 98% removal. This may be explained by further microbial adaptation or general hydrodynamic stability of the bioreactor system, such as a more homogeneous gas bubble-liquid slug length distribution among the twenty-five capillary channels. The increase in RE of both pinene and toluene occurred despite the slightly lower overall mass-transfer coefficient (K_La) of the capillary bioreactor system at a reduced superficial velocity (of the gas bubble-liquid slug) as determined in a previous study (Kraakman et al., 2023). The removal of hexane, on the other hand, did not increase but rather slightly decreased from 44 ± 7% to 33 ± 6%, which may be explained by further metabolite accumulation due to the absence of replenishment of the bioreactor liquid phase.

The results show that the operation and performance of the capillary bioreactor were stable without replacing the liquid in the reactor: steady VOC removal performance without foam formation while maintaining segmented flow in all capillary channels. In addition, the pH remained ~ 7.5 during the 150 days of the experiment (Stage I), which suggested that no acidic or alkaline degradation products were accumulated at substantial concentrations. The removal efficiencies of the VOCs observed in the capillary bioreactor were very high considering that the inlet VOC concentrations were relatively low (< 5 mg m^{-3}, with mass transfer proportional to gas concentration) and that the gas contact time was extremely low (~ 0.7 seconds). Conventional biological gas treatment systems typically require an empty bed residence time that is between one and two orders of magnitude higher for the abatement of hydrophobic compounds (Kennes and Veiga, 2013; Yu et al., 2021; Lebrero et al., 2012).

While the gas-liquid mass-transfer is intensified using segmented flow inside the capillaries, most of the biodegradation occurs within the reservoirs as they hold most of the

liquid containing the biomass. This would be like a conventional bioscrubber that has liquid recirculating between two reactor units. In the first reactor-unit, the gas contactor, compounds are absorbed from the gas-phase in the liquid phase, and in the second unit the compounds are further converted by microorganisms suspended in the liquid (suspended growth biomass).

The average VOC removal rate in the gas contactor was 43 ± 8 g VOC m^{-3} h^{-1} during Stage I and dropped to 35 ± 9 g VOC m^{-3} h^{-1} during Stage II. Similarly, the average biological degradation rate in the recirculating liquid was 0.9 ± 0.2 mg L^{-1} h^{-1} during Stage I and 0.7 ± 0.2 mg L^{-1} h^{-1} during Stage II. The results of Stage II are discussed further in **Chapter 7**.

Microbial Characterization

Liquid samples from the capillary reactor were taken at the beginning of Stage I and at the end of Stage II to analyse the microbial community. Microscopic investigations during Stage I revealed that nearly all the biomass resides inside or adhered to the silicone oil phase rather than in the water phase (see **Figure 6-3**). No biomass attached to any of the glass capillary channels was observed for the 150-days operation of the capillary bioreactor. This indicated that the main bacterial activity occurred nearly exclusively inside the silicone oil phase and/or adhered to the silicone oil-water interphase. The liquid-phase specific biocatalytic activity in the aqueous phase and the oil phase was not quantified in this study. The presence of micro-water droplets inside the silicone oil cannot be ruled out especially under the highly turbulent operating conditions inside the capillary channels. The finding was similar to the observation conducted by Hernandez and co-workers (2012) and Muñoz and co-workers (2013), who confirmed the activity of a hydrophobic microbial consortium inside and/or at the NAPL (silicone oil) when treating high concentrations of hexane in a continuously stirred bioreactor. They observed the highest enhancements in VOC elimination capacity when microbial cells were confined inside and/or adhered at the NAPL, which may also explain the superior elimination efficiencies obtained in our study. Microbial population changes over time in the capillary bioreactor have been confirmed in this study and changes in microbial cell hydrophobicity induced by the presence of silicone oil could also have played an important role for the biomass to adhere at the silicone oil phase rather than reside in the water phase. Liquid samples from the capillary bioreactor taken at the beginning (day 0) and at the end of Phase II were taken to analyse the microbial community. The results of this microbial characterisation are discussed in **Chapter 7**.

No accumulation of biomass on the walls of the capillary glass channels was observed for the 150-days operation of the multi-channel capillary bioreactor during Stage I. This observation is consistent with the findings in other studies where no biofilm formation was observed inside capillaries (Kraakman et al., 2023; Lopez de Leon, 2020) due to the relatively high shear forces. The prevention of biofilm formation was systematically investigated by Studer (2005), who showed that bacterial biofilm accumulation could be simply prevented with relatively low shear forces, which confirms the observations in the study discussed herein.

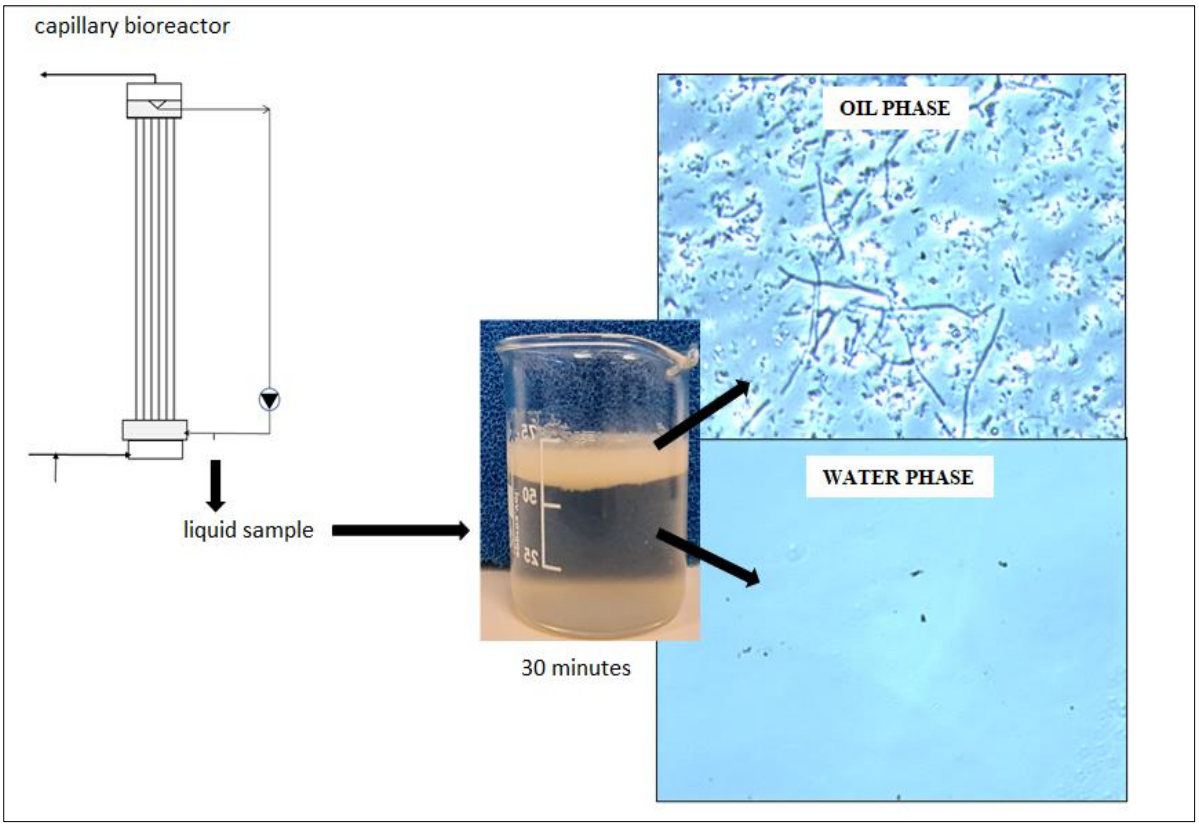

Figure 6-3 Photos of the microbial appearance in the recirculation liquid of the capillary bioreactor at the end of Phase I after separating the two-liquid phases.

6.4 Conclusions

Toluene, α-pinene and hexane removals up to 99, 98, and 55%, respectively, were achieved in the multi-channel capillary bioreactor with 10% (v/v) silicone oil dispersed in the recirculating liquid operated at a gas contact time lower than 1 second. The addition of silicone oil increased the RE of α-pinene from 45 ± 6% to 98 ± 2% over two days, likely due to the silicone oil alleviating biokinetic inhibition by acting as a buffer for the VOCs and their metabolites. For toluene, the RE gradually increased after silicone oil addition from 81 ± 3% to 99 ± 1% over eight weeks, likely due to microbial adaptation. The RE of hexane did not increase after silicone oil addition, potentially due to inhibition of hexane or its metabolites as the bioreactor was deliberately operated without replenishment of the recirculation liquid. Interestingly, the biomass adhered to the silicone oil phase rather than residing in the water phase.

7. HETEROTROPHIC–PHOTOTROPHIC SYNERGISM FOR VOC & CO_2 ABATEMENT

Chapter overview

An instant reduction of the outlet CO_2 concentration compared to the inlet CO_2 concentration was observed after the introduction of the microalgae into the capillary bioreactor. A slow natural increase of the pH caused by photosynthesis was recorded confirming photosynthetic activity. A net CO_2 consumption was observed achieving complete carbon sequestration from the removed VOCs with additional CO_2 removed (on average 10%) from the inlet ambient air. This confirms the feasibility of a capillary bioreactor as a platform for the biological gaseous co-abatement of CO_2 and hydrophobic VOCs. In addition, the bacterial diversity, an indicator of community stability and functional resilience, enhanced substantially during the 200-day operation and probably contributed to the observed stable performance of the capillary bioreactor. Longer-term operational requirements for the capillary bioreactor were identified, such as pH-neutralization and/or replenishment of the recirculation liquid.

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7.1 Introduction

With humans spending about 90% of their time indoors, effective simple indoor air purification methods are needed to obtain IAQ standards in addition to energy efficiency savings (Broderick et al., 2017). The types of indoor air pollutants and their current treatment methods are discussed elsewhere (Broderick et al., 2017; Gonzalez-Martin et al., 2021). The purification of typical indoor air contaminants was investigated and discussed in the previous chapter (**Chapter 6**) and provided an understanding of the removal of VOCs using a capillary bioreactor. However, in addition to VOC contaminants in indoor air, other contaminants including CO_2 should also be considered.

Because occupants produce CO_2, its concentration in indoor spaces occupied by humans and/or animals is higher than the concentrations outdoors. Concentrations above 1,000 ppm_v are defined as an indoor air pollutant by the American Society of Heating, Refrigerating and Air-Conditioning Engineers (ASHREA 2019) and in most green building certification schemes threshold CO_2 concentrations are considered (Wei et al. 2015). With the growing trend of constructing airtight buildings to provide energy consumption savings, the difference in indoor–outdoor CO_2 concentration increases as the ventilation rate per person decreases (i.e. rate of outdoor air supply to an indoor space). With the current global average outdoor concentration of about 400 ppm_v, CO_2 levels in urban areas can be expected to be higher (Persily 1997) and CO_2 concentrations inside occupied indoor spaces typically vary from outdoor levels up to several thousand ppm_v (Persily et al. 2008). Elevated CO_2 concentrations in office buildings can be expected especially in the afternoons and in meeting rooms where important decisions are sometimes made.

Several studies have shown that human performance is directly influenced by the CO_2 concentration. Indeed, a decline in workplace productivity and student academic performance have been shown with elevated CO_2 levels (Satish et al. 2012; Bakó-Biró et al. 2004; Seppänen et al. 2006; Shaughnessy et al. 2006). Satish et al. (2012) showed a moderate but statistically significant adverse effects of 1,000 ppm_v CO_2 in six out of a nine scales of human decision-making performance and a large reduction in seven scales at 2,500 ppm_v when compared to a baseline level of 600 ppm_v. Two previous studies with only 10 participants showed that they performed proofreading significantly more poorly at CO_2 concentrations of 4,000 ppm_v and marginally but significant differences were recorded at 3,000 ppm_v versus 600 ppm_v. The difference in reading performance was observed in the errors found, not in the reading speed. The quality of sleep is also affected by the CO_2 concentration in the sleeping room, alongside the freshness of the sleeping room air perceived and the next day performance (Strøm-Tejsen et al. 2016). In addition, negative symptoms like dry eyes, sore throat, nose congestion (related to the mucous membranes) and drowsiness, short breath, cough, and panting (related to the lower respiratory tract) have been associated with elevated CO_2 levels (Erdmann and Apte 2004).

Although many elevated CO_2 concentrations are the result of insufficient supply of ambient outside air as per current professional standards, even the ventilation rates in the leading ASHRAE standard (ASHREA 2019) can result in CO_2 concentrations higher than 1,000 ppm_v in generously occupied spaces (Satish et al. 2012).

Thus, the capillary bioreactor that successfully removed the hydrophobic indoor air model compounds discussed in the previous chapter was here explored as a potential platform to improve IAQ using synergistic algal-bacterial treatment of hydrophobic VOCs and CO_2. In an algal-bacterial bioreactor, microalgae can fix indoor CO_2 and CO_2 resulting from bacterial VOC mineralization, while producing oxygen during the photosynthetic process. This O_2 could be then utilized by heterotrophic bacteria mineralizing the VOCs. Studies on synergistic algal-bacterial treatment of hydrophobic VOCs and CO_2 are rare, especially in a multi-channel capillary reactor.

7.2 Material and Methods

Chemicals

The liquid medium used in the capillary bioreactor experiments consisted of a Brunner mineral salt media similarly as described in **Chapter 6**.

Capillary Bioreactor Set-up

The main part of the capillary bioreactor consisted of 25 glass capillary conduits (internal diameter of 2.4 mm and external diameter 4.4 mm) with a length of 1.5 m each similar as described in **Chapter 6**. **Table 7-1** provides an overview of the main operating parameters during the 200 days of operations of the capillary bioreactor at an extremely low gas contact time of less than 1 second.

Table 7-1 Key Operating Conditions in the Multi-Channel Capillary Bioreactor.

Stage	Gas Treatment	Days	Silicone Oil Addition (% v/v)	Recirculating Liquid Flow (L min^{-1})	Inlet Gas Flow Rate (L min^{-1})	Empty Channel Residence Time (s)
I Note 1)	VOCs	0-32	0	8	13.9	0.7
		33-95	5	8	13.9	0.7
		95-122	10	8	13.9	0.7
		122-150	10	6	13.9	0.7
II	VOCs + CO_2	150-200	10	6	13.9	0.7

Note 1 See Chapter 6

Combined VOC and Carbon Dioxide Removal in a Capillary Bioreactor

The capillary bioreactor was inoculated with a mixed microalgae consortium on day 150 (Stage II, see **Table 7-1**) with no changes made to the operating parameters of the bioreactor during the final stage of previous phase (which is discussed in Chapter 7) to explore the potential of VOC and CO_2 co-abatement. The heterotrophic–phototrophic synergism between microalgae and bacteria in the capillary photobioreactor was investigated from day 150 onwards to

elucidate whether it could be a sustainable platform for the biological removal of both CO_2 and VOCs in a single bioreactor. During the final period of Stage I, the operating parameters remained unchanged to explore the potential of VOCs and CO_2 co-abatement. The microalgae biomass (300 ml with a concentration of 2.6 g dry weight L^{-1} containing the main species *Pseudoanabaena sp*. (98%) and *Chlorella vulgaris* (2%) was obtained from a high-rate algal pond operated at the Institute of Sustainable Processes (University of Valladolid, Spain) increasing the overall biomass concentration in the capillary bioreactor by about 0.1 g dry weight L^{-1}. Additional illumination was provided with two cool white light emitting diodes (LEDs) strips (Mean Well, model LPV-100-12, 12 Volt, 8.5 Amp), which were wrapped around the bottom and top reservoirs, and the capillary channels. Aluminium foil was installed externally to direct the light towards the reactor surface. The average photosynthetic active radiation at the reactor wall was 100-150 $\mu E\ m^{-2}\ s^{-1}$. The inlet ambient airstream contained an average CO_2 concentration of 412 ± 51 ppm_v, to which CO_2 produced from the mineralized VOCs in the bioreactor was added. The biomass concentration, pH, conductivity of the recirculation liquid, and the inlet/outlet CO_2 and VOC concentrations were also periodically measured during the Stage II duration of 50 days. The CO_2 removal during Stage II was defined as the difference in CO_2 concentration between the inlet and outlet airflow of the capillary reactor and considered the formation of CO_2 from the mineralized VOCs inside the capillary reactor.

Analytical Methods

The VOC concentration in the inlet and outlet airstreams were measured using a GC-FID (BRUKER-3900) according to the method described in **Chapter 6**. The biomass concentration was determined according to Standard Method 2540 D.

Bacterial Community structure

The community structure of the bacterial community inside the capillary bioreactor was characterized at the start of Stage I (day 1) and at the end of Stage II (day 200). The DNA was extracted from each biological replicate with a FastDNA™ SPIN Kit (MP Biomedicals, USA). PCR amplification of regions 16S-V4-V5 was performed by using the primers GTGCCAGCMGCCGCGGTAA, CCGTCAATTCCTTTGAGTTT connecting with barcodes. Libraries were checked with Qubit and real-time PCR for quantification, while a bioanalyzer was used for size distribution detection. Quantified libraries were pooled and sequenced on a paired-end Illumina platform to generate 250bp paired-end raw reads in Novogene UK (Cambridge, UK). The whole process was performed through Python (V3.6.13) and adaptors were removed through cutadapt (V3.3). Paired-end reads were merged using FLASH (V1.2.11,http://ccb.jhu.edu/software/FLASH/). Data filtration and chimera removal were performed using the fastp (V0.23.1) software and the UCHIME Algorithm (http://www.drive5.com/usearch/manual/uchime_algo.html). Clustering of the sequences into Operational Taxonomic Units (OTUs) was as per the gene reference database SILVA (V138.1) and the ribosomal data base project (V18) (Quast et al., 2013) using QIIME (V 1.9.1). The sequences obtained have been deposited in Genbank as Bioproject PRJNA1020663. Bar graphs and heatmaps were plotted with R using the package ggplot2 (Wickman, 2009) and R

pheatmap (Kolde, 2019). Alpha diversity was calculated with QIIME (V 1.9.1) and displayed with R software (V 4.0.3). Function prediction according to marker genes was performed with the R package PICRUSt2 (V2.3.0) (Douglas et al., 2020).

7.3 Results and Discussion

Combined VOC and CO_2 Removal for IAQ Enhancement

The heterotrophic–phototrophic synergism between microalgae and bacteria in the capillary photobioreactor from day 150 onwards was investigated to elucidate whether it could be a sustainable platform for the biological removal of both CO_2 and VOCs in one reactor. Instant lower carbon dioxide concentrations were observed after the introduction of the microalgae to the capillary photobioreactor (**Figure 7-1**). This confirms a net CO_2 consumption despite the CO_2 produced from VOC mineralization by the bacteria achieving complete carbon sequestration from the removed VOCs. During the following 50 days, the outlet CO_2 concentration of the bioreactor remained in the range of 10 ± 5% lower than the inlet CO_2 concentration while observing a slow natural increase of the pH mediated by photosynthesis. The pH increased over a period of 30 days, from about 7.3 to 9.4, while CO_2 removal remained at 10.4 ± 4.8% until day 200, when the experiment was stopped. The increase in the pH of the cultivation broth can be explained by photosynthetic activity in the absence of replenishment of the bioreactor liquid in this study. Algae remove CO_2 from the recirculating liquid, reducing its alkalinity, which can subsequently raise the pH of the liquid.

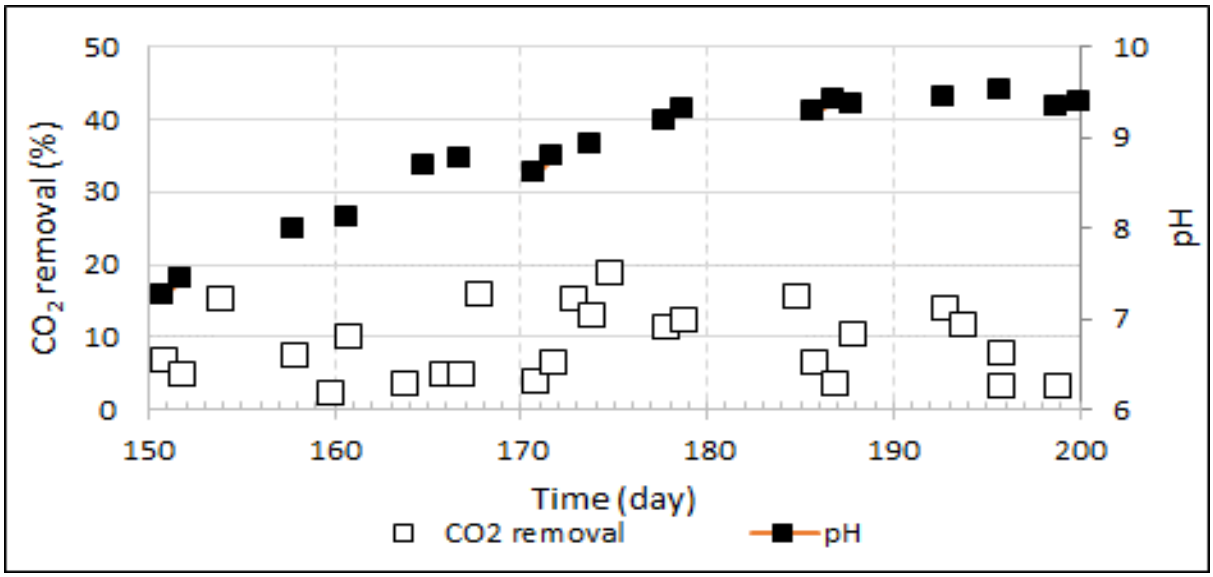


Figure 7-1 Time course of the removal efficiencies (□) of CO_2 and the pH (■) in the capillary photobioreactor during Phase II (day 150 – 200).

A net CO_2 consumption was observed during the entire Stage II achieving complete carbon sequestration from the removed VOCs. VOC removal during the initial phase of Stage II was similar to that during the final period of Stage I, but then changed, likely due to the pH slowly increasing from 7.3 to 9.4 over the course of 50 days (from day 150 to day 200). The

RE of α-pinene decreased from 99.5% to about 75% on day 158 when the increasing pH was ~ 8.0 (data not shown). The RE of toluene decreased from 95% on day 185 to about 70% when the pH reached ~ 9.3. During the same period, the RE of hexane increased from ~ 30% to 55% (data not shown). While both the RE of α-pinene and toluene decreased due to microbial inhibition at the high pH, the RE of hexane increased likely due to enzymatic changes within the microbial community removing toluene, as the changes in the removal performance occurred at the same time (~ day 185).

The potential of algal-bacterial symbiosis for the combined abatement of CO_2 and VOCs has not been investigated abundantly (Olivia et al., 2019), and especially not in relation to IAQ. Nonetheless, the technical feasibility of the combined VOCs and CO_2 consumption by a mixed microbial consortium of microalgae and bacteria in the capillary photobioreactor discussed herein agrees with observations of algae-bacterial treatment systems by other authors (Soreanu and Dumont, 2020; Olivia et al., 2019; Olivia et al., 2023; Lebrero et al., 2016). It is unlikely that there is severe competition between microalgae and bacteria. The bacteria dominating the bioreactor both are heterotrophic, so there is no competition for CO_2, and some microalgae can bio transform VOCs, but at a rate likely lower compared to the bacteria biotransformation rate of VOCs in our study. In algal-bacterial bioreactors, microalgae produce oxygen in the presence of light, and bacteria utilize the oxygen to oxidize the VOCs. The CO_2 produced as a by-product from aerobic VOCs degradation is concomitantly fixed by microalgae. On average, up to 24.8% of the CO_2 removed in the bioreactor is produced in-situ from VOC mineralization, while the rest of the CO_2 removed in the capillary bioreactor (at least 75.2%) comes from the inlet ambient air. Indeed, there is a net CO_2 consumption despite the CO_2 produced during VOC mineralization, achieving complete carbon sequestration from the removed VOCs along with additional CO_2 removed from the inlet ambient air.

The reduction of the inlet CO_2 concentration was about 10% (**Figure 7-1**), corresponding to a removal of 40 ppm_v between the inlet and the outlet CO_2 concentration in a single pass (less than 1 second) of the gas through the capillary bioreactor while treating VOCs. Thus, when the airflow is recycled, in a similar fashion to the recycling of ventilation air of an occupied room, this would still present a continuous removal of CO_2 from the room. The aim is not to achieve near-complete CO_2 removal is a single pass of the gas through the system, unlike end-of-pipe treatment technologies for industry emissions. The implementation of capillary photobioreactors to improve IAQ of occupied rooms could minimize or almost eliminate ambient air intake and significantly reduce the energy costs for heating and/or cooling typically required for conditioning outdoor air intakes. When a CO_2 RE of 10% is applied to a typical baseline ventilation rate of three air volume changes per hour in an occupied room, a constant CO_2 concentration can be maintained when the CO_2 production does not exceed a rate of 100 ppm_v CO_2 per hour. A higher CO_2 production rate would be feasible if the CO_2 concentration remains below 1,000 ppm_v, which is considered a safe value with no adverse effects on human health and well-being. This threshold is also the maximum limit in most green building certification schemes (ASHRAE, 2022; Wei et al., 2015). Alternatively, higher ventilation rates would be necessary to increase the overall CO_2 elimination capacity to maintain the required IAQ at a reduced outdoor air intake. The reduction in outdoor air intake while maintaining low enough levels of pollutants in a room

when an indoor air purifying system is employed is called the clean air delivery rate (*CADR*) of that system (Shaughnessy and Sextro, 2006). In summary, the overall purification capacity per volume of indoor space is a better performance criterium for indoor air purification systems than the single pass purification efficiency.

Maintaining low CO_2 levels in occupied spaces, in addition to maintaining low VOCs levels, is important as multiple studies have shown that human performance and wellbeing is directly negatively influenced by high CO_2 concentrations (Satish et al., 2012; Strøm-Tejsen et al., 2016). This involves workplace productivity, the quality of sleep alongside the next day performance and other negative symptoms like drowsiness, panting, and short breath. Moreover, when ambient outside air supply is maintained at the minimum ventilation rates per current professional standards such as ASHREA, generously occupied spaces can still result in CO_2 concentrations higher than the safe value of 1,000 ppm_v (Satish et al., 2012).

Biological approaches for improving IAQ are promising, but only when they can properly address the bioavailability of low concentrations of hydrophobic pollutants, provide CO_2-removal as well as guarantee microbial safety. A capillary bioreactor may provide an opportunity to improve IAQ via the co-abatement of VOCs and CO_2. Combining it with ultraviolet (UV) photolysis for the elimination of bioaerosols can further polish the biologically purified air, as reviewed elsewhere (Kraakman et al., 2021).

Microbial Characterization

Liquid samples from the capillary reactor were taken at the beginning of Phase I (see **Table 7-1**) and at the end of Phase II to analyse the microbial community. No accumulation of biomass on the walls of the capillary glass channels was observed for the 150-days operation of the multi-channel capillary bioreactor during Stage I. This observation is consistent with the findings in other studies where no biofilm formation was observed inside capillaries (Kraakman et al., 2023; Lopez de Leon et al., 2020) due to the relatively high shear forces. The prevention of biofilm formation was systematically investigated by Studer (2005), who showed that bacterial biofilm accumulation could be simply prevented with relatively low shear forces, which confirms the observations in the study discussed herein. However, the experiment was stopped by day 200 because of the clogging of three capillary channels mediated by the increase in algal biomass concentration during Stage II. The Stage II operation of the capillary bioreactor identified that operational adjustments would be required as microalgae, unlike bacteria in Stage I, seem capable of building a biofilm despite the relatively high shear-forces in the channels. These operational adjustments could involve placing the capillary channels in the dark and applying light only to the liquid recirculation reservoir or regular cleaning of the capillary channels. In addition, this study showed that pH-neutralization (and/or replenishment of the recirculation liquid) would be required to maintain a stable pH during co-abatement of VOCs and CO_2.

The bacterial diversities at the start and at the end of the experiment were determined and enhanced significantly during the 200-day operation of the capillary bioreactor. The Shannon and Simpson alpha diversity indexes increased from 5.1 to 5.6 and from 0.82 to 0.94, respectively (see diversity indexes in **Figure 7-2**). The bacterial diversity has been identified as an indicator of community stability and functional resilience towards perturbation (Saikaly and

Oerther, 2011) and could be an explanation of the stable performance during the 200-day operation of the capillary bioreactor.

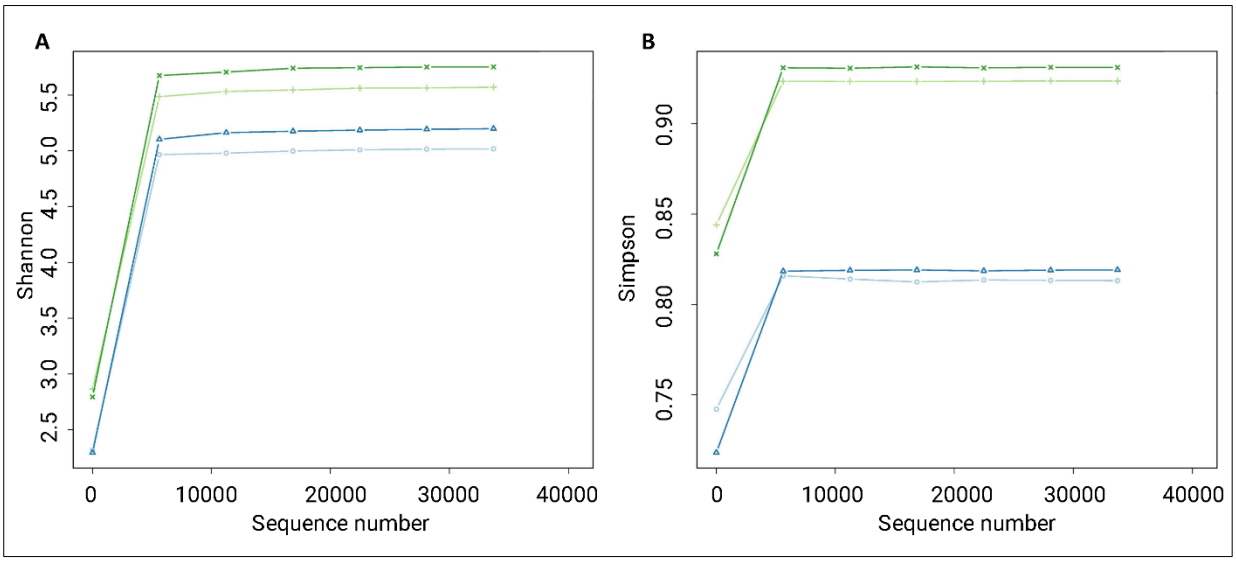


Figure 7-2 The Shannon (A) and Simpson (B) alpha diversity indexes at the start of Phase I (blue) and at the end of Phase II (green) both conducted in duplicate.

Metagenomic amplicon sequencing revealed that the bioreactor presented a more specialized and less diverse community at the start of Stage I, while bacterial richness and evenness significantly increased during the study (ANOVA < 0.05) (see **Figure 7-3, Figure 7-4, and Figure 7-5**). The community at the start of Stage I relied only on the recalcitrant VOCs treated (α-pinene, toluene, and n-hexane), while the addition of silicone oil and/or microalgae seems to have enhanced bacterial growth, diversity, and carbon co-metabolism potentially due to the algal characteristic release of dissolved organic compounds and phytohormones to the phycosphere (Tong et al., 2023). The variance between the bacterial genera found (per taxon) in each sample shows the great difference between the dominant bacterial communities at the start of Stage I and the end of Stage II (**Figure 7-3**).

The enrichment under the treated VOCs at the start of Stage I favoured the growth of a specialized community shaped by members of the uncultured OLB8 cluster from the family *Saprospiraceae* (42.1% ± 0.1 %) (see the genera abundance clustering bar plot in **Figure 7-4**). *Candidatus* genera from the family *Saprospiraceae* are known to be highly abundant in biological wastewater treatment processes. Recent shotgun genomic studies have confirmed that they have the capability of degrading complex and recalcitrant organic molecules (Kondrotaite et al., 2022), thus they were most likely involved in the catabolism of the target VOCs in Stage I. Other bacterial representative genera were members of the genus *Methylibium* (7.4% ± 0.5 %) and *Donkdonella* (2.2% ± 0.6 %). In contrast, these genera had almost negligible representation at the end of Stage II. Stage II was dominated by uncultured members of the family *Blastocatellaceae* (21.3% ± 0.01%). Microalgae (detected throughout chloroplast identification) and the cyanobacteria *Nodosilinea* were also representative in Stage II (17.3% ± 0.2% and 7.5% ± 0.01 %). Interestingly, bacteria previously related to α-pinene, toluene and n-hexane metabolism, such as the genera *Hydrogenophaga* (2.8% ± 0.4 %),

Pseudofulvimonas (1.0% ± 0.01 %) and *Pseudomonas* (0.7% ± 0.02 %) were detected in Stage II, but at low relative abundances (Cantera et al., 2022). This fact confirmed that the main metabolisms of Stage I were related to VOC removal, while in Stage II photosynthesis and chemoorganotrophy of the generated metabolites were most probably the prevalent metabolisms.

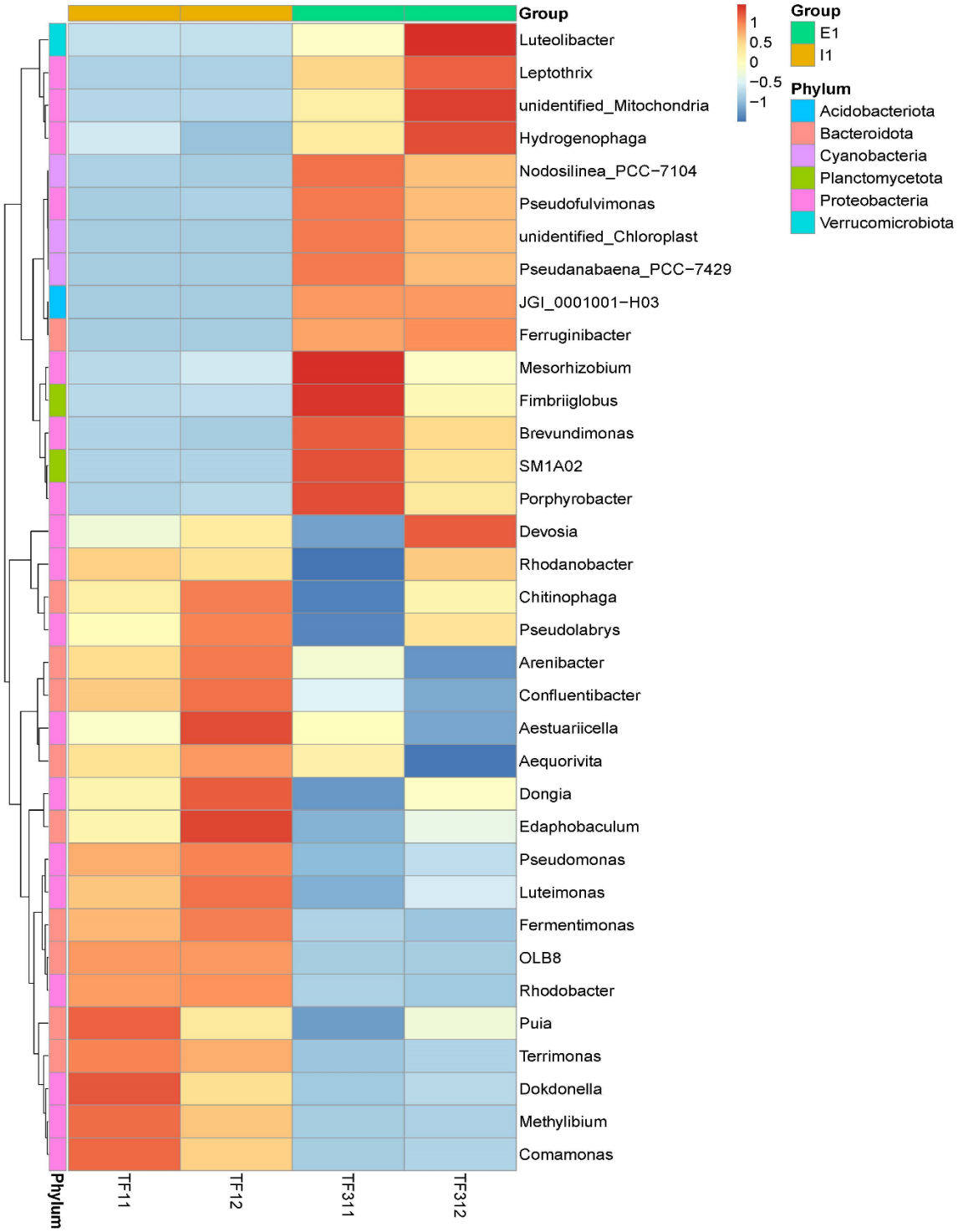


Figure 7-3 Heat map showing the comparison of each taxon at the start of Phase I and at the end of Phase II. The rows show the Z value obtained by standardizing the relative abundance of each row of genera. Group I1 (left two columns): start of Phase I; Group E1 (right two columns): end of Phase II.

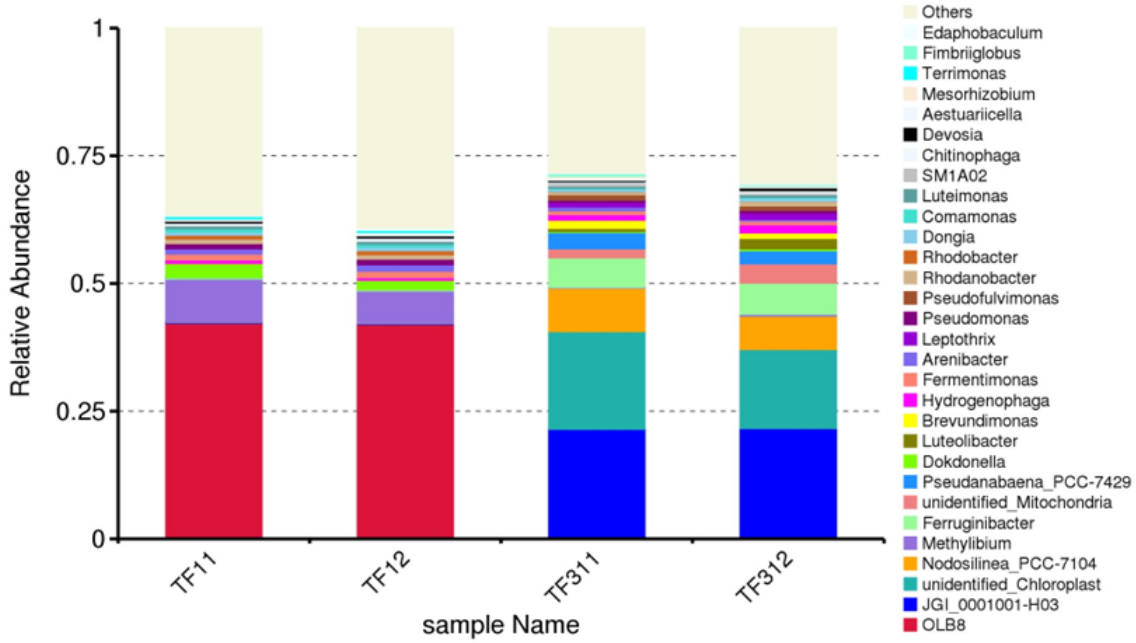


Figure 7-4 Species abundance clustering bar plot based on the annotation and abundance result of all samples at the genus level showing the top 35 genera in abundance ranking at the start of Phase I (TF1, left two bar columns) and at the end of Phase II (TF3, right two bar columns).

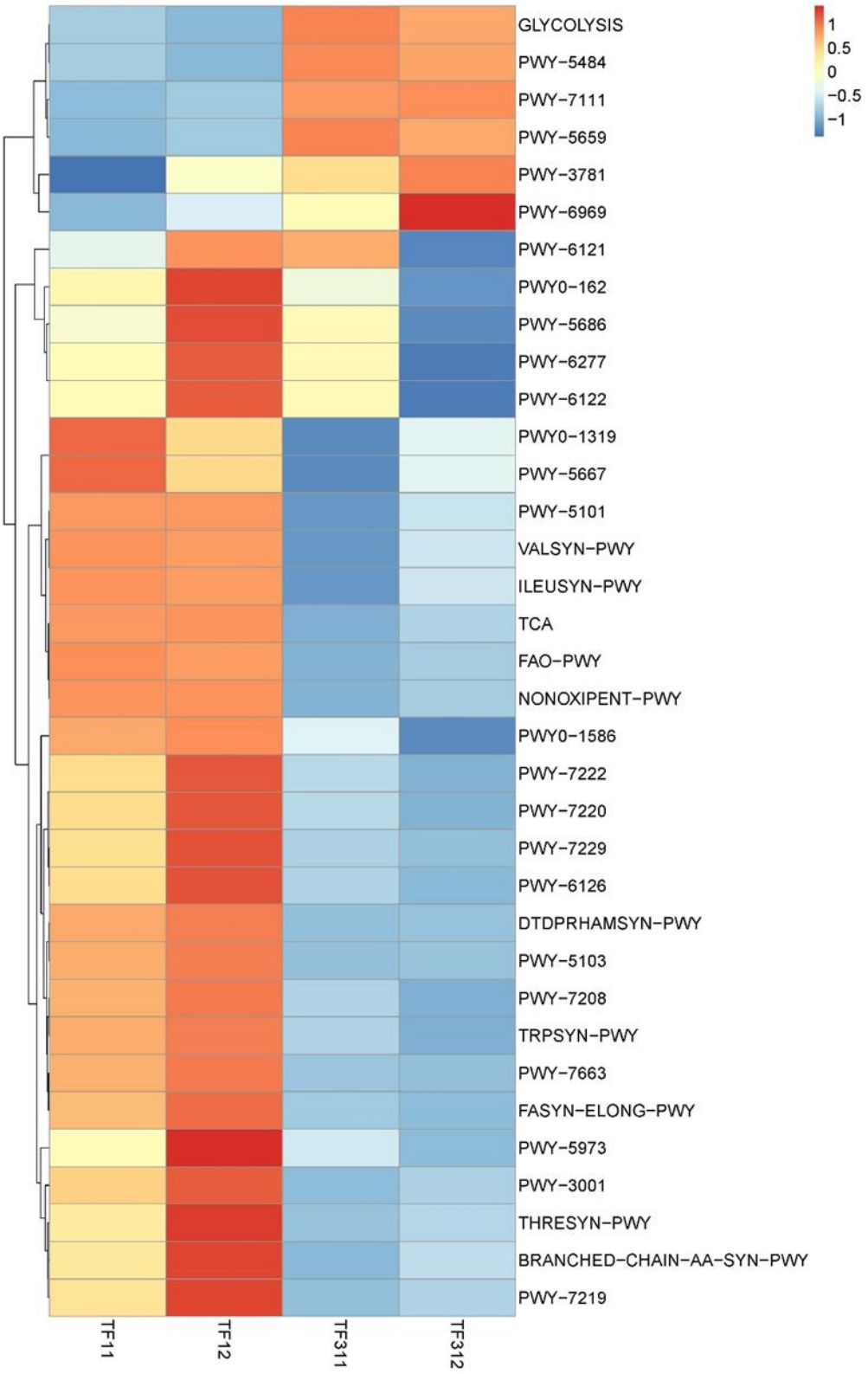


Figure 7-5 Heatmap of the metabolic functional prediction at the start of Phase I (TF1, left two columns) and at the end of Phase II (TF3, right two columns).

7.4 Conclusions

An instant reduction of the outlet CO_2 concentration compared to the inlet CO_2 concentration was observed after the introduction of the microalgae into the capillary bioreactor. A slow natural increase of the pH caused by photosynthesis was recorded confirming photosynthetic activity. A net CO_2 consumption was observed achieving complete carbon sequestration from the removed VOCs with additional CO_2 removed from the inlet ambient air. This confirms the feasibility of a capillary bioreactor as a platform for the biological gaseous co-abatement of CO_2 and hydrophobic VOCs.

In addition, the bacterial diversity, an indicator of community stability and functional resilience, enhanced substantially during the 200-day operation of Phase I and II and probably contributed to the observed stable performance of the capillary bioreactor. Longer-term operational requirements for the capillary bioreactor were identified, such as pH-neutralization and/or replenishment of the recirculation liquid.

PART VI

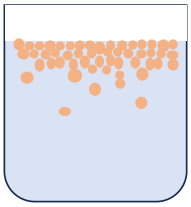
DILUTE METHANE MITIGATION USING A CAPILLARY BIOREACTOR

8. LIQUID PHASE MODIFICATION FOR DILUTE METHANE TREATMENT

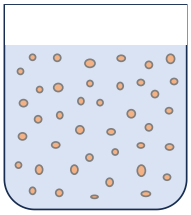
Chapter overview

Experiments were undertaken with the objective to optimise the liquid phase for dilute methane treatment in a capillary bioreactor. Three non-ionic surfactants were selected for their widespread availability and common use in many households or industries: BRIJ 58, TWEEN 60 and SDBS. The surfactants BRIJ 58 and SDBS, in contrast to TWEEN 60, both showed to be able to significantly enhance bioavailability of dilute methane at the concentrations tested. The lower apparent gas-liquid partition coefficient of methane and the enhanced cell hydrophobicity of the methane oxidizing consortium appear to be the main mechanism. The surfactant concentration required to obtain the maximum emulsion capacity of oil-in-water mixtures was low enough to prevent microbial inhibition for BRIJ 58 and TWEEN 60, but not for SDBS. This make SDBS less beneficial as additive in a bioreactor with silicone oil as non-aqueous phase, also because the foaming potential of SDBS is significantly higher than that of BRIJ 58 and TWEEN 60. BRIJ 58 was found to enhance the gas-liquid mass transfer by > 50% in a capillary channel under segmented (Taylor) flow regime, but the effect was significant only when combined with silicone oil. The improved emulsification of the oil by the surfactant combined with the enhanced cell hydrophobicity appeared to be the main mechanism, rather than the modification of the gas-liquid partial coefficient of methane.

Two immiscible liquids (water and oil), not yet emulsified



An unstable emulsion after mixing that progressively separates



Surfactant stabilised oil-in-water emulsion

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8.1 Introduction

Methane is the most abundant atmospheric organic gas released from major anthropogenic emission sources such as landfills, oil and natural gas systems, agricultural activities, coal mining, stationary and mobile combustion, and wastewater treatment processes. It is a significant greenhouse gas, responsible for ~ 30% of the rise in global temperatures since the Industrial Revolution. The need for methane mitigation has increased dramatically as research indicates that this gas has greater climatic impact than previously thought (O'Connor et al., 2010). In addition, as global efforts to mitigate CO_2 falter, aggressive methane mitigation is emerging as a lower cost strategy to curb climate change. Thus, reductions in methane emissions are imperative to controlling near-term global warming and improving air quality (IEA, 2023). However, approximately 55% of all the anthropogenic methane emissions have a concentration below the lower explosive limit of methane in air mixtures of 5% v/v and are incompatible for energy recovery or for physical-chemical oxidation abatement processes. The cost of mitigating methane emissions strongly varies depending on the sources (WMO, 2023; Harmsen et al., 2019), but the economic viability of mitigation is especially challenging when the methane concentration is below 5% v/v in air (Pecorini and Iannelli, 2020).

Microorganisms are capable of efficiently mineralising methane, but microbial activity is dependent on methane bioavailability in biological gas treatment systems. The treatment of methane-laden gaseous streams using biological methods presents challenges due to methane's poor solubility in water, together with its high volatility, and chemical stability. Conventional biological gas treatment systems such as biofilters and biotrickling filters operate as laminar contactors. As shown in **Table 3-2** (Section 3.3 of Chapter 3) conventional biological gas treatment systems are hampered by methane bioavailability and require extended gas residence times – often of several minutes – to achieve efficient removal due to the limited bioavailability of methane (Khabari et al., 2020; La et al., 2018; Stone et al., 2017; Kraakman et al., 2011). The laminar flow in conventional biological gas treatment systems is a flow regime characterized by high diffusion and low advection and is the opposite of turbulent flow. Improved convection by advection (i.e., the transport by the larger-scale motion of currents in a medium, for example through mixing) would improve mass transfer. In this context, capillary reactors when operated under segmented (Taylor) flow regime provide an internal liquid recirculation that combines enhanced mass transfer with low pressure drops, two important factors affecting cost effectiveness for many industrial applications (Bordel et al., 2024; Haase et al., 2016; Kreutzer et al., 2005).

The addition of a non-aqueous phase to gas-treatment bioreactors has been shown in multiple studies to enhance the removal of hydrophobic compounds (Lebrero et al., 2019; Cantera et al., 2016; Kraakman et al., 2024; Pascual et al., 2020). Silicone oil is generally considered the most suitable oil phase, with concentrations in the liquid media of the bioreactor of up to approximately 30% (v/v) (Lebrero et al., 2019(. However, operational problems such as foaming and adhesion to reactor internals have been reported when using silicone oil. Moreover, oils have a different viscosity and surface tension than water and can

therefore change the liquid physical characteristics and hydrodynamics, which can impact on the performance of many reactor types, including capillary reactors.

Surfactants have also shown to facilitate the removal of hydrophobic contaminants from contaminated soil and water, and to improve bioavailability through decreasing interfacial tension at the gas-liquid phase in gas treatment reactors (Lamprea et al., 2021; Wang et al., 2013). Indeed, different studies have demonstrated that the use of surfactant can improve performance in gas treatment bioreactors. However, these studies have mainly focused on the abatement efficiency, without analysing the mechanisms behind the improvements (Stone et al., 2017; Lamprea et al., 2021). In this sense, it is assumed that the addition of surfactants increases the solubility of the contaminant by reducing the surface tension at the immiscible phase and through micelles formation. However, other mechanisms have been also suggested that could enhance contaminant bioavailability, including increasing cell hydrophobicity, solubilization or emulsification of insoluble matter (such as biofilm material, grease, and oils), or promoting overall microbial metabolism if an easy-to-degrade surfactant is used (Lamprea et al., 2021). Conversely, surfactants can lead to substrate competition (i.e., degradation of the surfactant versus contaminant), can alter essential bacterial proteins and inactivate enzymes on the bacterial outer membrane or can cause cell membrane disruption resulting in a negative effect in the biological gas treatment system (Lamprea et al., 2021; Zhang et al., 2013).

Therefore, the addition of liquid phase additives in biological gas treatment reactors to improve overall performance in terms of removal efficiency and robustness requires a clear understanding of all the chemical, physical and biological processes involved. This study investigated the potential of dilute methane abatement using a capillary bioreactor and elucidated whether the liquid phase can be altered to improve its overall performance. To this aim, synthetic surfactants were investigated to assess their potential to enhance bioavailability and mass transfer, both with and without the presence of silicone oil. Three non-ionic surfactants were selected for their widespread availability and common use in many households or industries as detergents, wetting agents, emulsifiers, foaming agents, or antistatic additives: BRIJ 58, TWEEN 60 and SDBS. To date, no studies have tested the effect of surfactant addition in a capillary bioreactor treating dilute methane in the presence of silicone oil as non-aqueous liquid phase.

8.2 Materials and Methods

Mass-transfer study

This chapter explores the impact of liquid modifications on the gas-liquid mass transfer rate in a single capillary channel operated with segmented (Taylor) gas-liquid flow under abiotic conditions. Different surfactants with and without a non-aqueous liquid phase (silicone oil) are studied. Key steps included:

1. Selection of universally used surfactants that are readily available at low cost and known to be biodegradable. Three non-ionic surfactants were chosen based on lower toxicity to bacteria compared to ionic surfactants.

2. Toxicity assessment: surfactants were tested at concentrations known to minimize microbial inhibition.

3. Methane Bioavailability Test: The maximum specific methane oxidation rate of a mixed methanotrophic consortium was determined in bottles containing dilute methane in the headspace at two concentrations of each surfactant after an adaptation period of 10 weeks.

4. Cell hydrophobicity analysis: The microbial cell hydrophobicity was measured to link observed methane oxidation rate differences to the cell hydrophobicity of the methanotrophic consortium.

5. Oil-in-water mixtures with increasing silicone oil concentrations and increasing surfactant concentrations were prepared to determine their Emulsion Capacity, Emulsion Stability and Foaming Potential.

6. Surfactant selection: The best-performing surfactant was chosen based on its ability to enhance emulsion stability and capacity, improve bacterial hydrophobicity, and boost methane (CH4) bioavailability without microbial inhibition.

7. Determination of the mass transfer rate of the selected surfactant in a single capillary channel configuration under abiotic conditions with and without the presence of silicone oil.

Chemicals and Microorganisms

The medium used in this study consisted of a mineral salt medium containing KH_2PO_4 (0.7 g L^{-1}), $K_2HPO_4 \cdot 3\ H_2O$ (0.92 g L^{-1}), KNO_3 (3 g L^{-1}), NaCl (0.2 g L^{-1}), $MgSO_4 \cdot 7\ H_2O$ (0.35 g L^{-1}), $CaCl_2 \cdot 2\ H_2O$ (0.026 g L^{-1}) and 2 ml L^{-1} trace minerals solution containing EDTA (1 g L^{-1}), $FeSO_4 \cdot 7\ H_2O$ (0.08 g L^{-1}), $ZnSO_4 \cdot 7\ H_2O$ (0.005 g L^{-1}), $MnCl_2 \cdot 4\ H_2O$ (0.002 g L^{-1}), H_3BO_3 (0.001 g L^{-1}), $CoCl_2 \cdot 6\ H_2O$ (0.005 g L^{-1}), $CuCl_2 \cdot 2\ H_2O$ (0.001 g L^{-1}), $NiCl_2 \cdot 6\ H_2O$ (0.001 g L^{-1}) and $NaMoO_4 \cdot 2\ H_2O$ (0.002 g L^{-1}). The chemicals used for mineral salt medium preparation (PANREAC, Barcelona, Spain) had a purity of at least 99.0%. The silicone oil (polydimethylsiloxanes) that was used as second liquid phase exhibited a viscosity of 20 cSt (Sigma-Aldrich, Spain) or a viscosity of 220 cSt (Cogelsa, Spain). Surfactants were TWEEN 60, BRIJ 58, and sodium dodecyl benzene sulfonate (SDBS) (Sigma-Aldrich, Spain).

The inoculum was obtained from two sources: fresh activated sludge from Valladolid wastewater treatment plant (Spain) and post-composted anaerobically digested sludge from Five Ford wastewater treatment plant (United Kingdom). Both inocula were characterised as per methodology described in **Section 9.2** of Chapter 9, before adding each ~50% v/v in the final mixture.

Methane Bioavailability Test

From the mixed inoculum, methane oxidizing microorganisms were enriched in 2-L bottles containing 500 mL of medium while continuously stirred using a magnetic mixing plate at 400 rpm. An airflow of ~1 L min^{-1} containing methane at a concentration of ~ 500 ppm_v was continuously flowing through the headspace of the bottles. In total 10 bottles were used to which different additives (surfactant or oil) were periodically added to obtain the concentrations in the liquid shown in **Table 8-1**. The three selected surfactants TWEEN 80, BRIJ 58 and SDBS are all readily available at low cost and are biodegradable. In addition, these surfactants exhibit low potential for foaming and relatively low toxicity, and do not form salts with metallic ions when added to the nutrient solution to be dosed to a bioreactor due to their non-ionic character (Cattaneo and Astuto, 2024). The concentration of the surfactants was slowly increased over time to minimise the risk of microbial inhibition. The final surfactant concentration was chosen either to obtain the critical micelle concentration (CMC) of the surfactant in water (TWEEN 60 and BRIJ 58) or to avoid microbial inhibition (SDBS) as observed in other biological gaseous filtration studies with SDBS and sodium dodecyl sulfate (SDS) (Lamprea et al., 2021; Wu et al., 2022).

Table 8-1 Bottles with different additives to grow methane oxidizing microorganisms.

Bottle	Additive	Additive concentration (mg L^{-1})				
	Type	Week 1	Week 2	Week 3	Week 4	Final concentration (CMC[1)])
1	Control (medium only)					
2	Control (medium only)					
3	TWEEN 60 [2)]	9	18	36	36	1.25 CMC
4		9	18	36	72	2.5 CMC
5	BRIJ 58 [3)]	28	56	112	112	1.25 CMC
6		28	56	112	224	2.5 CMC
7	SDBS [4)]	3.1	6.3	12.5	12.5	0.013 CMC
8		3.1	6.3	12.5	25	0.026 CMC
9	Silicone oil only (5% v/v)					
10	Silicone oil only (5% v/v)					

[1)] CMC is the Critical Micelle Concentration in water with an increasing surface tension before reaching the CMC and a relatively constant surface tension after the CMC.

[2)] TWEEN 60 is a polyoxyethylenate sorbitol ester ($C_{64}H_{126}O_{26}$) with a HLB[5)] of 14.9

[3)] BRIJ 58 is a polyethylene glycol hexadecyl ether ($C_{56}H_{114}O_{21}$) with a HLB of 15.7.

[4)] SDBS is sodium dodecylbenzenesulfonate ($C_{18}H_{30}NaO_3S$) with a HLB of 19.9.

[5)] HLB is the Hydrophilic Lipophilic Balance number which is an indicator of surfactant hydrophilic or lipophilic character and a dominating factor to improve solubility of hydrophobic compounds in water (Lamprea et al., 2022).

The methane oxidation rate in the bottles was determined in Week 10, corresponding to 70 days after the initial addition of additives to the bottles. To measure the methane oxidation rate in each bottle, the continuous methane-containing air supply to the headspace was stopped, and the bottles were completely sealed with rubber stoppers and aluminium foil. The initial methane concentration in the headspace of each bottle was ~ 500 ppm_v (534 ± 12 ppm_v) and was measured in triplicate over time after 2, 5.5, 9, and 24 hours. By the end of the test, the microbial cell hydrophobicity was determined as described next.

Microbial Cell Hydrophobicity

The hydrophobicity was determined in duplicate according to a slightly modified method as described by Wu and co-workers (2022). A sample of 40 mL was taken from each bottle after vigorously shaking. The harvested biomass was centrifuged for 5 minutes at 5,000 rpm (Eppendorf, 5430 R) and then suspended in the original medium. Then the absorbance of the resuspended microorganisms (A1) was measured at 600 nm with UV-Vis spectrophotometer (Shimadzu UVmini-1240). The absorbance was maintained at 0.5 - 0.6 with samples being diluted when necessary. Then 3 mL of the above suspended microorganism's solution was taken, and 0.75 mL of n-hexadecane was added, mixed using an advanced vortex mixer at 2400 rpm (ZX3, Velp Scientifica) while regularly shaking for exactly 2 minutes, and then stand for 30 minutes. Finally, the absorbance of the aqueous phase (A2) at 600 nm was measured and the cell surface hydrophobicity of microorganisms was calculated by the following Equation (8-1):

$$\textit{Cell Hydrophobicity (\%)} = 100 \times (1 - A2 / A1) \qquad \text{(Equation 8-1)}$$

The measurement was repeated for each bottle the next day and the results were averaged.

Emulsion Activity and Stability of Oil-in-Water Liquid

Emulsions are mixtures of two or more liquids that are immiscible and are inherently unstable. Emulsions do not tend to form spontaneously and requires input of energy (e.g., stirring) to be formed and generally also to be maintained. The Emulsion Activity of oil-in-water mixtures containing surfactant was here determined in duplicate, which is a measure of the ability to form an emulsion, according to a methodology adapted from Kempka and co-workers (2015). In addition, the Emulsion Stability was determined in duplicate, which refers to the ability of an established emulsion to resist change in its properties over time. An appropriate surfactant can increase the stability of an emulsion so that the oil droplets dispersed in the dispersion medium do not change significantly with time as surfactants reduce the interfacial tension between the liquids.

The Emulsion Activity and Emulsion Stability were here determined for silicone oil in the medium solution (demineralised water containing a nutrient solution as defined previously in this section under *Chemicals and Microorganisms*) to which different concentrations of surfactant were added. Silicone oil (20 cSt) was added to the medium in various ratios to obtain different concentrations of silicone oil. Surfactant was added in concentrations ranging from 0 mg L^{-1} to above its CMC. After that, the liquids were mixed using an advanced vortex mixer (VELP Scientific, ZX 3) for exactly 90 seconds at 3,000 rpm.

The Emulsion Activity was determined after 6 minutes by measuring the serum volume (A) and the total volume of the liquid after mixing (B) and calculated as per Equation 8-2:

$$\textit{Emulsion Activity (\%)} = (B - A) / B \qquad \text{(Equation 8-2)}$$

The Emulsion Stability was determined after 60 minutes and 24 hours by measuring the serum volume (A) and the total volume of the liquid (B) as per Equation 8-3:

$$\textit{Emulsion Stability (\%)} = (B - A) / B \qquad \text{(Equation 8-3)}$$

In addition, the Foaming Potential was determined after 30 seconds by measuring the foam volume (C) and the total volume of the liquid before mixing (D) as per Equation 8-4:

$$Foaming\ Potential\ (\%) = C / D \qquad \text{(Equation 8-4)}$$

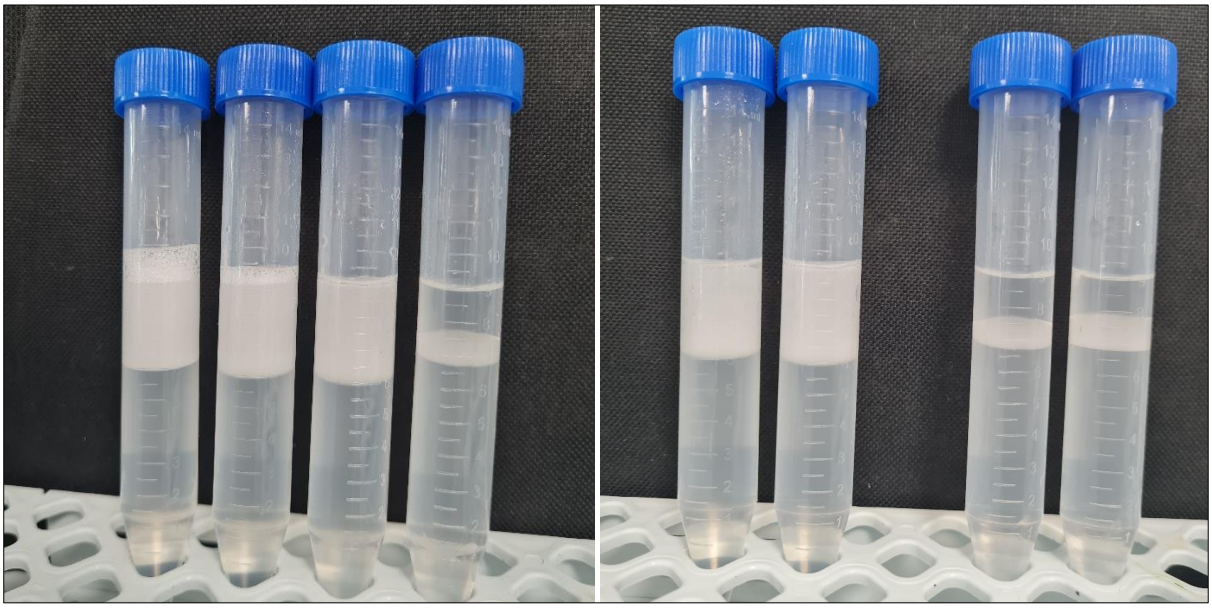


Figure 8-2 Examples of the impact of the surfactant concentrations (left) and duplo results (right).

Abiotic Mass-Transfer Rate in a Single Capillary Channel

The gas-to-liquid mass-transfer rate of methane was measured in duplicate in a 0.54 m single capillary channel under segmented flow (Taylor flow) conditions. A glass capillary channel with an internal diameter of 2.4 mm was used through which the gas-liquid bubble train moved downwards. Air and water were introduced to the capillary channel via a simple T-connector at the top of the capillary channel and the air and liquid were disengaged at the bottom in a glass flask containing two overflows; one for the water in the bottom and one for air in the top (see set-up **Figure 8-3**). A pump (Watson Marlow 323) was used to set the gas flow rate at 7.09 L h^{-1} and a second pump (Watson Marlow 323) was used to set the liquid flow rate at 5.44 L h^{-1}. This resulted in a gas-to-liquid ratio of 1.3, an empty channel gas contact time of 0.7 s, and a superficial slug face velocity of approximately 0.77 m s^{-1} in the capillary channel. The airflow was recirculated through the capillary channel (internal loop), while the liquid was flowing only once through the capillary channel. A known amount of methane was injected in the recirculated air stream and its concentration was measured several times to confirm stable methane concentration in the recirculating airflow before starting the liquid pump. At t=0 the liquid pump was started and the time course of methane concentration in the recirculating airflow was measured to determine the gas-to-liquid mass transfer of methane in the capillary channel. The gas-to-liquid mass transfer rate was determined for different liquid mixtures: (1) water only, (2) water and silicone oil (20 cSt at 10% v/v), (3) water and BRIJ 58 (120 mg L^{-1}), and (4) mixtures of water, BRIJ 58 (120 mg L^{-1}) and silicone oil different in concentration (10% and 25% v/v) or viscosity (20 cSt and 200 cSt).

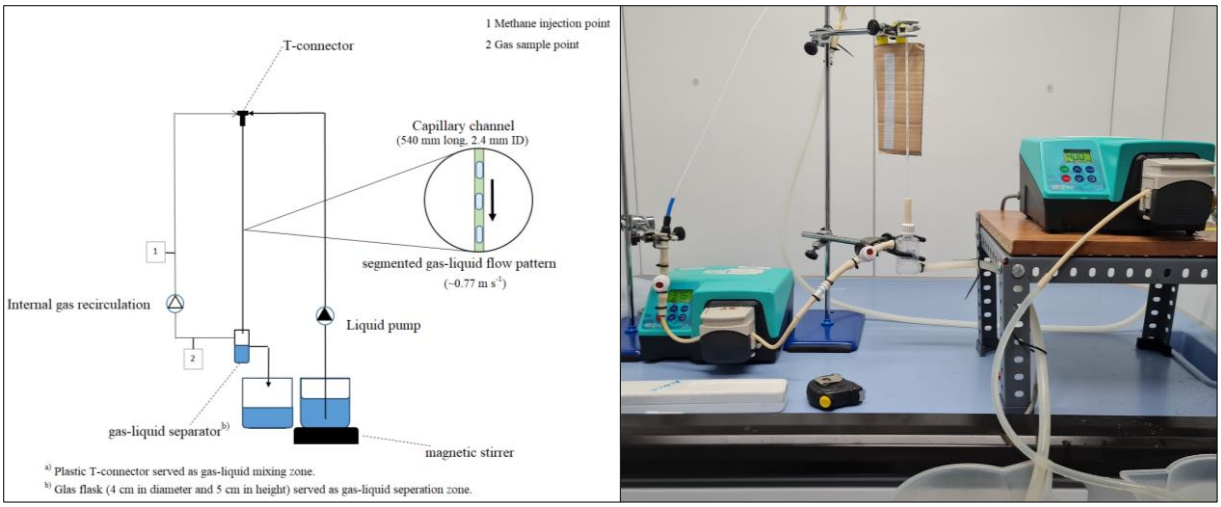


Figure 8-3 Schematic representation of the experimental set-up (left) and the actual set-up of the single capillary channel mass transfer measurements.

8.2 Results and Discussion

Methane Bioavailability Test

The methane oxidation rate in the bottles containing methane oxidizing microorganisms was determined 10 weeks after the initial addition of additives to the bottles as per schedule shown in **Table 8-1**. To measure the methane oxidation rate in each bottle, the continuous air supply containing methane to the headspace was stopped and the methane concentration in the headspace of all bottles containing different liquid additives was measured over time as shown in **Figure 8-4**. The biomass concentration in the liquid of the bottles ranged between 0.5 and 1 g L^{-1} to determine the maximum specific methane oxidation rate (MOR) which is defined as the mmol CH_4 removed per gram dry weight of biomass per day at the initial methane concentration of ~500 ppm_v. The maximum specific methane removal rate of the controls (Bottles 1 and 2 without any liquid additive) was the lowest, while being significantly higher in Bottles 7 and 8, reaching values up to 18 and 12 times higher when supplemented with SDBS at 12.5 and 25 mg L^{-1}, respectively, and in Bottle 5, achieving 15 times higher removal rates at the lower BRIJ 58 concentration of 112 mg L^{-1}. The specific methane removal rate of both bottles containing Tween 60 and the bottle with the higher BRIJ 58 concentration are only slightly higher when compared to the controls.

The results of the methane oxidation rate in the bottles containing SDBS in this study agrees with the observations conducted in the study of Wu and co-workers in a biotrickling filter treating n-alkane and methane. In their study, the methane removal efficiency (RE) increased from 35% to 74% with the addition of SDBS at a surfactant concentration of 15 mg L^{-1}, which was shown not to inhibit microbial growth (Wu et al., 2022).

Biological gas treatment studies testing surfactants from the BRIJ group have also shown an enhancement of removal performance consistent with the findings in our experiment with BRIJ 58. Ramirez and co-workers (2012) observed an increase of methane removed between 6% and 35% when different surfactants of the BRIJ group were added to a conventional biofilter treating methane. In addition, Miller and co-workers (2018) reported a nearly 20%

improvement of a biofilter treating toluene after the addition of BRIJ 35. Moreover, Dhamwichukorn and co-workers (2001) observed an increase of α-pinene removal from 26% to 95% when treating a mixture of α-pinene and methanol in a thermophilic biofilter after addition of a mixture of non-ionic surfactants, including BRIJ 35 and BRIJ 58. On the other hand, although bioavailability and biodegradation can be enhanced, the microbial growth rate can be inhibited at already relatively low BRIJ concentrations (< 1 CMC) as illustrated for BRIJ 30 (Dhamwichukorn et al., 2001).

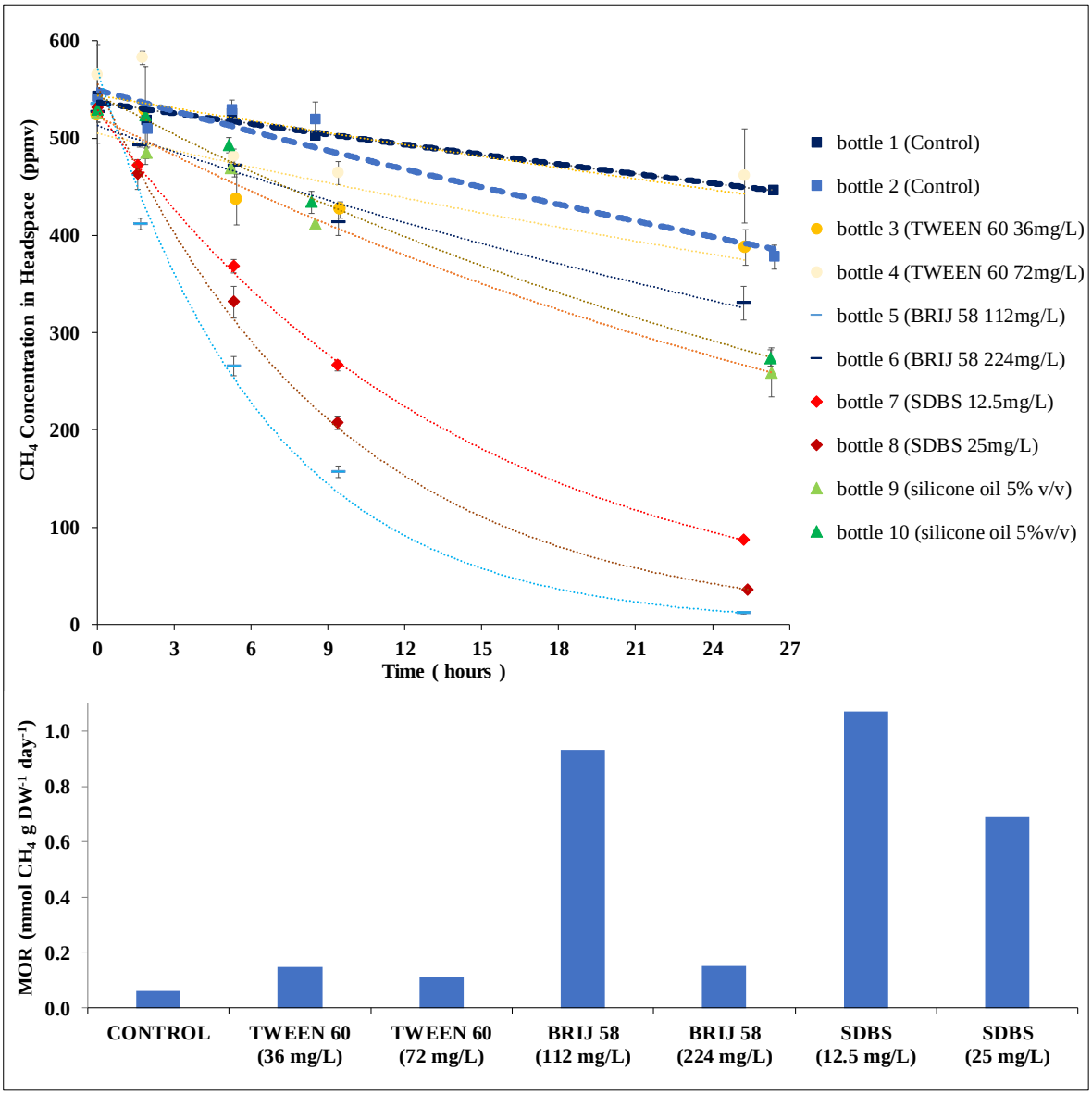


Figure 8-4 Time course of the reduction of the methane concentration in the headspace of the bottles (upper graphic) and maximum specific methane oxidation rate (MOR) (lower graphic) after 10 weeks containing methane oxidizing microorganisms and different liquid phase additives.

The relatively small increase in methane oxidation rate observed in this study when TWEEN 60 was supplemented is consistent with findings from other studies, where the effect of a surfactant from the TWEEN group was neutral or only minor (either positive or negative). For example, TWEEN 20 neither affected the RE nor affected the development of the microbial

community in a conventional biofilter treating toluene (Chan and Wu, 2010). Similarly, it was observed that TWEEN 80 exerted an either neutral or a slightly positive effect on the mass transfer of conventional biofilters (Miller et al., 2020). This may be explained by the observed lower influence of TWEEN surfactants on the apparent gas-water partitioning coefficient constant of contaminants compared to other type of surfactants (Lamprea et al., 2023). Conversely, Ramirez and co-workers (2012) showed an increase between 19 to 35% in methane removal in a conventional biofilter when adding TWEEN surfactants intermittently to the system as part of the nutrient solution.

In addition, the toxicity of non-ionic surfactants has shown to be higher as their molecular weight (MW) increases, which makes the surfactant TWEEN 60 (MW 1312) potentially less suitable compared to SDBS (MW 348) and BRIJ 58 (MW 1122). Similarly, the effect in terms of removal efficiency (positive, neutral, negative) has shown to be strongly dependent on the concentration of the TWEEN surfactant added, as illustrated by Wang and co-workers (2022). Their study showed that while an increase in the TWEEN 20 concentration from 3.7 mg L^{-1} to 7.4 mg L^{-1} (~ 0.1 CMC) did enhance the RE of ethylbenzene in a biotrickling filter, a further increase to 37 mg L^{-1} and 74 mg L^{-1} (~ 1 CMC) resulted in a reduction of the RE. In a subsequent study, these authors observed an improvement in m-xylene removal in a biotrickling filter when TWEEN 80 was added at a relative high concentration of 100 mg L^{-1} (~ 6.7 CMC), but this was mainly attributed to the higher inlet m-xylene concentrations (Lamprea et al., 2024). Deng and co-workers observed a 20% increase of the hexane RE when treating hexane and dichloromethane in a biotrickling filter with TWEEN 20 at a relatively low concentration of 30 mg L^{-1} (= 0.5 CMC) in the recirculating liquid (Deng et al., 2023). This increase in RE is comparable to the study of Amin and co-workers (2016), who showed a slight (~14%) improvement of xylene removal in a conventional biofilter when TWEEN 20 was applied daily as part of the nutrient solution at a concentration of 150 mg L^{-1} (= 2.5 CMC).

The highest specific methane removal rates for each surfactant in our study were observed at the lower rather than the higher surfactant concentration. This might also explain the large difference in specific methane removal rate in the bottles with the BRIJ 58 additive, with Bottle 5 containing half the concentration of Bottle 6. This observation supports reports from other studies regarding the risk of microbial inhibition by surfactants at higher concentrations (Zhang et al., 2013; Wu et al., 2022; Miller et al., 2018).

The methane removal rate in the headspace of both bottles containing only silicone oil (Bottle 9 and Bottle 10) only slightly increased when compared to the bottles containing no additive (Control Bottles 1 and 2). The specific methane removal rate in the bottles containing silicone oil could not be confirmed because the biomass concentration was not determined. However, it can be inferred that silicone oil had a limited beneficial effect in our set-up, which was probably attributed to the low degree of emulsification of the oil-water mixture. A high degree of emulsification entails that tiny oil droplets stay suspended within the water phase, while a low degree of emulsification progressively separates the oil from the water phase and forms an oil layer on top of the water phase. When properly emulsified, oil in tiny droplets would increase the methane liquid-oil and the gas-oil mass transfer due to its larger interfacial surface area.

This study confirms that surfactants can significantly improve bioavailability of dilute methane, with both BRIJ 58 and SDBS showing an increased bioavailability by one to two orders of magnitude at the concentrations tested. This improvement can be attributed to a reduction in the gas-liquid surface tension when the surfactant was added, and the formation of micelles that decrease the apparent Henry's law constant of the contaminants (Wu et al., 2022; Lamprea et al., 2023). On the other hand, surfactants can adsorb onto the bacterial cell or may increase the bacterial cell membrane hydrophobicity, which enhances the bioavailability of hydrophobic contaminants (Lamprea et al., 2021; Wu et al., 2022).

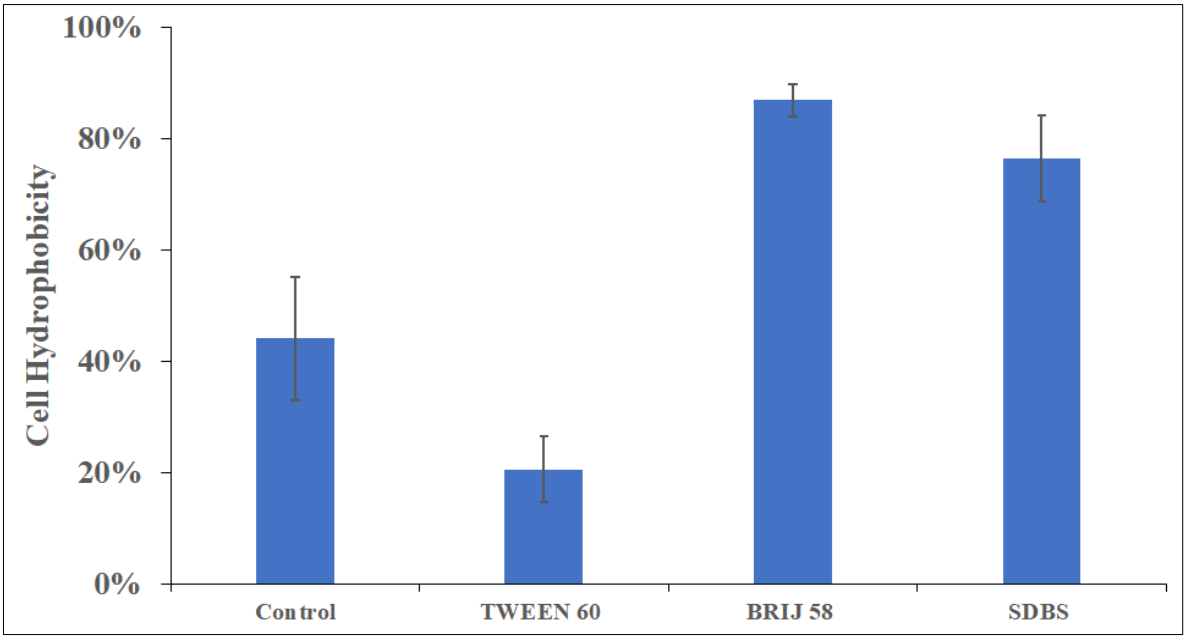


Figure 8-5 The cell hydrophobicity of the microorganisms after growth on dilute methane in the presence of different surfactants.

Therefore, the day after measuring the bioavailability in the bottles, the cell hydrophobicity of the microorganisms was determined after having grown on methane for ten weeks (**Figure 8-5**). The cell hydrophobicity of the microorganisms grown in the presence of the surfactant BRIJ 58 was ~87% regardless of the concentration, and for those grown in the presence of SDBS was ~ 75%, both significantly higher than the cell hydrophobicity of the methane oxidizing microorganisms in the controls (44%). In contrast, the cell hydrophobicity of the microorganisms in the bottles containing TWEEN 60 was not enhanced, remaining at only 21%. It was concluded that BRIJ 58 and SDBS in our experiment increased the cell hydrophobicity by nearly a factor of two when compared to the controls (without any additive), while TWEEN 60 did not increase the cell hydrophobicity at the concentrations tested, which was actually lower when compared to the control (no surfactant).

Emulsion Activity and Stability of Oil-in-Water Mixtures

The Emulsion Capacity and Emulsion Stability as well as the Foaming Potential were determined for oil-in-water mixtures containing the three selected surfactants. The water was in this case demineralised water containing nutrients and the oil was silicone oil (20 cSt). **Figure**

8-6 shows the results for the different oil-in-water mixtures for increasing silicone oil concentrations and increasing surfactant concentrations.

The Emulsion Capacity and Emulsion Stability are 0% when no surfactants are added, confirming that the oil-in-water mixture is not very stable when 20 cSt silicone oil and the medium solution are respectively used as oil and water phase. On the contrary, and as expected, the Emulsion Capacity increases with oil when surfactants are supplemented to the medium. In the particular case of BRIJ 58, the required surfactant concentration to form a stable emulsion does not need to exceed 80 mg L^{-1}. This can be explained by its CMC value (~90 mg L^{-1}), beyond which the surface tension between the liquids does not further decrease and remains relatively constant. Similarly, the higher CMC of SDBS (~960 mg L^{-1}) explains why the Emulsion Capacity increases at the higher surfactant concentrations tested, as the surface tension between liquids reduces with increasing surfactant concentration up till the CMC of the surfactant. Furthermore, the Emulsion Stability is highest for BRIJ 58, while the Foaming Potential is negligible for both BRIJ 58 and TWEEN 60 but significantly higher for SDBS.

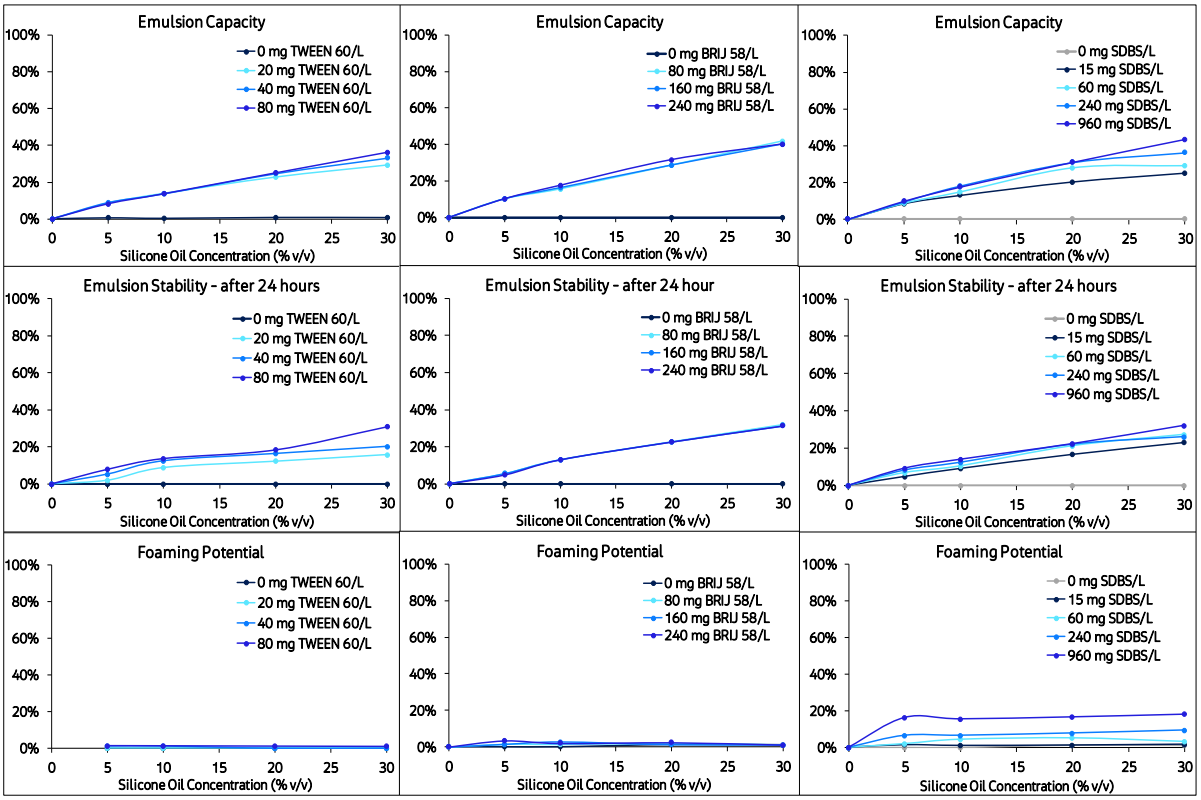


Figure 8-6 The Emulsion Capacity (top), Emulsion Stability (middle), and Foaming Potential (bottom) of TWEEN 60 (left), BRIJ 58 (middle), and SDBS (right) at increasing silicone oil percentages.

Abiotic Mass-Transfer Rate in a Single Capillary Channel

The gas-to-liquid mass-transfer rate of methane in a single capillary channel was measured under segmented (Taylor) flow regime conditions at methane concentrations of ~ 5,000 ppm_v (= 0.5% v/v) in ambient air for different liquids: (1) water, (2) water + silicon oil, (3) water + BRIJ 58 and (4) water + silicone oil + BRIJ 58, with the oil at two concentrations (10 % v/v and 25% v/v) and two viscosities (20 cSt and 200 cSt). The results are summarized in **Figure 8-7** and show that the addition of only BRIJ 58 or only silicone oil did slightly (< 10%) increase the gas-to-liquid mass transfer of methane in the capillary channel. The combined addition of

surfactant (BRIJ 58) and 10% (v/v) silicone oil (both 20 cSt and 220 cSt) did significantly (~70%) increase the gas-to-liquid CH_4 mass transfer in our set-up when compared to the control (water). The combined addition of the surfactant BRIJ 58 and 25% (v/v) silicone oil (both 20 cSt and 220 cSt) did still increase the gas-to-liquid mass transfer, but less (~30%) when compared with the control (water).

It can be concluded that the addition of the surfactant BRIJ 58 can significantly enhance the gas-liquid mass transfer in the capillary channel but only when combined with silicone oil, which may be explained by the improved emulsion capacity as observed in the results obtained on emulsion capacity and stability **(Figure 8-7)**. The enhancement of the methane gas-liquid mass transfer in the capillary channel was most noticeable when the amount of silicone oil was 10%, rather than 25%, while the viscosity (20 cSt or 200 cSt) did not made much of a difference.

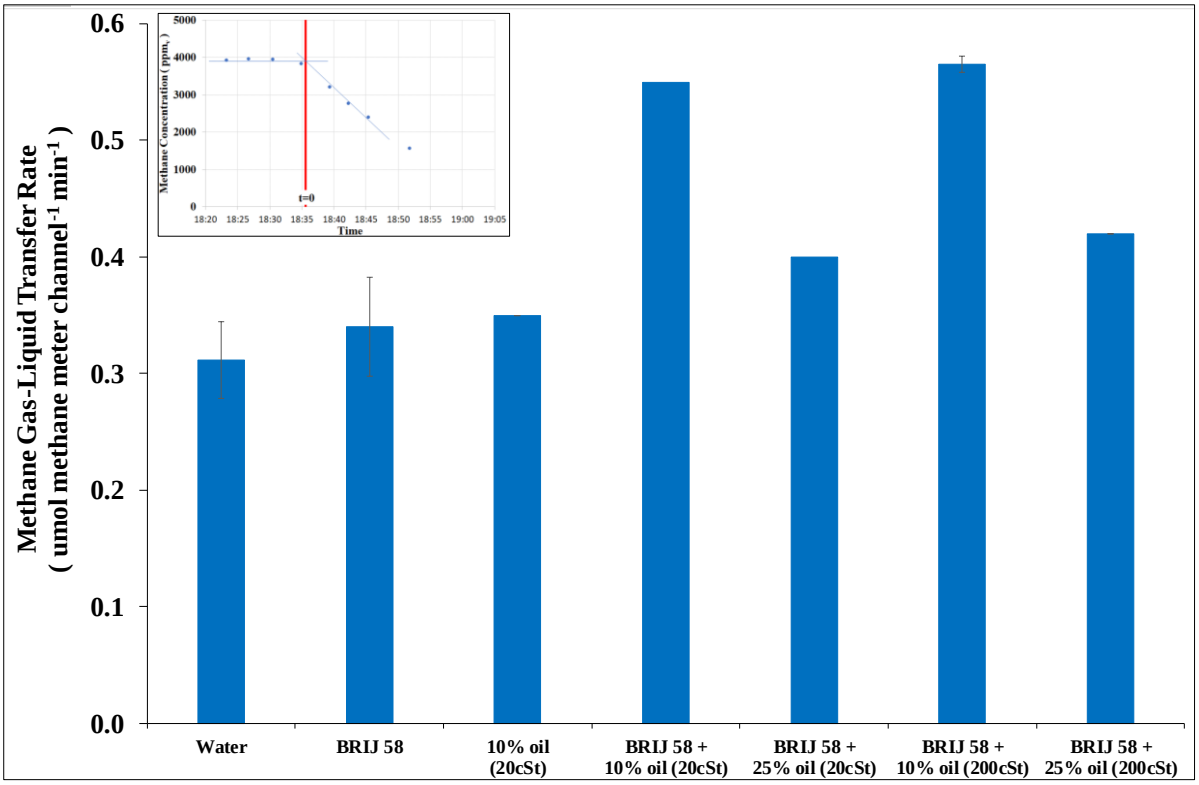


Figure 8-7 Mass-transfer rate of methane in the single capillary channel with liquids containing different additives. Graphic in the top left corner showing an example of the gaseous methane concentration over time with t=0 the start of the liquid recirculation.

The slight increase (12%) in methane mass-transfer when only 10% v/v 20 cSt silicone oil was added may be explained by the lower gas-oil partition coefficient of methane ($H_{Gas/Silicone\ Oil}$ = 0.82) compared to the gas-water partition coefficient of methane ($H_{Gas/Water}$ = 28). It can be calculated that an oil-water mixture containing 10% (v/v) silicone oil could theoretically provide a partition coefficient ($H_{Gas/Water\text{-}Silicone\text{-}Oil\text{-}Mixture}$) for methane of 25.3, which is 11% lower than the gas-water partition coefficient of methane ($H_{Gas/Water}$) of 28 and thus corresponding with the 12% increase in methane mass-transfer measured in our study.

The observed 9 % increase in methane mass-transfer when only BRIJ 58 (120 mg L^{-1}) was added can only partly be explained by the ~ 4% increase in methane solubility in water

expected by adding the BRIJ surfactant, as discussed elsewhere (Garcia-Aguilar et al., 2011). The remaining increase may be attributed to experimental analysis error in our study, which is estimated to be a few percent.

A larger increase in methane mass-transfer was observed when the surfactant and the silicone oil were combined, an improvement seen in all silicone oil combinations tested, regardless the volume of the oil or the viscosity of the oil. The explanation is most likely related to the improved emulsification of the oil in the water where the surfactant stabilises the oil-in-water emulsion maintaining smaller oil droplets in the water phase. Smaller oil droplets enhance gas-to-oil mass transfer, which creates higher methane carrying capacity because the $H_{Gas/Silicone\ Oil}$ (= 0.82) is much smaller than the $H_{Gas/Water}$ (= 28). The oil-in-water emulsion is a mixture of two liquids that are immiscible and are inherently unstable and in which the oil tends to separate out from the water in the absence of the surfactant.

The enhancing effect of oil volume was larger than the effect of oil viscosity, as 10% v/v volume provides better mass-transfer than 25% v/v volume (regardless the viscosity of the oil) and 200 cSt viscosity provides slightly better mass-transfer than 20 cSt (regardless the volume of the oil). The higher methane mass transfer observed with 10% v/v silicone oil and surfactant compared to the 25% v/v silicone oil with surfactant appears to be the result of a more optimal segmented flow patron. Increasing the silicone oil fraction from 10 to 25% v/v made the length of the gas bubble (L_b) and the length of the liquid slug (L_s) combined become significantly longer ($L_b + L_s = L_u$ which is also called the one total unit length). In our study, the average total unit length (L_u) increased from about 1 cm to more than 3 cm (**Figure 8-8**). A shorter L_u may increase mass transfer as it reduces the risk that the liquid film surrounding the gas bubble get saturated, limiting further mass transfer as discussed elsewhere (Bordel et al., 2024). The higher viscosity of the oil provided slightly better mass-transfer (regardless the oil volume) and might be explained by the impact of viscosity on the liquid film thickness surrounding the gas bubbles. Increasing the liquid viscosity of the oil-in-water emulsion increases the liquid film thickness as explained elsewhere (Aussillous and Quere, 2000), which increases the methane carrying capacity of the liquid film each time a gas bubble passes it in the segmented flow in the capillary channel. The liquid film thickness flowing around gas bubbles is critical for gas-liquid mass transfer in a capillary channel under segmented (Taylor) flow regime. On the other hand, higher liquid viscosity can also hamper the gas-liquid mass transfer in a capillary channel under segmented (Taylor) flow regime, with the optimum viscosity dependent on the operating conditions and the liquid surface tension (Bordel et al., 2024). Moreover, higher viscosity increases the viscous drag forces relative to the surface tension forces, which may compromise capillarity. The Capillary number (*Ca*) represents this relation between viscous drag forces and capillary forces (Equation 8-5):

$$Ca\ (-) = \mu\, v\, /\, \gamma \qquad \text{(Equation 8-5)}$$

where μ is the viscosity (Pa s), v the liquid velocity (m s^{-1}), and γ the surface tension of the liquid in the gas phase (N m^{-1}). Increased viscous drag forces slows down the internal liquid recirculation, the vortex that enhances mass transfer through convection rather than diffusion. Thulasidas and co-workers (Thulasidas et al., 1997) found that the liquid internal recirculation velocity reduces sharply and ultimately becomes zero with increasing the Ca number, with Ca

> 0.6 being the theoretical value where the internal vortex becomes zero in a downward flow. In our experiments with the 20 cSt viscosity silicone oil the calculated Ca numbers were 0.06 and 0.12 for the 10% v/v and 25% v/v oil, respectively, while with the 200 cSt viscosity silicone oil 0.5 and 1.1 for the 10% v/v and 25% v/v oil, respectively. This assumes that the overall liquid viscosity is proportional to the oil-liquid fraction and the gas-liquid surface tension is 35.7 mN m^{-1} as per Peters and Arabali (2013) This assumption is a simplification but shows that adding more silicone oil, and especially adding silicone oil with a higher viscosity, may increase the Capillary number beyond the threshold where internal recirculation is reduced, and mass transfer is compromised.

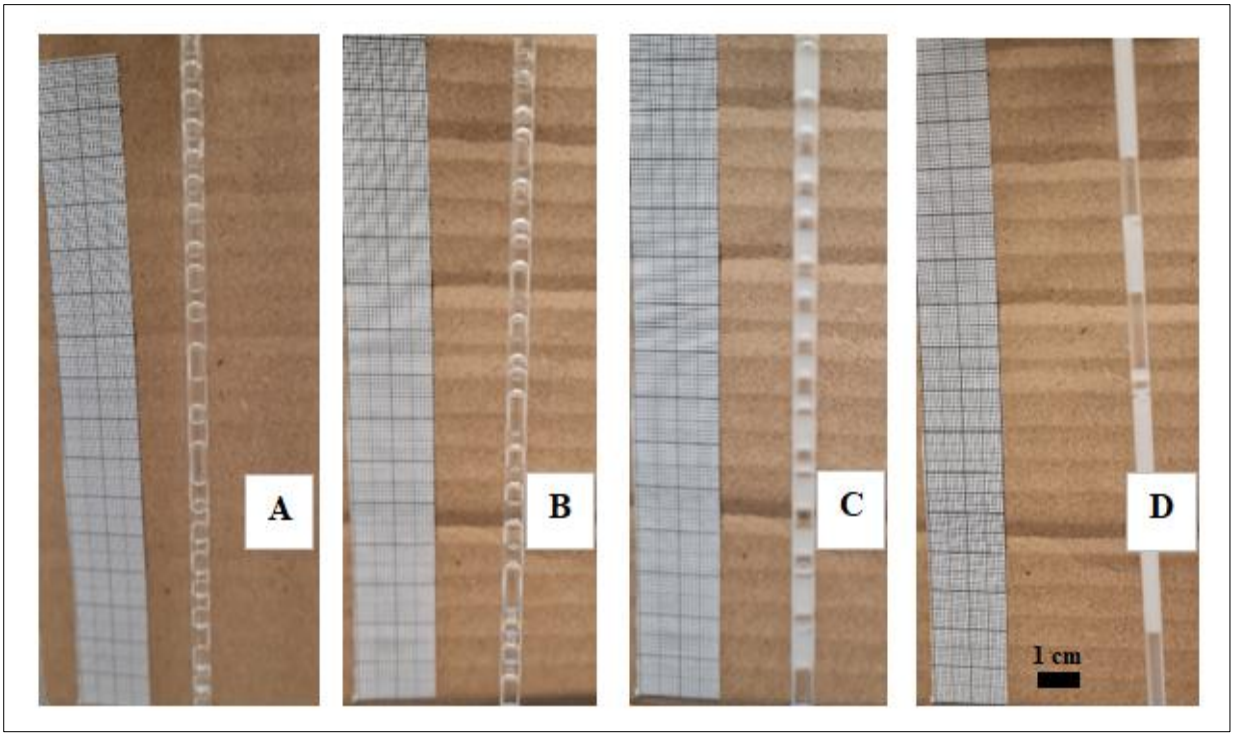


Figure 8-8 Photos of the segmented flow patrons in the single capillary channel during the abiotic mass-transfer rate experiment of water only **(A),** water + BRIJ 58 **(B),** water + BRIJ 58 + 10 % v/v silicone oil **(C)**, and water + BRIJ 58 + 25 % v/v silicone oil **(D).**

8.4 Conclusions

The experiments elucidated that the liquid phase can be optimized to improve its overall performance dilute methane abatement using a capillary reactor. Synthetic surfactants were investigated to assess their potential to enhance bioavailability and mass transfer, both with and without the presence of silicone oil. Three non-ionic surfactants were selected for their widespread availability and common use in many households or industries: BRIJ 58, TWEEN 60 and SDBS. The surfactants BRIJ 58 and SDBS, in contrast to TWEEN 60, both showed to be able to significantly enhance bioavailability of dilute methane at the concentrations tested. The lower apparent gas-liquid partition coefficient of methane and the enhanced cell hydrophobicity of the methane oxidizing consortium appear to be the main mechanism. The surfactant concentration required to obtain the maximum emulsion capacity of oil-in-water

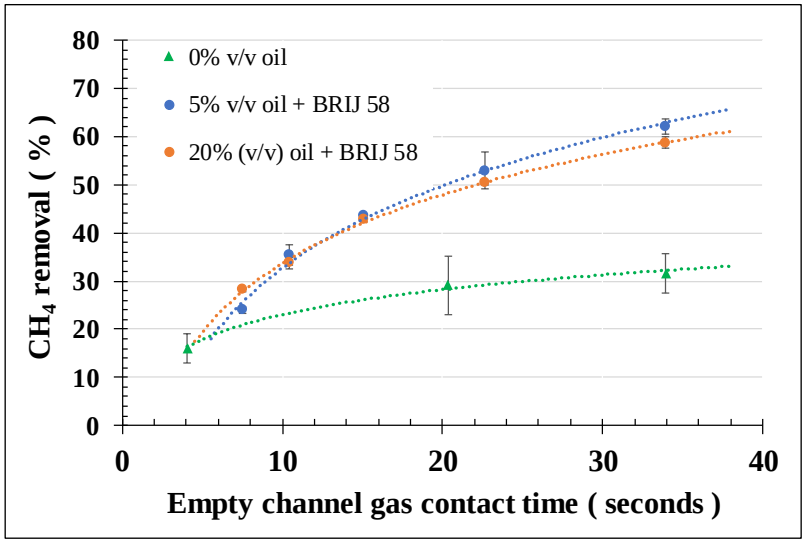
mixtures was low enough to prevent microbial inhibition for BRIJ 58 and TWEEN 60, but not for SDBS. This make SDBS less beneficial as additive in a bioreactor with silicone oil as non-aqueous phase, also because the foaming potential of SDBS is significantly higher than that of BRIJ 58 and TWEEN 60. BRIJ 58 was found to enhance the gas-liquid mass transfer in a capillary channel, but the effect was significant only when combined with silicone oil. The improved emulsification of the oil by the surfactant combined with enhanced cell hydrophobicity appeared to be the main mechanism for this enhancement, rather than the modification of the gas-liquid partial coefficient of methane.

9. CAPILLARY BIOREACTOR OPERATING EVALUATIONS

Chapter overview

The potential for dilute methane abatement of a capillary bioreactor was investigated and discussed in this chapter. The removal of gaseous methane was investigated in different capillary bioreactor configurations and evaluated for operating conditions and parameters relevant to input requirements (e.g., energy) and reliable long-term performance. Biotic experiments were performed in multi-channel capillary bioreactors to study different capillary channels, changes in gas-liquid slug velocities, gas-liquid ratios, methane inlet loading rates, gas contact times, and with/without internal gas recirculation. Although all reactors showed a high methane removal capacity, the addition of only surfactant (Experiment A) or only silicone oil (Experiment B) did not show any enhancement in methane removal. The capillary bioreactor containing silicone oil and surfactant BRIJ 58 (Experiment C) treated dilute methane the best at an elimination capacity of 231 ± 30 g methane per m^3 internal capillary channel per hour at an efficiency of 52.8 ± 6.1% at an empty channel gas contact time of 23 seconds. The optimised liquid phase consisted of water containing nutrients, silicone oil (20% v/v and a viscosity of 20 cSt), and BRIJ 58 (160 mg L^{-1} = 1.8 CMC).

The silicone oil acting as a buffer for methane was confirmed in a test that showed no deterioration in methane removal in the CBR following the methane supply interruption of six days. The use of surfactants and silicone oil, along with the improved bioavailability of methane, promoted a strong microbial specialization by the end of the operation of the CBR with the most abundant aerobic methanotroph belonging to the genus *Methylosarcina* with an increase in the relative abundance of *Lacunisphaera*. No accumulation of biomass on the walls of the capillary glass channels was observed during the entire period of more than 300-days operation of the CBR. It appears that a CBR with an optimized liquid phase, when operated with internal gas recirculation and thus decoupling optimal conditions for mass transfer from the gas contact time, may be a useful platform for further exploring the abatement of dilute methane.



Parts of this chapter have been submitted for publication together with of the content of Chapter 9 as: Kraakman N.J.R., Villarrael-Heras, L., González-Martína, J., Cantera, S., Muñoz, R., Lebrero, R. (2024). **Enhancing Dilute Methane Treatment Through Liquid Phase Alteration in a Capillary Bioreactor.** *Chemical Engineering Journal.*

9.1 Introduction

Capillary gas-liquid bioreactors can be effective gaseous treatment systems, as shown and discussed in previous chapters, and may be promising for environmental applications (such as air quality control, dilute methane abatement, and gas-phase biorefineries). However, further studies on capillary gas-liquid bioreactors would be required to fully understand operating conditions of the treatment of hydrophobic gaseous compounds, especially in terms of input requirements (e.g., energy) and aspects relevant for long-term reliable performance, important factors affecting the ultimate cost effectiveness and acceptance for most applications.

In this chapter, the removal of gaseous methane is investigated in different capillary bioreactor configurations and its results are evaluated for operating conditions relevant to input requirements (e.g., energy) and reliable long-term performance. Biotic experiments were performed in multi-channel CBRs to study:

- different capillary channels
    - diameters (1.7mm and 2.4mm)
    - lengths (1.5m and 1.0m)
- different operational modes
    - changes in gas-liquid slug velocities, gas-liquid ratios, methane inlet loading rates, gas contact times, with/without internal gas recirculation.
- different liquid characteristics
    - with/ without surfactants
    - with/ without silicone oil
- conditions relevant for reliable long-term performance
    - sudden methane load increases
    - methane supply interruption
    - nutrient requirements
    - biomass control.

The observation that no biomass accumulated on the walls of the capillary glass channels of the multi-channel capillary bioreactor for the 300-days operation under high methane loading rates was further evaluated. Furthermore, the dynamics of microbial population structure was monitored in one of the CBR with the optimized liquid phase (see **Chapter 8**) is discussed in this chapter.

9.2 Material and Methods

Chemicals

The medium used in this study consisted of a mineral salt medium containing KH_2PO_4 (0.7 g L^{-1}), $K_2HPO_4 \cdot 3\ H_2O$ (0.92 g L^{-1}), KNO_3 (3 g L^{-1}), NaCl (0.2 g L^{-1}), $MgSO_4 \cdot 7\ H_2O$ (0.35 g L^{-1}), $CaCl_2 \cdot 2\ H_2O$ (0.026 g L^{-1}) and 2 ml L^{-1} trace minerals solution containing EDTA (1 g L^{-1}), $FeSO_4 \cdot 7\ H_2O$ (0.08 g L^{-1}), $ZnSO_4 \cdot 7\ H_2O$ (0.005 g L^{-1}), $MnCl_2 \cdot 4\ H_2O$ (0.002 g L^{-1}), H_3BO_3 (0.001 g L^{-1}), $CoCl_2 \cdot 6\ H_2O$ (0.005 g L^{-1}), $CuCl_2 \cdot 2\ H_2O$ (0.001 g L^{-1}), $NiCl_2 \cdot 6\ H_2O$ (0.001 g L^{-1}) and $NaMoO_4 \cdot 2\ H_2O$ (0.002 g L^{-1}). The chemicals used for mineral salt medium preparation (PANREAC, Barcelona, Spain) had a purity of at least 99.0%. The silicone oil (polydimethylsiloxanes) that was used as second liquid phase exhibited a viscosity of 20 cSt (Sigma-Aldrich, Madrid, Spain)

Capillary Reactor Set-up

Three biotic experiments were undertaken to study dilute methane removal in a CBR according to the schedule shown in **Table 9-1**.

- Experiment A involved a CBR containing capillary channels with an internal diameter of 1.7 mm and 1.5 meter in length. The primary object was to quantify the effect of the addition of silicone oil (3% v/v silicone oil with a viscosity of 20 cSt).
- Experiment B contained capillary channels with an internal diameter of 2.4 mm and 1.0 meter in length. This experiment was focused on the addition of a surfactant (SDBS at a concentration up to 27.5 mg L^{-1}).
- Experiment C contained capillary channels with an internal diameter of 2.4 mm and 1.0 meter in length. The aim was to quantify the effect of the combined addition of a surfactant and silicone oil (Brij 58 at concentrations of 80 and 160 mg L^{-1} and silicone oil concentration of 5% and 20%). The incentives for Experiment C were the limited methane removal efficiencies obtained in Experiment A and Experiment B (RE up to about 30% only) and the promising results of the experimental work studying the combined addition of a surfactant and silicone oil as reported in **Chapter 8**.

The schematic representation of the CBR set-up in the three experiments is shown in **Figure 9-1**. In Experiment A and Experiment B the gas-liquid mixing was conducted by pushing air into the liquid through a flat 3 mm thick PDMS membrane through which about 400 needle holes were perforated using a 0.4 mm diameter needle. In Experiment C the gas-liquid mixing was conducted by injecting the air via the 4mm supply tubing into the liquid that contained 6 mm scrubber Kaldness K1 packing rings. Internal gas recirculation was only applied in Experiment C by using an EVO 10 compressor (EAD, Model H5P3 P 1, Spain) where the recycled gas stream was subsequently mixed with fresh inlet air containing methane before resupplied into the bottom liquid reservoir as illustrated in **Figure 9-1**. Internal gas recirculation had shown to be beneficial for methane removal in a biotrickling filter study (Estrada et al., 2014) and was here adapted as a potential strategy to enhance methane removal in the CBR. The fresh inlet air was clean dry air from which all the CO_2 was removed before methane was introduced using a flow control meter (Aalborg, Model GFC 17). The clean

dry supply airflow and the recirculating gas flow were measured with a rotameter (Aalborg, S/N 51588-2).

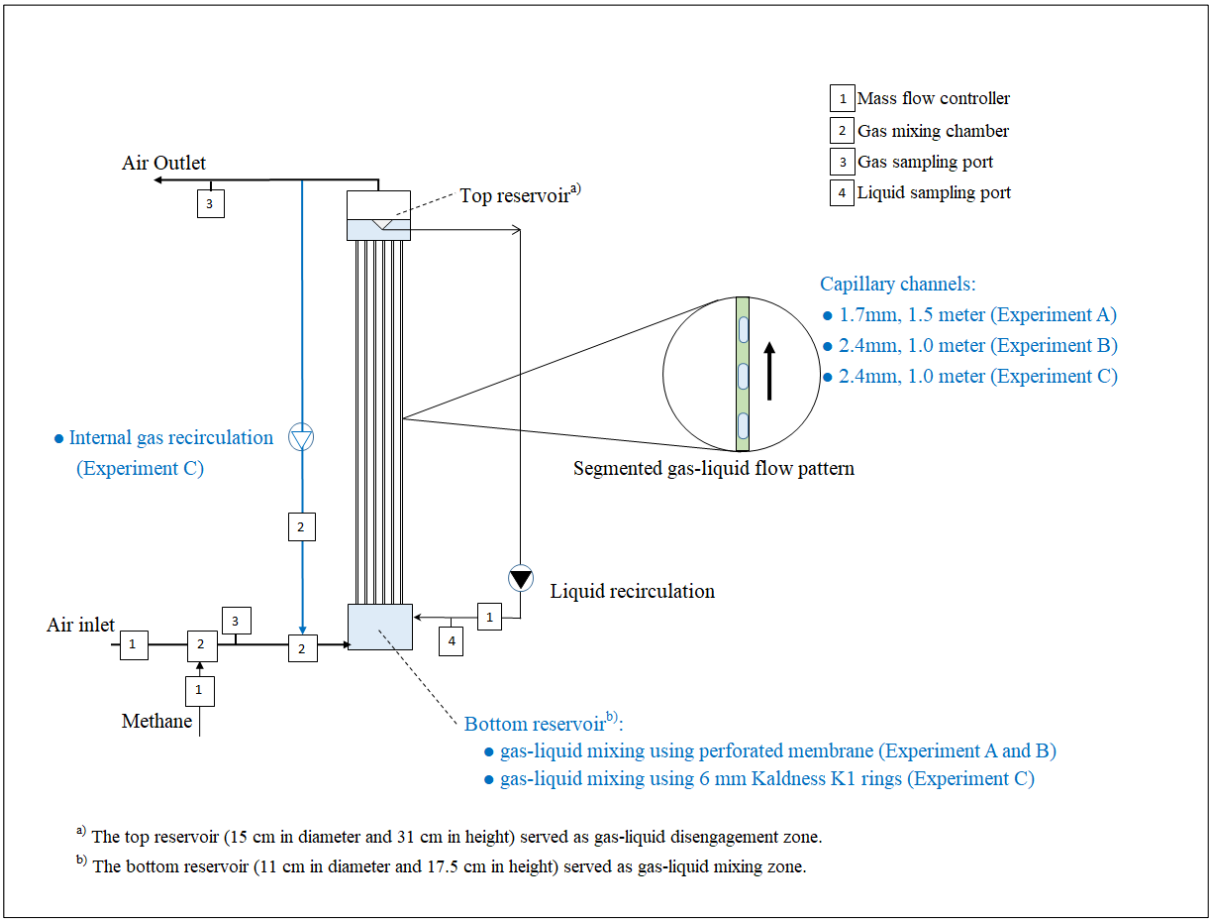


Figure 9-1 Set-up of the capillary bioreactor to study dilute methane removal.

The temperature of the recirculation liquid of the CBR was the temperature of the room (maintained ~ 20 ºC) during Experiment A and Experiment B, while controlled and constantly maintained at 24 ºC during Experiment C. The pressure of the gas flows (inlet, outlet and recycled) was periodically measured with a pressure sensor (IFM PN7097).

The capillary reactor was inoculated with fresh activated sludge from Valladolid wastewater treatment plant (Spain) in Experiment A and Experiment B. In Experiment C a mixed inoculum was used from two sources: fresh activated sludge from Valladolid wastewater treatment plant (Spain) and post-composted anaerobically digested sludge from Five Ford wastewater treatment plant (United Kingdom). These inocula were characterised as per methodology described under *Analytical Methods* further down in this **Section 9.2**, before adding each ~50% v/v in the final mixture. The microbial consortium in Experiment C was acclimatised in the CBR for the first 175 days before starting the experiment on Day 175 to determine the effect of surfactant addition and silicone oil addition to the recirculating liquid in the capillary reactor on the methane removal capacity.

Table 9-1 Operational conditions of the capillary bioreactor to study dilute methane removal.

Experiment	Days (#)	CBR Channels Diameter[1]	Length	Channels	Slug Face Velocities ($m\ s^{-1}$)	ECRT (sec)	Internal Gas Recirculation (Yes / No)	G/L Ratio in Channel (-)	Methane IC (ppm_v)	Methane IL[3] ($g\ m^{-3}\ h^{-1}$)	Liquid Medium of CBR[4]
A	98	1.7 mm (PTFE[2])	1.5 m	25	1.7 – 6.0	0.5 – 4.0	No	0.5 – 1.9	~ 250	125 - 1250	Medium only **(Stage I)** 3% v/v Silicone oil (20 cSt) **(Stage II)**
B	238	2.4 mm (glass)	1.0 m	25	0.15 – 0.84	4.5 – 9.0	No	0.4 – 2.5	350 – 7850	100 - 2000	Medium only **(Stage I)** SDBS (27.5 mg L^{-1}) **(Stage II)**
C	305	2.4 mm (glass)	1.0 m	25	1.3 - 2.5	4.1 - 33.9	Yes	0.5 – 2.0	900 - 6500	300 - 1100	Medium only **(Stage I)** BRIJ 58 (80 mg L^{-1}) **(Stage II)** BRIJ 58 (80 mg L^{-1}) 5% v/v Silicone oil (20 cSt) **(Stage III)** BRIJ 58 (160 mg L^{-1}) 5% v/v Silicone oil (20 cSt) **(Stage IV)** BRIJ 58 (160 mg L^{-1}) 20% v/v Silicone oil (20 cSt) **(Stage V)**

[1] Internal diameter

[2] PTFE = polytetrafluoroethylene (Teflon™)

[3] Inlet methane load per total internal volume of all capillary channels

[4] Concentration of the liquid phase in the CBR

No medium was replaced during Experiment A and Experiment B, while during Experiment C 800 mL of recirculating liquid was removed from the CBR five days per week from day 87 onwards and replaced with fresh medium to avoid nutrient limitation and accumulation of inhibitory metabolites. During this medium replacement, the biomass and silicone oil were recovered and returned to the capillary reactor through centrifugation of the liquid twice (5000 rpm for 10 minutes) in a refrigerated centrifuge (Eppendorf, Model 5439 R). The performance of the CBRs was evaluated using the following parameters:

- The inlet methane load (IL), which is defined as follows (Equation 9-1):

$$IL\ (g\ m^{-3}\ h^{-1}) = Q_g \times C_i / (V_c \times n_c) \qquad \text{(Equation 9-1)}$$

  with Q_g is the inlet air flow rate ($m^3\ h^{-1}$) and C_i is the inlet methane concentration ($g\ m^{-3}$), V_c is the internal volume of a capillary channel (m^3), and n_c the number of capillary channels in the CBR (-).

- The methane elimination capacity (EC), which is defined as follows (Equation 9-2):

$$EC\ (g\ m^{-3}\ h^{-1}) = (C_i - C_o) \times Q_g / (V_c \times n_c) \qquad \text{(Equation 9-2)}$$

  with C_o the outlet methane concentration ($g\ m^{-3}$).

- The removal efficiency (*RE*), which is defined as follows (Equation 9-3):

$$RE\ (\%) = (C_i - C_o)/ C_i \times 100 \qquad \text{(Equation 9-3)}$$

- The empty channel residence time (*ECRT*) is defined as follows (Equation 9-4):

$$ECRT\ (s) = (V_c \times n_c) / (Q_g) \qquad \text{(Equation 9-4)}$$

The same operating conditions were maintained in Experiment C during the last 130 days testing of the liquid additives: an up-flow segmented flow face velocity inside the capillary channels of 2.2 m s^{-1} and an internal gas recirculation (recycled gas to fresh inlet air) ratio of 15, which resulted in an ECRT of 23 seconds. The inlet methane concentration was maintained at a ~4500 ppm_v, while the surfactant BRIJ 58 was selected based on results of the experimental work reported in **Chapter 8**.

Evaluation of factors important for stable bioreactor operation

The following parameters were investigated to get an understanding of the impact of factors that might be important for stable bioreactor operation:

- Methane inlet load interruption or inlet load increases (transient conditions)
- Nutrient concentration (minimum total nitrogen concentration)
- High surfactant concentration (beyond threshold causing microbial inhibition)
- Biomass control (risk of biomass accumulation inside capillary channels)

Microbial studies are often focussed on conversion rates under optimal conditions, while microbial responses to transient conditions are less common, though very valuable to fundamentally understand a microbial reactor system. Moreover, reliability is important when applying (biological) gas treatment processes. Reliability is the combination of robustness and resilience. The process robustness reflects the capacity of a treatment system to maintain functionality with certain changes such fluctuations in inlet loading rate, loading interruptions,

or operational upsets. The resilience is the rate at which a treatment system returns to its original state after being disturbed. Biological systems may be impacted by sudden changes or longer-term changes in parameters such as nutrients or accumulated biomass.
In addition, the pressure drop has been calculated and evaluated for different CBR designs (i.e., capillary channel diameter) and different CBR operation conditions (i.e., slug velocity and gas-liquid ratio).

Analytical Methods

Methane concentrations were measured at the inlet and outlet of the CBRs typically twice a day and where each measurement entails the average of three gas samples. Each gas sample was analysed in a Bruker 430 GC-TCD (Palo Alto, USA) equipped with a thermal conductivity detector, and a CP-Molsieve 5A and a CP-PoraBOND Q columns. The oven, injector and detector temperatures were maintained at 40 ^{o}C, 150 ^{o}C and 250 ^{o}C, respectively. Helium was used as the carrier gas at 3.9 mL min $^{-1}$.

The biomass, total nitrogen (TN), and total organic carbon (TOC) concentrations in the liquid phase were periodically quantified according to Standard Method 2540 D. The dissolved TN and TOC were determined after filtration of the sample through a 0.45 μm pore size filter in a TOC-VCSH analyser (Japan) with a TNM-1 chemiluminescence module. The pH (Crison BASIC-20+) and conductivity (Crison BASIC-30) in the liquid media were also monitored (APHA, 2017).

The concentration CO_2 of inlet and outlet gas stream of the CBR was measured using a GC-TCD (Agilent 8860, Santa Clara, USA) equipped with a CP-Molsieve 5A and a CP-PoraBOND Q columns. The oven temperature was maintained at 80 ^{o}C for 2.3 minutes after which it increased with 20 ^{o}C per minute to 150 ^{o}C. Helium was used as the carrier gas at 3.9 mL min^{-1}.

During Experiment C the community structure of the two inocula (Activated Sludge Inoculum (InAS) and post-composted anaerobically digested sludge (InCS)), as well as that at the end of Phase I (prior to adding surfactant, BR) and at the end of Phase V (end of operation, TR), was analysed. Genomic DNA was extracted using FastDNA™ SPIN Kit for Soil (MP Biomedicals, USA). PCR amplification of regions 16S-V4-V5 was performed by using the primers GTGCCAGCMGCCGCGGTAA, CCGTCAATTCCTTTGAGTTT connecting with barcodes. PCR products of the appropriate size were selected by agarose gel electrophoresis. Equal amounts from each sample were pooled, end-repaired, A-tailed, and ligated with Illumina adapters to create sequencing libraries. These libraries were quantified using Qubit and real-time PCR, with size distribution checked by Bioanalyzer. Finally, the quantified libraries were pooled and sequenced on an Illumina platform to generate 250 bp paired-end reads at Novogene UK (Cambridge, UK). Paired-end reads were assigned to samples based on unique barcodes, and barcodes and primer sequences were trimmed using Python (V3.6.13) and Cutadapt (V3.3). FLASH (V1.2.11) was used to merge the paired-end reads, while fastp (V0.23.1) and the UCHIME algorithm handled data filtration and chimera removal (Edgar et al., 2011; Magoc et al.,2011). Sequences were clustered into Operational Taxonomic Units (OTUs) using QIIME2 (202202) with the SILVA (V138.1) and RDP (V18) gene reference databases (Quast et al., 2012). The top 35 taxa at genus level were selected to plot relative abundance histograms in Perl (V5.26.2) using SVG, and heatmaps in R (V4.0.3) using

pheatmap (Kolde, 2019). Shannon alpha diversity index and Beta diversity were calculated using QIIME2. Functional predictions based on marker genes were performed with the R package PICRUSt2 (V2.3.0) (Douglas et al., 2020). The sequences obtained have been deposited in Genbank as Bioproject PRJNA1162485.

9.3 Results and Discussion

CBR performance evaluation Experiment A – including the addition of silicone oil

During Experiment A, a relatively small capillary channel (internal diameter 1.5 mm) was tested. The ECRT was initially maintained very short (<1 second) as illustrated in **Table 9-1**, similarly as to the previous experiments when treating the hydrophobic compounds hexane, toluene, and α-pinene (**Chapter 5**, **6, and 7**). The inlet dilute methane concentration was maintained relatively low and on average 250 ± 15 ppm_v during the entire experiment. No medium was added during the entire 98 day of the experiment, only demineralised water was occasionally added to maintain the about 8.5 Liter liquid in the reactor. The pH of the recirculated liquid was ~ 7.4 ± 0.05.

The results of the CBR operation are summarised in **Table 9-2**. The RE during Stage I (Medium only) was on average 21 ± 7%, and only 8 ± 5% on average during Stage II (with 3% v/v silicone oil). When compared for the exact same operational conditions (0.6 second ECRT, a slug face velocity of 4.6 m s^{-1}, and a gas-to-liquid ratio between 1.0 and 1.1), the RE during Stage I (Medium only) ranged between 16 and 25%, while the RE during Stage II (with 3% v/v silicone oil) was lower, which averaged between 4 and 13%. Even when the ECRT was in Stage II increased from the 0.6 seconds to 2.6 seconds and then to 5.1 seconds, the RE increased only slightly to 10 ± 2% and 16 ± 5%, respectively. It can be concluded that the addition of silicone only as second liquid phase to a CBR treating dilute methane does not provide any improved removal efficiency under the conditions tested, and actually may hamper its performance.

The reduction in performance of the CBR after silicone oil addition may be explained in this case by the increase in liquid viscosity due to the oil added. A higher viscosity increases the viscous drag forces relative to the surface tension forces, which may compromise capillarity. The Capillary number (Ca) represents this relation between viscous drag forces and capillary forces (Equation 9-5):

$$Ca\ (-) = \mu \times u / \gamma \qquad \text{(Equation 9-5)}$$

where μ is the viscosity (Pa s), u the liquid velocity (m s^{-1}), and γ the surface tension of the liquid in the gas phase (N m^{-1}). Increased viscous drag forces slow down the internal liquid recirculation, the vortex that enhances mass transfer through convection rather than diffusion.

Thulasidas and co-workers (1997) found that the liquid internal recirculation velocity reduces sharply and ultimately becomes zero with increasing the Ca number, with Ca > 0.6 being the theoretical value where the internal vortex becomes zero in a downward flow. In this experiment with the 20 cSt viscosity silicone oil, the calculated Ca numbers were 0.06 and 0.19 for the 0% v/v and 3% v/v oil, respectively. This assumes that the overall liquid viscosity is proportional to the oil-liquid fraction and the gas-liquid surface tension is 35.7 mN m^{-1} as per Peters and Arabali (2013). This assumption is a simplification but shows that adding more

silicone oil may increase the Capillary number beyond the threshold where internal recirculation is reduced, and mass transfer is compromised.

Table 9-2 Summary of the results of the CBR operations during the Experiment A.

Slug Face Velocity ($m\ s^{-1}$)	Count[1)] (#)	ECRT (sec)	Gas flow IN ($L\ min^{-1}$)	Liquid flow ($L\ min^{-1}$)	Gas to Liquid ratio (-)	IC (ppm_v)	IL ($g\ m^{-3}\ h^{-1}$)	RE (%)	EC (channels) ($g\ m^{-3}\ h^{-1}$)	EC_{Liquid} (liquid) ($mmol\ L^{-1}\ h^{-1}$)
Stage I (Medium only)										
4.7	3	0.6	8	7.9	1	252 ± 13	916 ± 47	17 ± 6	153 ± 59	0.12 ± 0.05
4.6	**1**	**0.6**	**8**	**7.6**	**1.1**	**263**	**955**	**20**	**186**	**0.15**
4.6	**3**	**0.6**	**8**	**7.6**	**1**	**238 ± 3**	**864 ± 10**	**25 ± 8**	**213 ± 66**	**0.17 ± 0.05**
4.6	**6**	**0.6**	**8**	**7.7**	**1**	**246 ± 6**	**893 ± 23**	**21 ± 3**	**182 ± 24**	**0.15 ± 0.02**
4.6	**1**	**0.6**	**8**	**7.8**	**1**	**261**	**947**	**16**	**147**	**0.12**
4.5	1	0.7	7.6	7.6	1	275	950	29	264	0.22
4.5	4	0.7	7.7	7.6	1	245 ± 14	857 ± 65	15 ± 7	125 ± 64	0.10 ± 0.05
4.5	1	0.7	7.7	7.6	1	265	927	26	235	0.19
4.5	1	0.6	7.9	7.6	1	231	830	27	220	0.18
4.4	1	0.7	7.5	7.6	1	253	861	36	303	0.25
Stage II (3% v/v Silicone Oil, 20 cSt)										
4.6	**7**	**0.6**	**8**	**7.6**	**1.1**	**254 ± 11**	**924 ± 38**	**4 ± 3**	**35 ± 28**	**0.03 ± 0.02**
4.6	**1**	**0.6**	**8**	**7.6**	**1**	**261**	**947**	**8**	**76**	**0.06**
4.6	**2**	**0.6**	**8**	**7.7**	**1**	**249 ± 1**	**904 ± 3**	**13 ± 11**	**114 ± 95**	**0.09 ± 0.08**
4.6	**1**	**0.6**	**8**	**7.8**	**1**	**257**	**932**	**8**	**75**	**0.06**
4.5	2	0.6	8	7.2	1.1	240 ± 6	871 ± 23	8 ± 5	64 ± 37	0.05 ± 0.03
4.5	4	0.6	8	7.3	1.1	255 ± 15	926 ± 55	5 ± 5	46 ± 45	0.04 ± 0.04
4.5	5	0.6	8	7.4	1.1	261 ± 13	949 ± 46	11 ± 3	106 ± 32	0.09 ± 0.03
3.6	17	0.6	8	4.2	1.9	260 ± 9	944 ± 34	8 ± 5	69 ± 48	0.06 ± 0.04
3	11	0.9	6	4.2	1.4	252 ± 10	688 ± 26	9 ± 5	58 ± 33	0.05 ± 0.03
2.4	12	1.3	4	4.2	1	244 ± 9	443 ±16	6 ± 3	27 ± 11	0.02 ± 0.01
1.8	5	2.6	2	4.2	0.5	228 ± 11	207 ± 10	10 ± 2	19 ± 5	0.02 ± 0.00
0.9	6	5.1	1	2.1	0.5	230 ± 24	104 ± 11	16 ± 5	16 ± 5	0.01 ± 0.00

[1)] Count is defined as the number of analyses performed at the same CBR operating conditions.

Increasing the ECRT from 2.6 seconds and then to 5.1 seconds increased somewhat the RE, which may be explained by the lower liquid velocity, which were 1.8 m s^{-1} and 0.9 m s^{-1}, respectively, and thereby reducing the Capillary number from 0.19 to 0.07 and 0.04, respectively.

Despite the low REs during Experiment A with only 8% during Stage II and 21% during Stage I), the overall EC was nevertheless reasonably with 46 ± 29 g m^{-3} h^{-1} and 188 ± 45 g m^{-3} h^{-1}, during Stage II and Stage I, respectively. These elimination capacities are reasonably high compared to conventional biological gas treatment system treating methane (see **Table 3-1** in Chapter 3), especially when considering the extreme short ECRT (~1 to ~5 seconds) and relatively low inlet concentrations (~250 ppm_v).

After 100 days, Experiment A was stopped because 3 of the 25 capillary channels became non-functional. This failure was attributed to biomass aggregates detaching from the recirculation liquid tubing and/or pump, which subsequently obstructed the inlet side of the capillary channels preventing liquid flow.

Overall, it can be concluded from Experiment A that under the conditions tested (relatively high slug velocities of 2.4 – 4.6 m s^{-1} and short gas contact time of 0.6 to 5.1 seconds), the addition of silicone oil (3% v/v, 20 cSt) does not improve the methane gas-liquid mass transfer at low inlet methane concentrations (~250 ppm_v).

CBR performance evaluation Experiment B – including the addition of surfactant

During Experiment B, the CBR with larger diameter (2.4mm) but shorter (1.0m) channels was tested under lower slug velocities (between 0.15 and 0.8 m s^{-1}) when compared to Experiment A, and thus associated higher ECRTs (between 4.5 and 9.0 seconds). Furthermore, the addition of a surfactant was investigated according to the schedule in **Table 9-1**. The inlet concentration was in general ~1400 ppm_v but was changed up to a maximum concentration of 3818 ppm_v. The surfactant tested in this Experiment B was sodium dodecylbenzenesulfonate (SDBS, $C_{18}H_{30}NaO_3S$) at a concentration of 27 mg L^{-1}. A concentration of less than 30 mg L^{-1} has shown to avoid microbial inhibition while increasing the RE in a conventional biotrickling filter treating methane and various other hydrophobic short-chain (C2-C6) alkanes (Wu et a., 2022). Additional medium was occasionally added to maintain the about 8.5 Liters liquid in the reactor, which on average represented 154 ml per week (which represented ~2% per week of the total liquid volume in the reactor). The pH and the electric conductivity of the recirculating liquid were on average 8.0 ± 0.4 and 179 ± 22 uS cm^{-1}, respectively, while the Total Suspended Solids (SST) and Total Volatile Solids (TVS) were also measured in Experiment B, which averaged 1.78 ± 0.88 and 1.33 ± 0.67.

The results of the CBR operation are summarised in **Table 9-3**. The RE during Stage I was (Medium only) 19 ± 14% and similar (19 ± 11%) during Stage II (with surfactant SDBS). When compared for the exact same operational conditions (9.0 second ECRT, a slug face velocity of 0.18 m s^{-1}, and a gas-to-liquid ratio of 1.5), the RE during Stage I (Medium only) accounted for 16 ± 8%, while the RE during Stage II (with surfactant SDSB) was slightly less, which averaged 11 ± 6%. It can be concluded that the addition of the surfactant SDSB to a CBR treating dilute methane does not provide any improved removal efficiency under the conditions tested. Note that the RE slightly increased both during Stage I and Stage II when the slug velocity was increased to a value between 0.26 and 0.29 m s^{-1}, and to 27 ± 7% (Stage II) and 28 ± 10% and 33 ± 5% (Stage I for two different Gas-to-Liquid ratios).

Despite the low REs during Experiment B, the overall EC was nevertheless slightly better than the overall EC in Experiment A, and were on average 186 ± 166 g m^{-3} h^{-1} and 72 ± 52 g m^{-3} h^{-1}, during Stage I and Stage II, respectively. The experiment lasted 238 days, while 12 days before (day 226) an additional supplementation of 13 mg SDSB L-1 was added, which did not exert a positive nor a negative effect on the REs. During the entire 238-day duration of Experiment B none of the 25 capillary channels got blocked, which indicate that 2.4 mm diameter channels (Experiment B) are more appropriate than 1.5 mm diameter channels (Experiment A).

Table 9-3 Summary of the results of the CBR operations during Experiment B.

Slug Face Velocity ($m\ s^{-1}$)	Count[1)] (#)	ECRT (sec)	Gas flow IN ($L\ min^{-1}$)	Liquid flow ($L\ min^{-1}$)	Gas to Liquid ratio (-)	IC (ppm_v)	IL ($g\ m^{-3}\ h^{-1}$)	RE (%)	EC (channels) ($g\ m^{-3}\ h^{-1}$)	EC_{Liquid} (liquid) ($mmol\ L^{-1}\ h^{-1}$)
Stage I (Medium only)										
0.18	16	**9.0**	**0.75**	**0.50**	**1.50**	**1388 ± 142**	**361 ± 37**	**16 ± 8**	**57 ± 33**	**0.06 ± 0.04**
0.21	4	6.8	1	0.40	2.50	3481 ±37	1208 ± 13	16 ± 7	179 ± 81	0.19 ± 0.09
0.22	38	6.8	1	0.50	2.00	3067 ±848	1065 ± 294	20 ± 7	212 ± 114	0.23 ± 0.12
0.24	1	6.8	1	0.60	1.67	3691	1281	14	169	0.18
0.27	3	6.8	1	0.80	1.25	3811 ± 247	1323 ± 86	**28 ± 10**	354 ± 112	0.38 ± 0.12
0.29	4	6.8	1	1.00	1.00	3818 ± 246	1325 ± 85	**33 ± 5**	420 ± 51	0.46 ± 0.06
0.39	11	6.8	1	1.67	0.60	3326 ± 274	1155 ± 95	13 ± 4	142 ± 44	0.15 ± 0.05
0.45	1	4.8	1.4	1.67	0.84	1603	779	13	93	0.10
0.47	1	4.5	1.5	1.67	0.90	2006	1044	5	45	0.05
0.52	8	6.8	1	2.50	0.40	3438 ± 155	1193 ± 54	10 ± 5	118 ± 57	0.13 ± 0.06
0.84	1	4.5	1.5	4.17	0.36	1382	720	10	71	0.08
Stage II (SDBS surfactant 27 mg L^{-1})										
0.15	1	9.0	0.75	0.30	2.50	1406	366	11	38	0.04
0.17	2	9.0	0.75	0.40	1.88	1429 ± 31	372 ± 8	14 ± 2	50 ± 8	0.05 ± 0.01
0.18	12	**9.0**	**0.75**	**0.50**	**1.50**	**1432 ± 172**	**373 ± 45**	**11 ± 6**	**40 ± 22**	**0.04 ± 0.02**
0.20	3	9.0	0.75	0.60	1.25	1470 ± 80	383 ± 21	13 ± 5	49 ± 17	0.05 ± 0.02
0.206	3	9.0	0.75	0.65	1.15	1501 ± 84	391 ± 22	10 ± 5	37 ± 17	0.04 ± 0.02
0.214	5	9.0	0.75	0.70	1.07	1428 ± 67	372 ± 17	15 ± 6	53 ± 21	0.06 ± 0.02
0.22	3	9.0	0.75	0.75	1.00	1402 ± 34	365 ± 9	17 ± 6	58 ± 21	0.06 ± 0.02
0.23	5	9.0	0.75	0.80	0.94	1417 ± 68	369 ± 18	9 ± 7	33 ± 24	0.04 ± 0.03
0.26	31	9.0	0.75	1.00	0.75	2063 ±1895	537 ± 493	**27 ± 7**	127 ± 80	0.14 ± 0.09

[1)] Count is defined as the number of analyses performed at the same CBR operating conditions.

Table 9-4 Summary of the Results of the CBR operations during the first 175 days of Experiment C.

Slug Face Velocity ($m\ s^{-1}$)	Count[1)] (#)	Gas flow IN ($L\ min^{-1}$)	Gas flow RECIRC ($L\ min^{-1}$)	Liquid flow RECIRC ($L\ min^{-1}$)	Gas RECIRC to GAS IN ratio (-)	Gas RECIRC to Liquid RECIRC ratio (-)	IC (ppm_v)	IL ($g\ m^{-3}\ h^{-1}$)	RE (%)	EC (channels) ($g\ m^{-3}\ h^{-1}$)	EC_{Liquid} (liquid) ($mmol\ L^{-1}\ h^{-1}$)
2.7 seconds ECRT											
1.1	2	2.5	0	7.5	0.0	0.0	974 ± 10	845 ± 9	5 ± 2	39 ± 14	0.03 ± 0.01
1.6	8	2.5	3.5	7.5	1.4	0.5	953 ± 48	827 ± 41	10 ± 4	86 ± 42	0.08 ± 0.04
1.8	4	2.5	5	7.5	2.0	0.7	976 ± 37	847 ± 32	13 ± 4	114 ± 40	0.10 ± 0.04
2.2	3	2.5	7.5	7.5	3.0	1.0	1047 ± 16	909 ± 14	16 ± 3	147 ± 30	0.13 ± 0.03
2.5	7	2.5	9.5	7.5	3.8	1.3	900 ± 30	781 ± 26	11 ± 3	83 ± 26	0.07 ± 0.02
4.5 seconds ECRT											
2.2	1	1.5	7.5	7.5	5.0	1.0	1552	808	16	125	0.11
6.8 seconds ECRT											
1.9	4	1	5.5	7.5	5.5	0.7	2308 ± 142	853 ± 65	17 ± 6	168 ± 26	0.13 ± 0.04
1.9	5	1	7.5	5.5	7.5	1.4	2456 ± 187	801 ± 49	19 ± 3	147 ± 50	0.15 ± 0.02
1.9	10	1	7.5	5.5	7.5	1.4	4854 ± 195	1685 ± 68	26 ± 3	126 ± 26	0.20 ± 0.02
13.6 seconds ECRT											
1.3	73	0.5	5	3.75	10.0	1.3	4621 ± 452	802 ± 78	22 ± 7	180 ± 58	0.16 ± 0.05
1.7	4	0.5	7.5	3.75	15.0	2.0	4873 ± 360	846 ± 62	17 ± 2	148 ± 24	0.13 ± 0.02
2.2	28	0.5	7.5	7.5	15.0	1.0	4342 ± 373	754 ± 65	29 ± 6	217 ± 33	0.19 ± 0.03
2.2	3	0.5	7.5	7.5	15.0	1.0	6479 ± 72	1125 ± 12	26 ± 1	288 ± 10	0.25 ± 0.01
2.5	6	0.5	9.5	7.5	19.0	1.3	4477 ± 104	777 ± 18	28 ± 2	221 ± 17	0.20 ± 0.02
22.6 seconds ECRT											
2.2	7	0.3	7.5	7.5	25.0	1.0	4738 ± 393	493 ± 41	32 ± 4	158 ± 26	0.14 ± 0.02

[1)] Count is defined as the number of analyses performed at the same CBR operating conditions.

Table 9-5 Summary of the results of the CBR operations during the last 130 days of Experiment C.

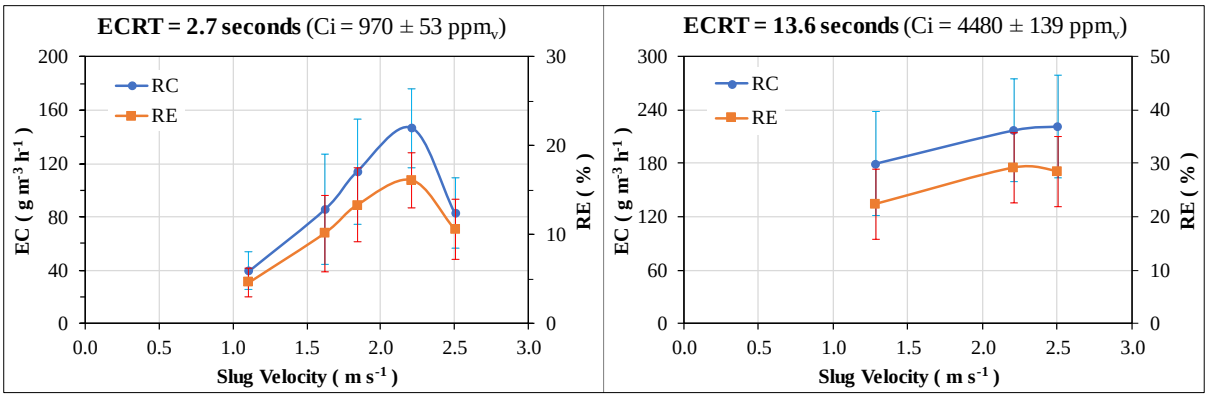
Stage	Count[1)] (#)	Gas flow IN ($L\ min^{-1}$)	Gas flow RECIRC ($L\ min^{-1}$)	Liquid flow RECIRC ($L\ min^{-1}$)	Gas RECIRC to GAS IN Ratio (-)	Gas RECIRC to Liquid RECIRC Ratio (-)	IC (ppm_v)	IL ($g\ m^{-3}\ h^{-1}$)	RE (%)	EC (channels) ($g\ m^{-3}\ h^{-1}$)	EC_{Liquid} (liquid) ($mmol\ L^{-1}\ h^{-1}$)
22.6 seconds ECRT and 2.2 m s^{-1} slug face velocity											
I	8	2.2	0.3	7.5	7.5	25	4692 ± 414	489 ± 43	32 ± 4	157 ± 26	0.14 ± 0.02
II	13	2.2	0.3	7.5	7.5	25	4446 ± 237	463 ± 25	34 ± 2	159 ± 18	0.14 ± 0.01
III	13	2.2	0.3	7.5	7.5	25	4581 ± 500	477 ± 52	46 ± 4	222 ± 45	0.20 ± 0.04
IV	59	2.2	0.3	7.5	7.5	25	4310 ± 295	449 ± 31	47 ± 4	214 ± 26	0.19 ± 0.02
V	34	2.2	0.3	7.5	7.5	25	4191 ± 209	436 ± 21	51 ± 6	224 ± 12	0.20 ± 0.03

[1)] Count is defined as the number of analyses performed at the same CBR operating conditions.

CBR performance evaluation – Experiment C – including the addition of oil and surfactant

During Experiment C, the CBR with the 2.4 mm diameter and 1.0 m long channels was tested under medium slug velocities (between 1.1 and 2.5 m s^{-1}), while internal gas recirculation was applied to decouple the optimal gas-liquid turbulence conditions inside the capillary channel from the actual gas retention time. BRIJ 58 was selected as the surfactant to be tested in the CBR because of its potential to enhance CH_4 gas-liquid mass transfer in the presence of silicone oil (as illustrated in **Section 8.3** in Chapter 8) as well as its ability to enhance the oil-in-water Emulsion Capacity and oil-in-water Emulsion Stability at a concentration low enough to eliminate the risk of microbial inhibition (as discussed in **Section 8.3** in Chapter 8). Moreover, BRIJ 58 showed to enhance the cell hydrophobicity of methane oxidizing bacteria and to improve overall the bioavailability of dilute methane (as illustrated in **Section 8.3** in Chapter 8).

During the first 130 days of Experiment C, and prior the testing of surfactant and silicone oil as additives in the CBR, the microbiology was exposed to methane as the sole energy and carbon source, in which optimal and stable process conditions of the CBR were established. During this period, the operating conditions were changed in terms of gas contact time, slug velocity, internal gas recirculation rate and G/L ratio. The results of the CBR operation are summarised in **Table 9-4**. The RE was in general lower than 15% during operation at a short ECRT of 2.7 seconds and was ~25-30% at a higher ECRT of 13.6 and 23.6 seconds. Changing the G/L ratio did not significantly change the performance under the conditions tested. The slug velocity was changed at two different ECRTs (2.7 and 13.6 seconds) by changing the internal gas recirculation rate, which allowed decoupling of the slug velocity from the overall gas retention time in the channels. Interestingly, the optimum slug velocity at both ECRTs appear to be between 2.0 and 2.5 m s^{-1} as illustrated in **Figures 9-2**. It was concluded that the optimum slug velocity for the CBR set up in Experiment C was ~2.2 m s^{-1} and this operating condition was applied as such during the testing of liquid additives in the CBR.



Figures 9-2. Methane removal efficiency and methane elimination capacity at 2.7 s of gas contact time (left) and 13.6 seconds gas contact time (right) during the initial 130 days of Experiment C.

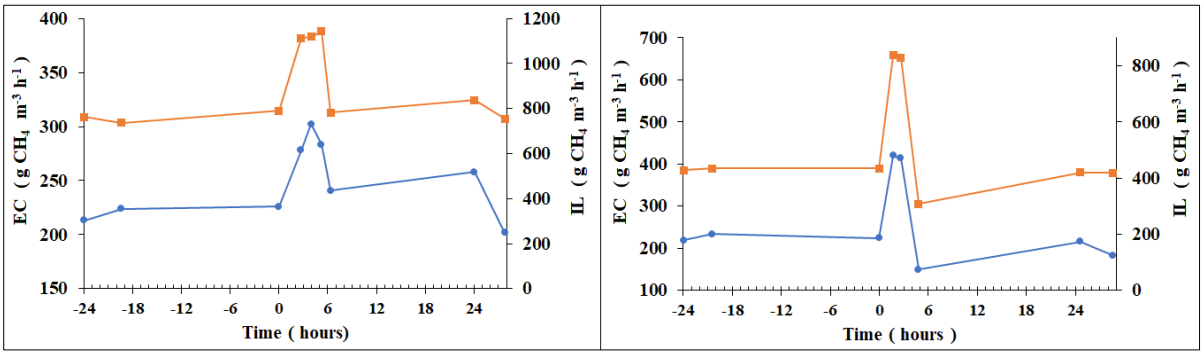
During the testing of the liquid additives in the CBR the same operating conditions were maintained: an up-flow segmented flow face velocity inside the capillary channels of 2.2 m s^{-}

^{1} and an internal gas recirculation (recycled gas to fresh inlet air) ratio of 25, which resulted in an ECRT of 22.6 seconds. The inlet methane concentration was maintained at a ~4500 ppm_v. Just prior the start of testing surfactant and silicone oil as additives in the CBR, the biomass concentration was measured multiple days and showed a TSS of 1.8 ± 0.3 g L^{-1}, of which 82 ± 11% was VSS. The pH and the electrical conductivity of the recirculating medium at the start were 7.3 ± 0.04 and 5.1 ± 0.1 mS cm^{-1}, respectively, and remained relatively constant during the entire test period of 120 days (7.4 ± 0.1 and 4.7 ± 0.2 mS cm^{-1}). The TN concentration was maintained between 40 and 90 mg N L^{-1} for the whole experiment and was on average 62 ± 15 mg N L^{-1}. At the beginning of Stage I, the TN concentration was ~90 mg N L^{-1}, slowly decreasing over time despite medium replenishment, reaching a concentration of 40 mg N L^{-1} by day 60 after the start of Stage I. Thus, 50 mg N L^{-1} as sodium nitrate was added to restore the initial nitrogen concentration of 90 mg N L^{-1}, steadily decreasing again to ~40 mg N L^{-1} by the end of Stage V. The TOC was measured once a week and was on average 189 ± 40 mg C L^{-1}. TOC contains all soluble organic carbon including any methane metabolites and may be an indication of metabolic product accumulation. The TOC slowly increased at the beginning of Stage I, then decreased gradually after the initial surfactant addition (Stage II). A slow increase of the TOC was again recorded, followed by another decrease after the second surfactant addition (Stage IV). This observation may be explained by previous studies indicating that surfactants can solubilise storage polymers, such extracellular polymetric substances (EPS) from biofilms, due to their detergent character, thereby limiting EPS accumulation (Ramirez et al., 2012; Lamprea et al., 2024).

During Stage I, the methane EC during a step increase (by a factor of 1.4) in inlet methane concentration was monitored to elucidate whether the process was mass transfer or kinetically limited before supplementing additives to its liquid phase (**Figure 9-3a**). The EC directly increased from ~225 to ~290 g m^{-3} h^{-1} (increase by a factor of 1.3) during this sudden methane load increase and decreased to previous steady state values when the inlet methane concentration was restored. This test confirmed that methane removal was mass transfer limited and not biologically limited. In addition, the determination of methane concentration in the liquid phase at the top reservoir of the CBR revealed a value of 0.0007 g m^{-3}, which is much lower than the theoretical equilibrium concentration of 0.0785 g m^{-3} calculated by the Henry's law, confirming that methane mass transfer from the gas to the liquid phase was the limiting mass transfer process.

The influence of the addition of surfactant and silicone oil as on methane removal was tested according to **Table 9.1** (Section 9.2). The results of the methane removed in the CBR during the different phases are summarised in **Table 9-4**. During Stage I, when no additives were added, the operational conditions of the CBR resulted in a RE of 32.0 ± 4%, corresponding to an EC of 156 ± 26 g m^{-3} h^{-1}. The addition of the surfactant in Stage II did not result in any significant change in the RE and the EC, remaining at 34.3 ± 2.5% and 159 ± 18 g m^{-3} h^{-1}, respectively. In contrast, when silicone oil at 5 % was added in Stage III, both the RE and the EC increased by ~40% up to 45.9 ± 4.4% and 222 ± 45 g m^{-3} h^{-1}, respectively. These results are summarized in **Figure 9-4.** BRIJ 58 showed to enhance the gas-liquid mass transfer in a

capillary channel, but only when combined with silicone oil. The surfactant enhanced emulsification of the oil in the medium, which appears to be the main mechanism rather than altering the gas-liquid partial coefficient of methane.



Figures 9-3 Methane (●) elimination capacity (EC) and the methane (■) inlet load (IL) in the capillary bioreactor during the mass transfer limitation test before (Stage I, Figure 9-2a, left) and after (Stage V, Figure 9-2b, right) the supplementation of additives to the liquid phase.

No significant enhancement on the methane removal performance was observed after the increased surfactant addition in Stage IV, with average RE and EC values in this stage of 47.6 ± 4.2% and 214 ± 27 g m^{-3} h^{-1}, respectively. However, increasing the silicone oil to 20% (v/v) in Stage V did further increase, though slightly, the RE and the EC to 52.8 ± 6.1% and 231 ± 30 g m^{-3} h^{-1}, respectively. This confirmed that the addition of silicone oil beyond 5% v/v is beneficial in this case, especially since during this Stage V the inlet concentration was somewhat lower compared to the average concentration in earlier stages in Experiment C (4,195 ± 195 ppm_v during Stage V vs 4,404 ± 250 ppm_v on average during Stages I to IV).

After Stage V, the methane EC under a sudden increase in CH_4 concentration by a factor of 1.93 was tested to elucidate the limiting mass transfer mechanisms (**Figure 9-3b**). The EC directly increased from ~226 to ~417 g m^{-3} h^{-1} (increase by a factor of 1.85) during this sudden methane load increase and decreased to previous steady state values when the inlet methane concentration was restored to its original concentration. The determination of methane concentration in the liquid phase at the top reservoir of the CBR also revealed a value of 0.0016 g m^{-3}, which is much lower than the theoretical equilibrium concentration of 0.0941 g m^{-3} calculated by the Henry's law, confirming that methane mass transfer from the gas to the liquid phase was the limiting mass transfer process.

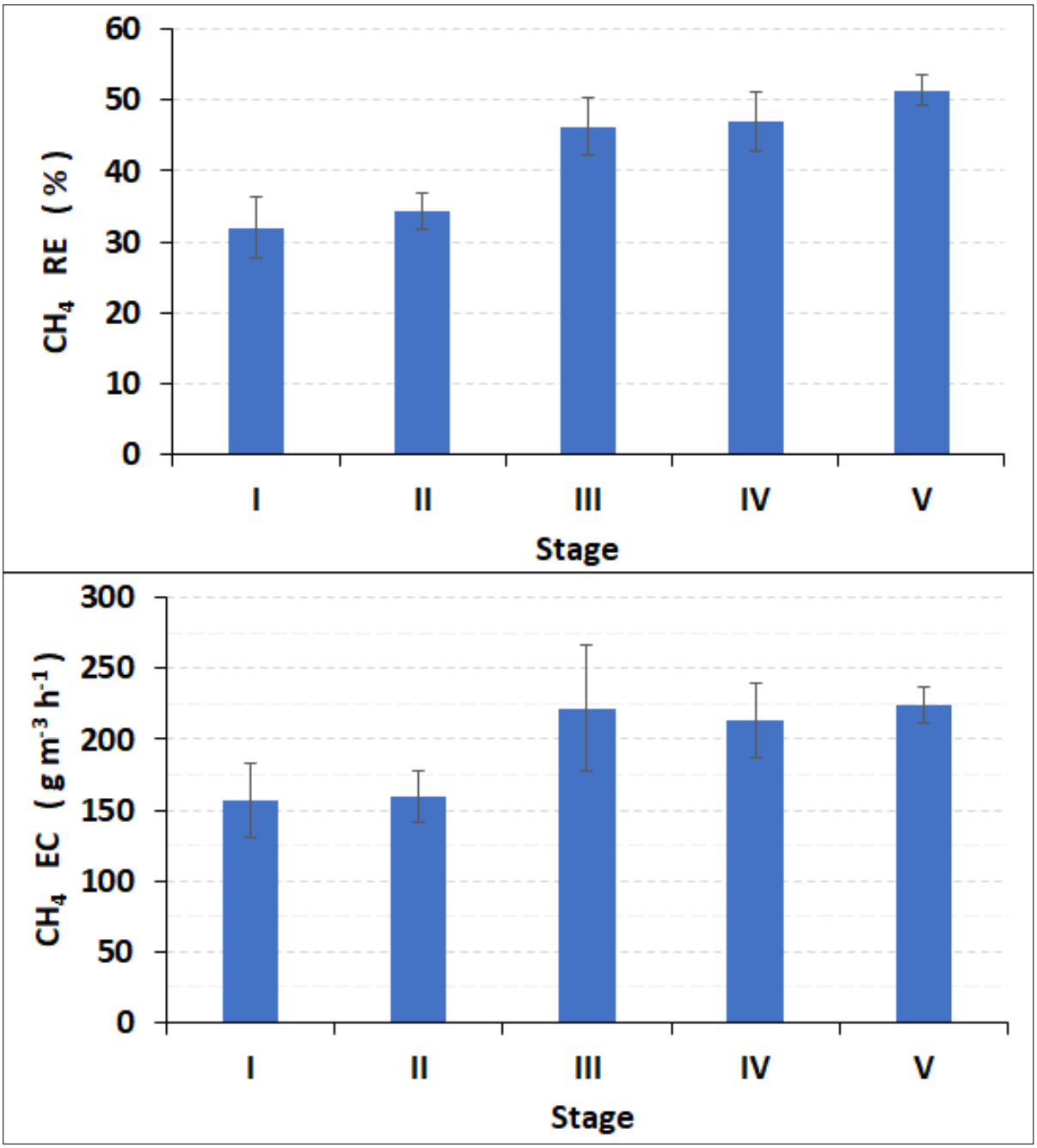


Figure 9-4. Methane removal efficiency (upper) and methane elimination capacity (lower) in the capillary bioreactor during the different experimental stages of quantifying the influence surfactant and silicone oil addition.

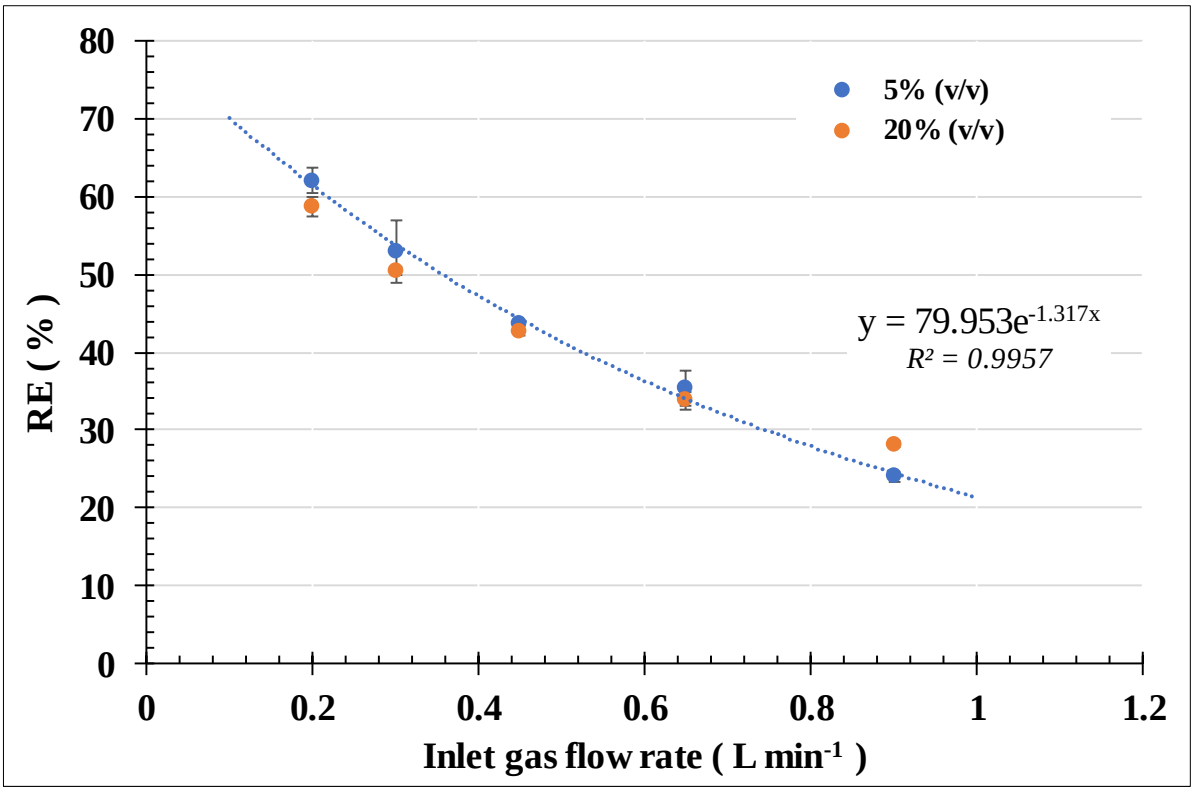


Figure 9-5 Methane removal efficiency in the capillary bioreactor operated at a constant inlet methane loading rate and constant channel gas-liquid slug velocity while only the inlet gas flow rate was increased resulting in reduced internal gas recirculation rates and reduced overall gas contact time, and reduced inlet methane concentration during Stage IV (5% v/v oil) and Stage V (20% v/v oil).

The methane RE and the methane EC in the CBR during the different experimental stages (**Figure 9-4**) are determined under similar operating conditions: an up-flow segmented flow face velocity inside the capillary channels of 2.2 m s^{-1} and an internal gas recirculation (recycled gas to fresh inlet air) ratio of 25, which resulted in an empty channel gas residence time of 22.6 s. The performance of the CBR was also determined when operated at constant inlet methane load while only the inlet gas flow rate was changed resulting in different inlet concentrations and different gas contact times. The inlet gas flow rate was changed during the day. Methane inlet and outlet concentrations were measured three times one hour after the change in inlet gas flow rate. The measurements were repeated the next day under the same conditions showing similar results. **Figure 9-5** shows the results where a low inlet gas flow rate of 0.2 L min^{-1} (= 33.9 seconds ECRT) resulted in a removal efficiency ~ 60% (62 ± 1.5% during Stage IV and 59 ± 1.3% during Stage V), while at the high inlet gas flow rate of 0.9 L min^{-1} (= 7.5 seconds ECRT) the removal efficiency was ~ 25% (24 ± 0.7% during Stage III and 28 ± 0.3% during Stage V). It can be concluded that the performance in both stages is similar regardless of the amount of silicone oil applied. The 5% v/v silicone oil (Stage IV) resulted in a slightly higher RE at the low inlet gas flow rate (high ECRT), while the 20% v/v silicone oil (Stage V) resulted in slightly higher RE at the high inlet gas flow rate (low ECRT).

The results are also illustrated in **Figures 9-6**, where the ECRT is plotted against the RE and the EC with the inlet methane concentrations at the different ECRTs. A similar correlation

was determined from the measurements during Stage I and proves the significant enhancement when the liquid contained silicone oil in combination with the surfactant.

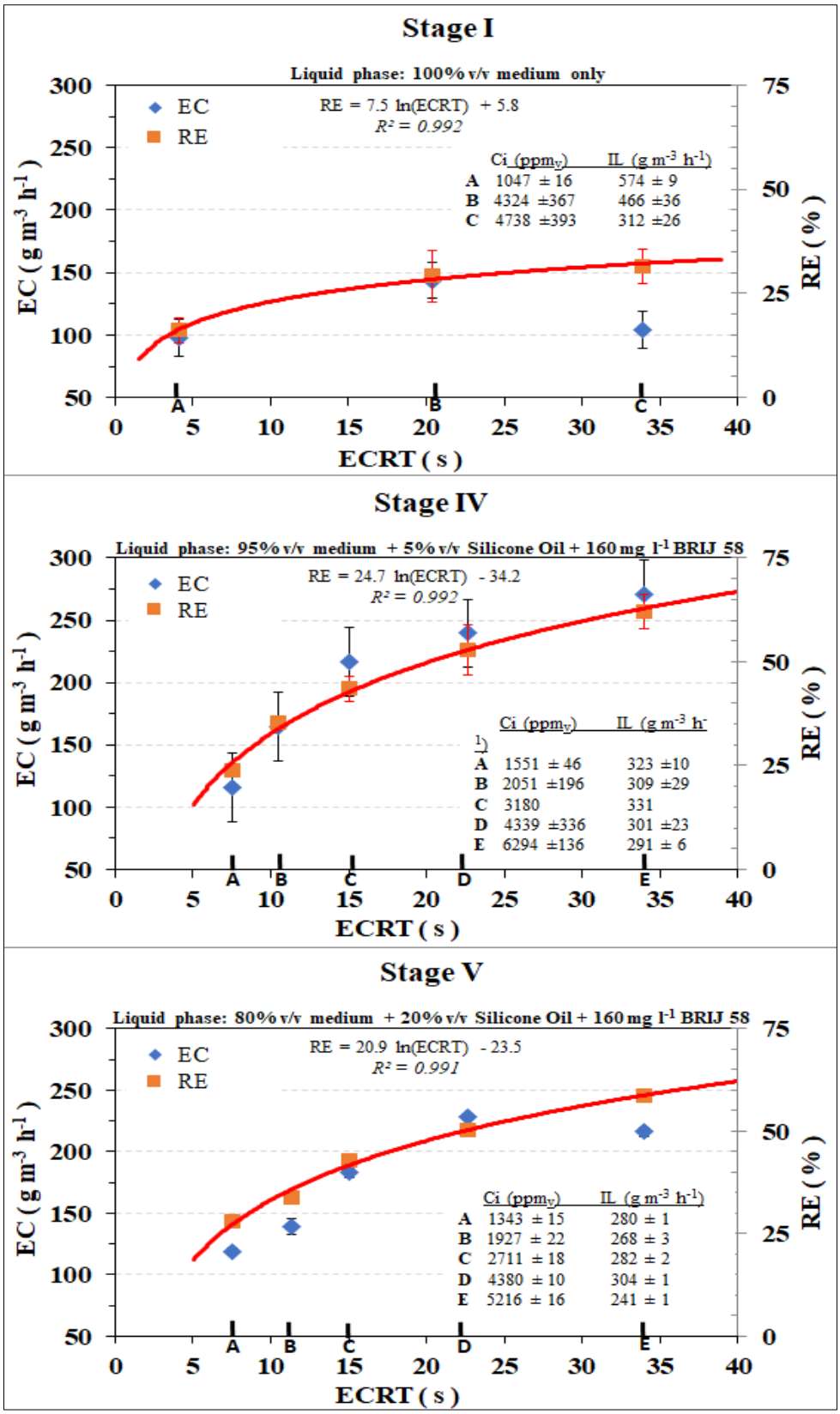


Figure 9-6 Methane removal efficiency (RE) and methane elimination capacity (EC) in the capillary bioreactor during Stage I (upper), Stage IV (middle), and Stage V (lower), and operated under different internal gas recirculation rates resulting in different overall gas contact times and different inlet concentrations.

Microbial Characterisation – Experiment C

Metagenomic amplicon sequencing revealed that the use of surfactants and silicone oil, along with the high bioavailability of methane, promoted a strong specialization by the end of the operation of the CBR (**Figure 9-7**). This effect has been observed in previous studies that used silicone oil to enhance methane transfer in continuous stirred tank reactors (Cantera et al., 2015). This diversity is phylogenetically represented in **Figures 9-8 and 9-9**.

By the end of Phase I, during reactor operation without the addition of surfactants and silicone oil (BR), the most abundant aerobic methanotroph belonged to the genus *Methylosarcina*, comprising 6% of the total relative abundance. However, after transitioning to operations that included surfactants and silicone oil (TR), this population declined to 3% relative abundance. Previous studies have demonstrated that the presence of silicone oil can significantly impact methanotrophic communities, often promoting the growth of certain genera, such as *Methylosarcina*, due to its capacity to form aggregates adhered to silicone oil (Cantera et al., 2015). However, the findings from this experiment indicate that the relative abundance of proteobacterial methanotrophs decreased when silicone oil and surfactants were introduced.

Interestingly, in the later stages of operation, there was a marked increase in the relative abundance of *Lacunisphaera*. This genus is known to play a role in the dynamics of methanotrophic communities, and some species, such as *L. limnophila*—the species detected in this study— has been recently recognized as a potential verrucomicrobial methanotroph (Zheng et al., 2020). This increase may indicate a shift in the methanotrophic community dynamics driven by the addition of surfactants and silicone oil.

In addition to these shifts, there was a notable rise in methylotrophic populations, particularly within the genus *Hyphomicrobium*. This genus is capable of oxidizing methanol and formaldehyde using unique dehydrogenases, enabling it to utilize these carbon sources without requiring NAD(P). The likely scenario here is that *Hyphomicrobium* cross-fed on methanol and formaldehyde, byproducts of the methane oxidation process, thereby contributing to the detoxification of the reactor environment. This cross-feeding likely had a synergistic effect, enhancing overall methane oxidation rates (Martineau et al., 2015; Kuloyo et al., 2020).

By the end of phase V, other microbial genera such as, *Edaphobaculum*, *Parvibaculum*, and *Obscuribacter* also showed increased abundance. These genera are known for their ability to degrade a wide array of complex carbon sources, suggesting they may have metabolized not only the byproducts of methane degradation but also the surfactant added during reactor operations (Wang et al., 2020). In fact, the main predicted functions obtained by the end of the operation, outside of pathways necessary for basic metabolism, consisted of metabolic pathways related to fatty acid oxidation, which could be related to the degradation of the surfactant (**Figure 9-10**). However, further studies, including gene upregulation and multiomics, should be performed to confirm the degradability of the surfactant under the conditions present in the CBR.

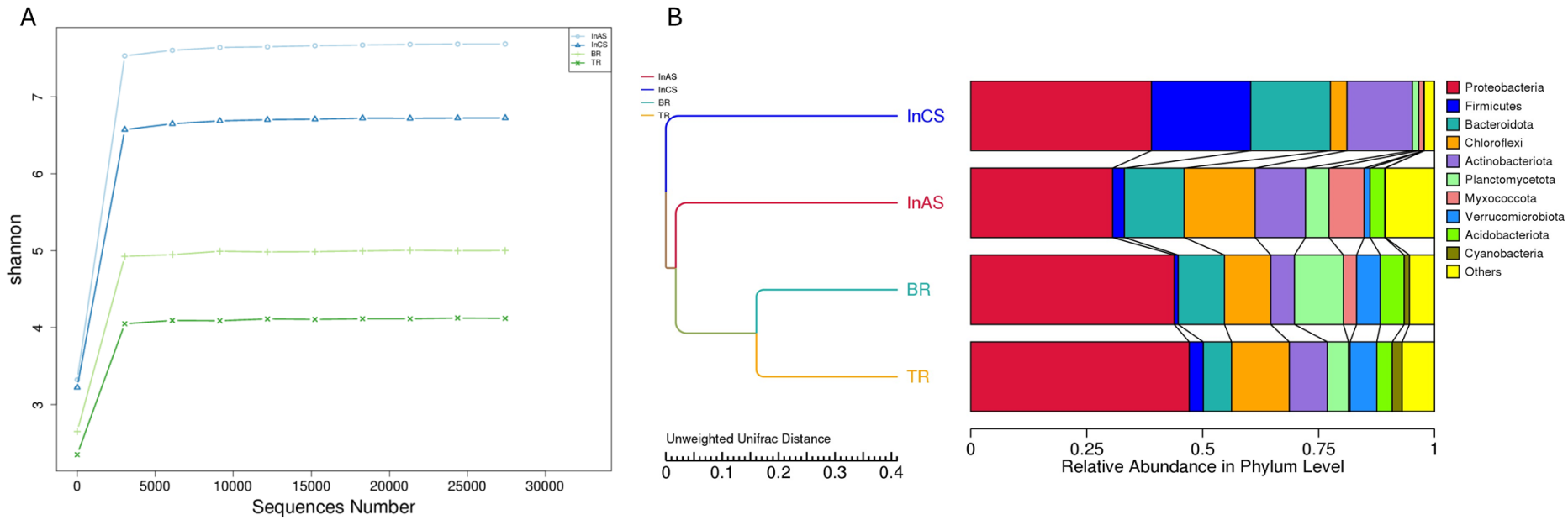


Figure 9-7 The Alpha diversity Shannon index **(A)** of the microbial community in the activated sludge inoculum (Light Blue), the post-composted anaerobically digested sludge (Blue), end of phase I (Light green) and end of operation (Green). The beta diversity **(B)** representing the similarity among the different samples in a cluster tree created throughout UPGMA.

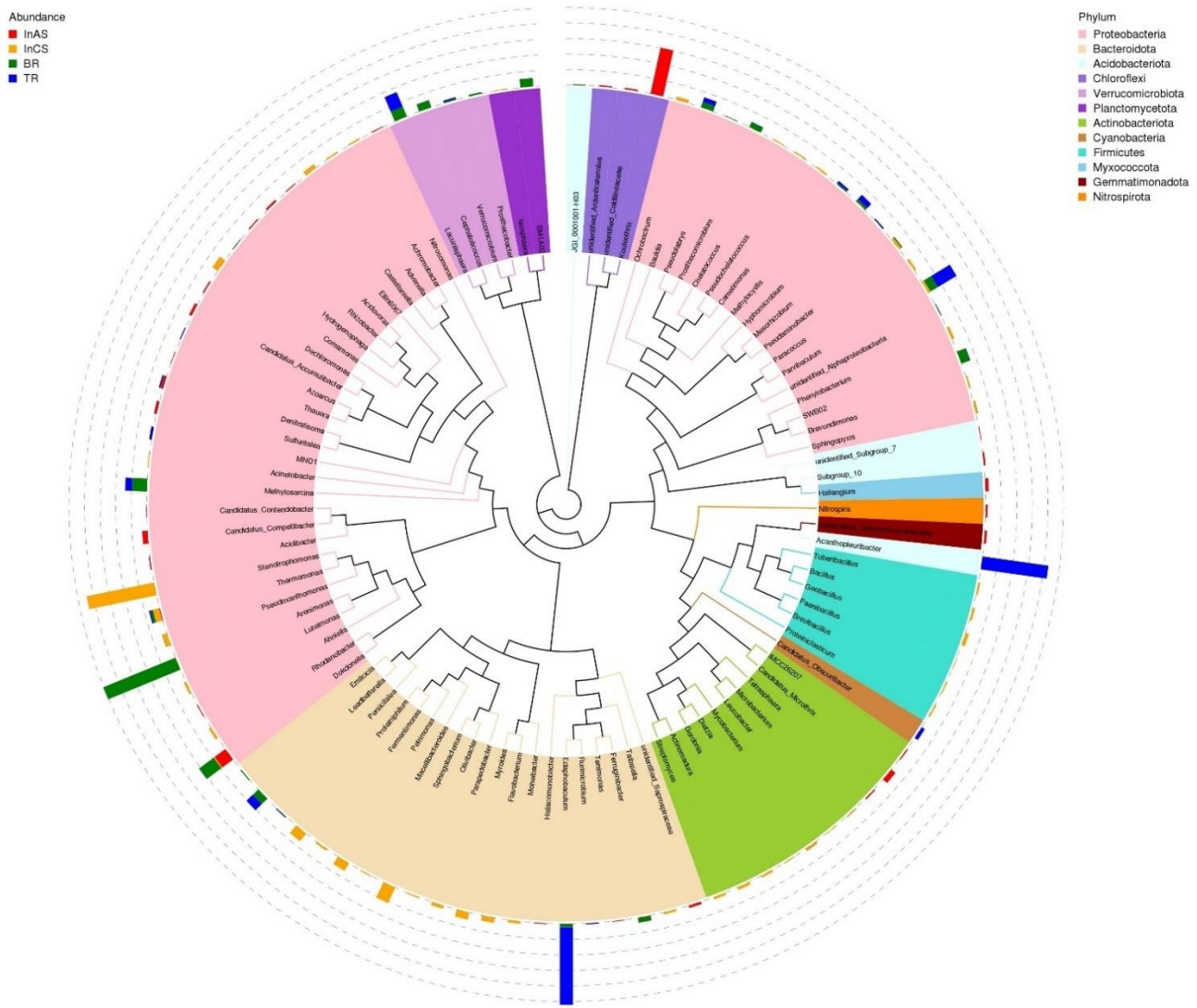


Figure 9-8 Evolutionary tree representing the phylogenetic relationship (top 100 genera). Different colors of the branches represent different phyla. Relative abundance of each genus in each group was displayed outside the circle and different colors represent different samples.

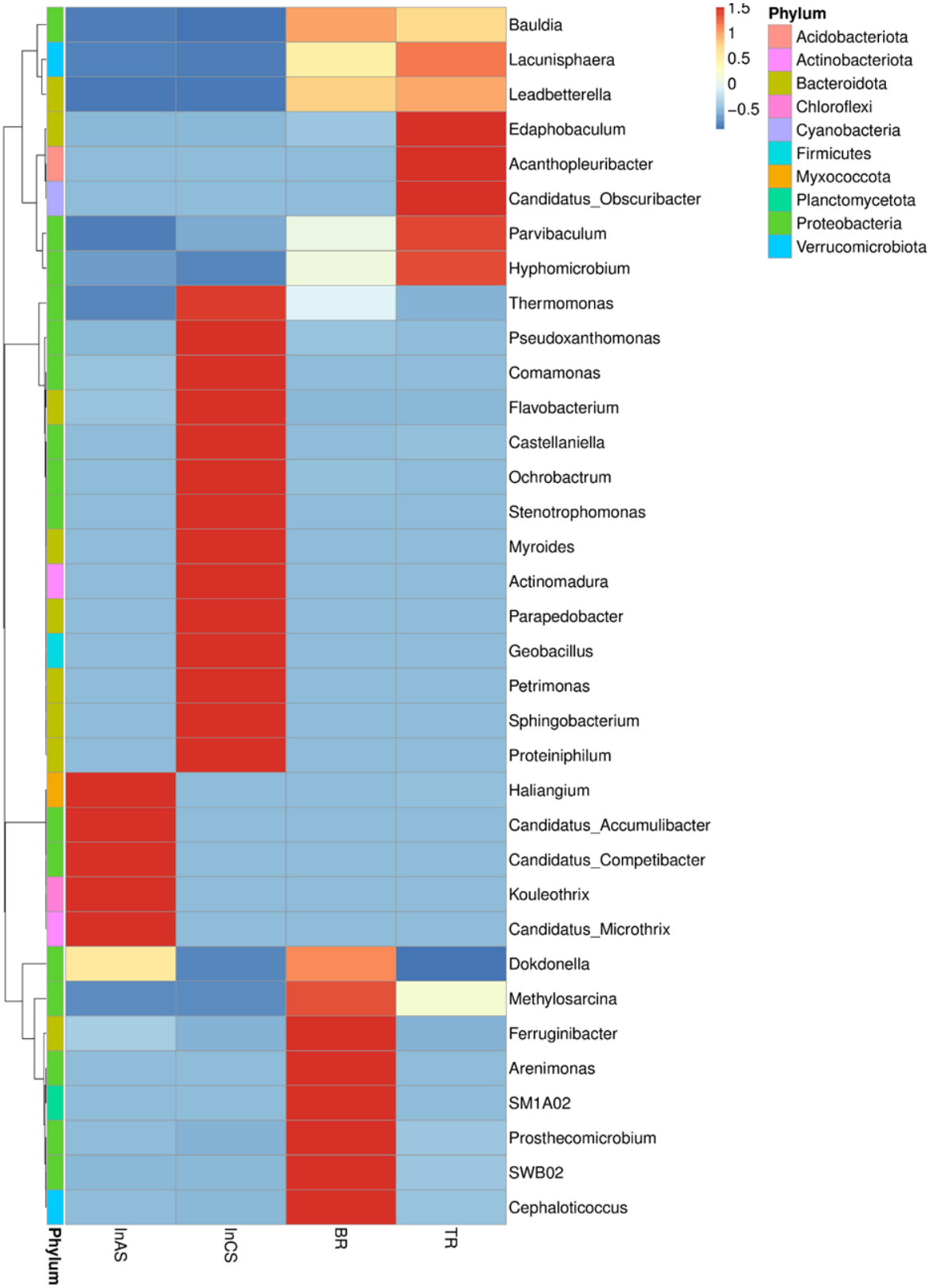


Figure 9-9 Heatmap showing the comparison of each taxon in the inocula (InAS and InCS), at the end of Phase I (BR) and at the end of Phase V (TR). The rows show the Z value obtained by standardizing the relative abundance of each row of genera.

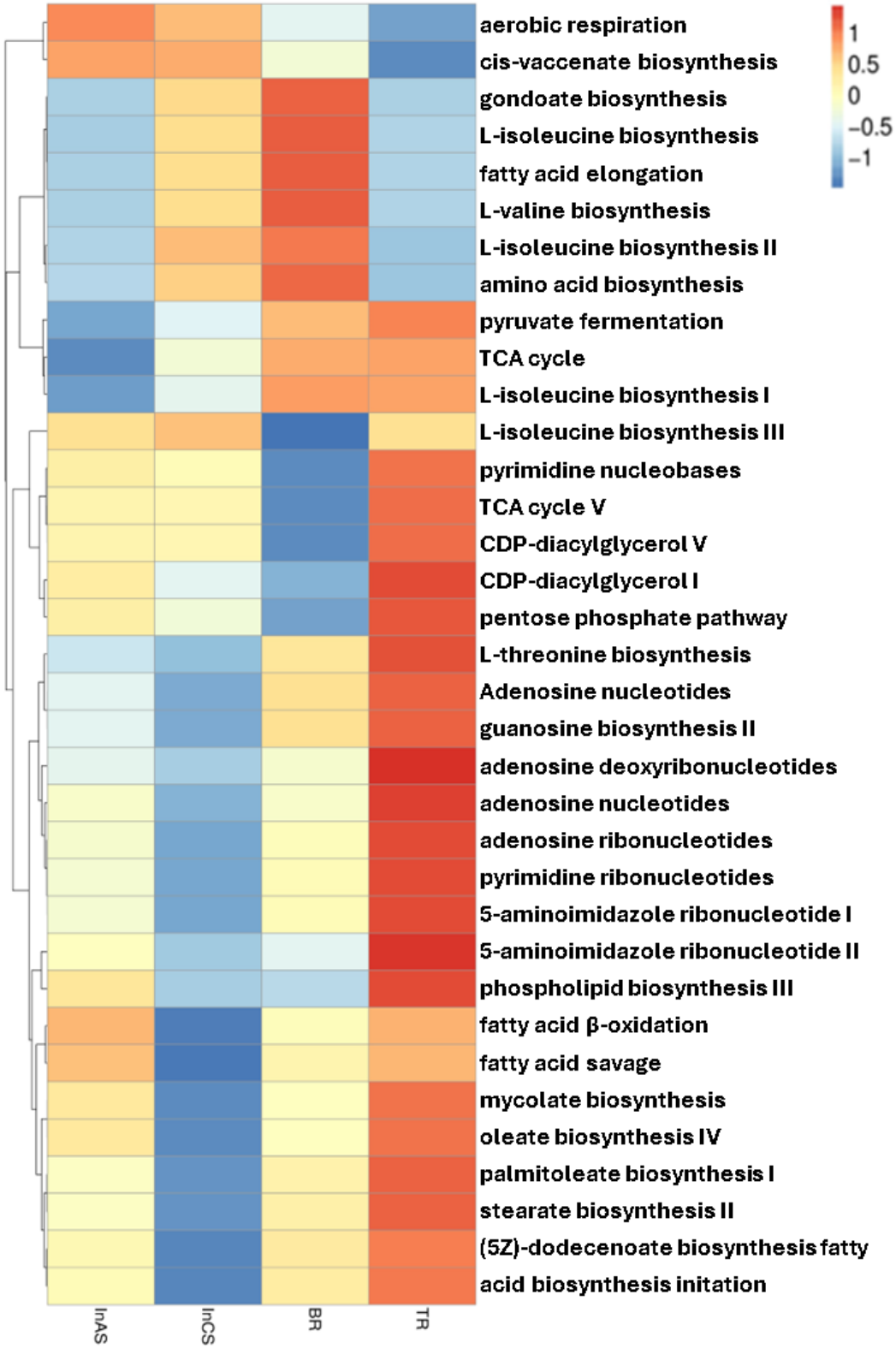
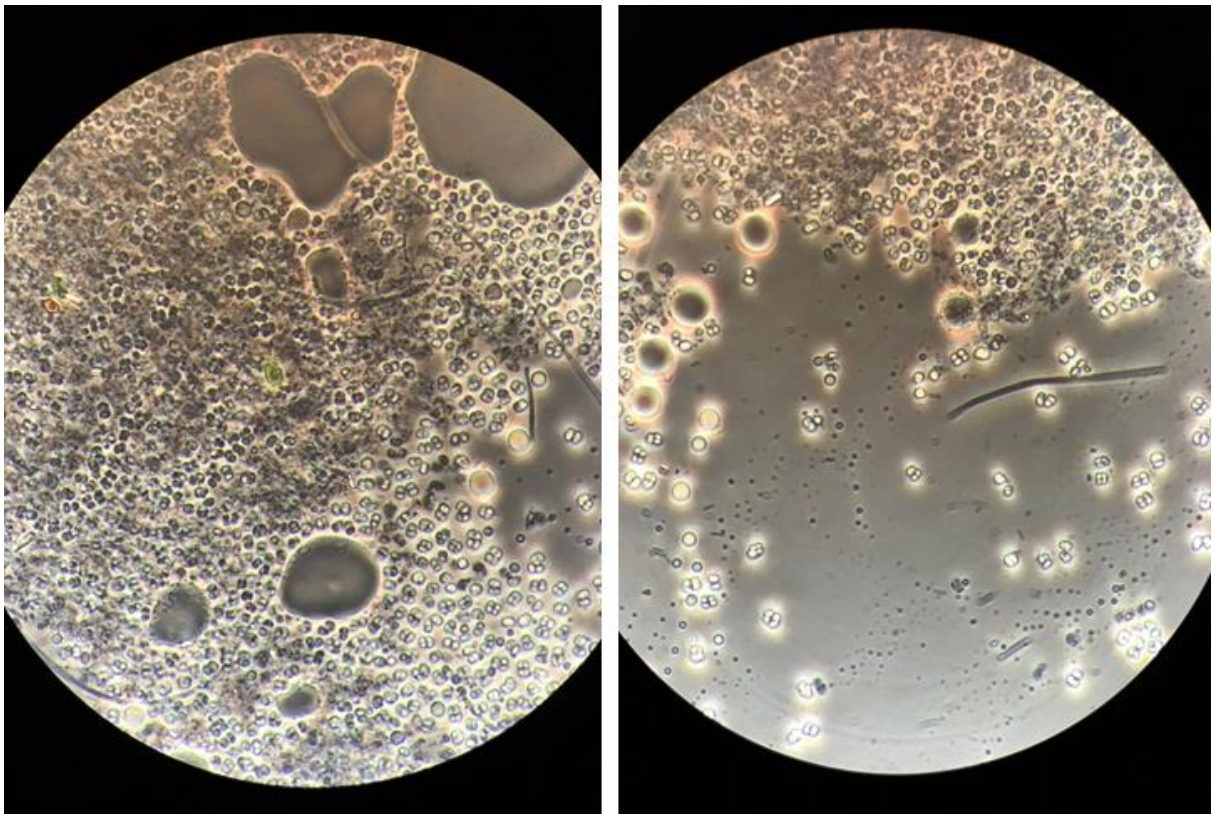


Figure 9-10 Heatmap of the metabolic functional prediction in the inocula (InAS and InCS) and at the end of Phase I (BR) and end of operation (TR).



Figures 9-11 Microscopic (100 x magnification) images of the recirculation liquid of the CBR during Experiment C after the addition of 5% v/v 20 cSt silicone oil (Stage III) about 15 minutes after taking the sample showing small silicone oil conglomerates.

The recirculating liquid showed fast separation of the oil-liquid phase within less than 30 minutes in the previous experiment in the CBR treating hexane, toluene and pinene (see **Figure 7-3** in Chapter 7). On the contrary, the recirculating liquid in Experiment C showed no separation of the oil-liquid phase after 24 hours, which confirms that a more stable emulsion is produced when the silicone-oil is combined with the BRIJ surfactant. **Figure 9-11** above illustrates the very small silicone oil conglomerates in the recirculation liquid of the CBR during Experiment C.

In the previous experiment in the CBR treating hexane, toluene and pinene, nearly all biomass adhered to the silicone oil (see **Figure 7-3** in Chapter 7). Whether the biomass was adhered to the silicone oil as well in Experiment C couldn't be confirmed. However, the fact that biomass was adhered to the silicone oil was expected in Experiment C as other studies have also shown that methanotrophs preferably reside on the oil-aqueous interface in reactor systems where a non-aqueous phase was added to the liquid phase. Han and co-workers (2009) as well as Lebrero and co-workers (2015) proved the growth of methanotrophs on the oil-aqueous interface in a stirred-tank and a biotrickling filter removing methane, respectively (**Figures 9-12**). This implies that the main bacterial activity occurred nearly exclusively adhered to the silicone oil-water interphase. These observations agree with the findings of Muñoz and co-workers (2013) and Hernandez and co-workers (2012), who confirmed the activity of a hydrophobic microbial consortium at the silicone oil-aqueous interface when

treating high concentrations of hexane in a continuously stirred bioreactor. These authors observed the highest enhancements in VOC elimination capacity when microbial cells were confined adhered at the silicone oil and may also explain the superior elimination efficiencies obtained in this study.

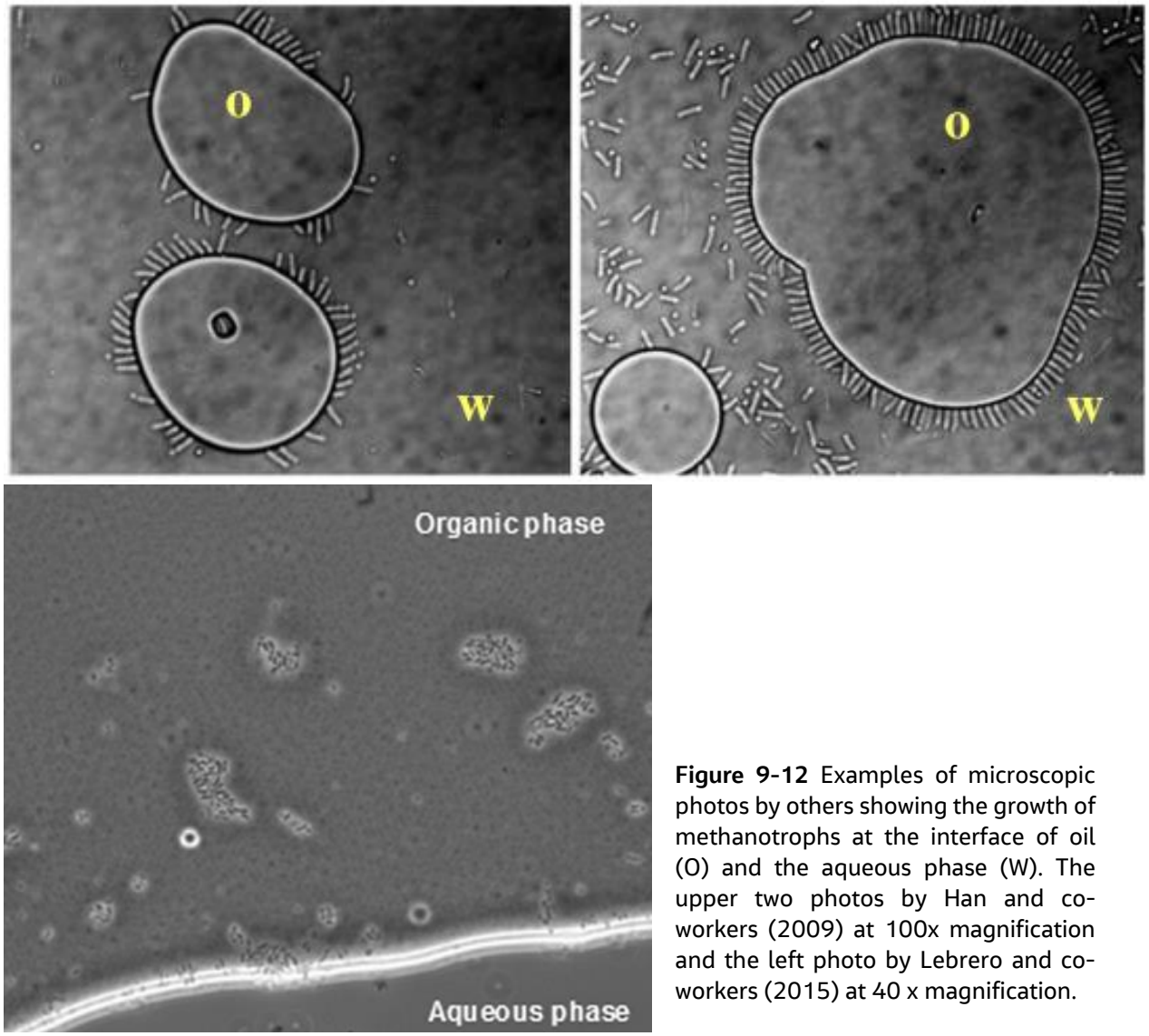


Figure 9-12 Examples of microscopic photos by others showing the growth of methanotrophs at the interface of oil (O) and the aqueous phase (W). The upper two photos by Han and co-workers (2009) at 100x magnification and the left photo by Lebrero and co-workers (2015) at 40 x magnification.

Experiment C – Evaluation of factors important for stable bioreactor operation.

Methane Supply Interruption

The methane supply was stopped on day 291 of Experiment C and was resumed again on day 297. The potential of silicone oil to act as a buffer for methane was confirmed in this test, where the inlet methane load was interrupted for six days, while keeping the rest of the CBR operational without any changes. No deterioration in methane removal was observed following the methane supply interruption of six days, when measured 30 minutes after the restart of

the methane supply to the CBR as illustrated in **Figure 9-13**. The methane eliminations before and directly after the six-day interruption were equal (the RE was 52 ± 2% before *vs* 51 ± 1% after and the EC was 219 ± 9 g m^{-3} h^{-1} before *vs* 227 ± 4 g m^{-3} h^{-1} after).

The silicone oil buffering capacity was further confirmed by the CO_2 produced during the following days after resuming methane supply from the six-day interruption. CO_2 production increased from 76 ± 6.5% of the amount of CH_4 removed recovered as CO_2 to 122 ± 11.4% after supply resumption. Indeed, more CH_4 was converted by the methanotrophic bacteria in the CBR than CH_4 was removed from the air stream by the CBR during the following days after resuming CH_4 supply.

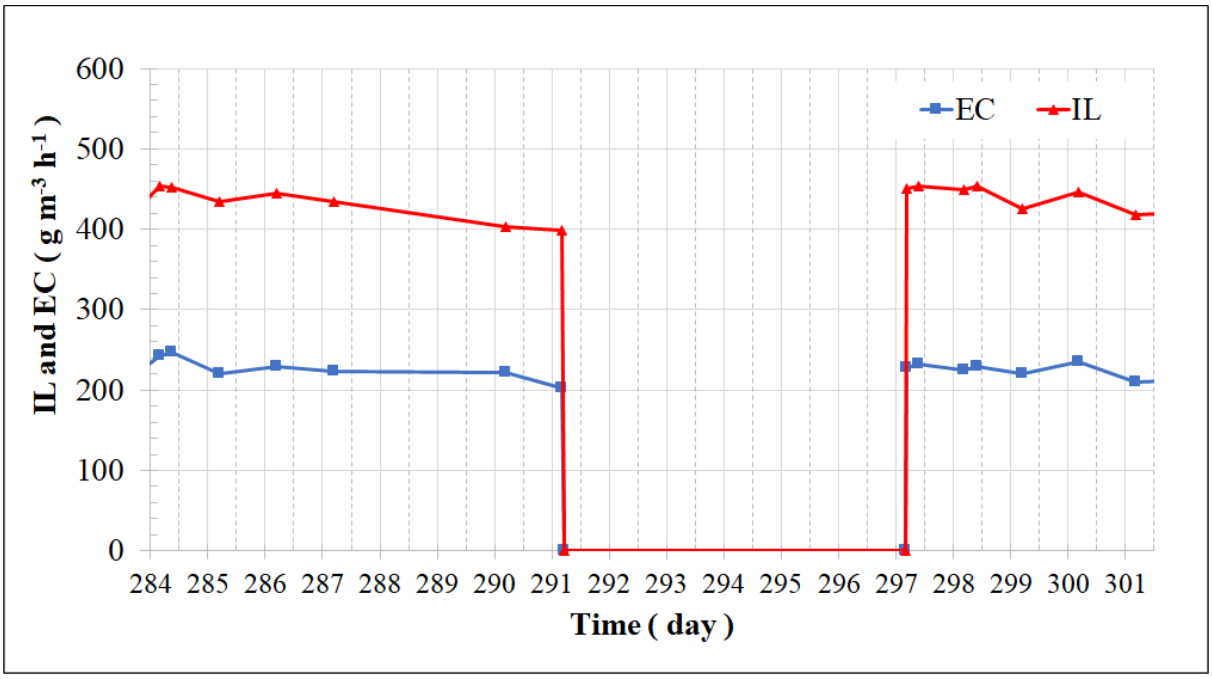


Figure 9-13 Methane Elimination Capacity (EC) and Inlet load (IL) before and after a six-day methane supply interruption.

Different studies have shown the benefit of silicone oil addition when treating dilute methane in terms of removal efficiency (see **Table 3-2** in Chapter 3), but none of these studies have demonstrated the beneficial buffering capabilities of silicone oil during methane supply interruption and thereby overcoming a starvation period. However, there are studies with other VOCs that have demonstrated the effectiveness of organic solvent to overcome starvation periods and transient VOC loading conditions. For example, Boudreau and Daugulis (2006) demonstrated as one of the first that the addition of an organic solvent (33% v/v n-hexadecane) creates a buffer during transient conditions of large fluctuations in inlet load and thereby improves the overall performance in terms of RE and RE recovery times. Moreover, Lebrero and co-workers (2013) demonstrated that the recovery times were shorter after a 'starvation period' when silicone oil was added to the recirculating liquid in biotrickling filters treating several VOCs.

Sudden Methane Loading Increases

Transient conditions of large fluctuations in inlet load were investigated during Stage I and Stage V. The methane EC was quantified by suddenly increasing methane inlet loading rate to determine whether the CBR operation was mass transfer or kinetically limited. It was confirmed that methane mass transfer from the gas to the liquid phase was the limiting mass transfer process in both Stage I and Stage V (see this Section 9.3 *CBR performance evaluation – Experiment C*). When we compare the methane removal of Stage I and Stage V during the initial measurement of the transient condition, it appears that the initial response of the CBR during Stage V (with silicone oil) was slightly quicker than during Stage I (without the silicone oil). This is illustrated in **Figure 9.2** in this Section 9.3. This may be an indication of the beneficial buffering capabilities of silicone oil in the CBR, which agrees with the observation above when, after six-day methane interruption, methane was buffered after the restart of the methane supply to the CBR as illustrated in **Figure 9-13**.

TOC and Total Nitrogen Concentrations Changes

The TOC in the recirculating liquid of the CBR, typically measured twice a week, was on average 189 ± 40 mg C L^{-1}. The TOC contains all soluble organic carbon including any methane metabolites and may be an indication of metabolic product accumulation. The TOC also includes extracellular polymeric substances such as polysaccharides when suspended in the aqueous phase. The TOC slowly increased at the beginning of Stage I, then decreased gradually after the initial surfactant addition (Stage II). A slow increase of the TOC was again recorded, followed by another decrease after the second surfactant addition (Stage IV).

The observation of the gradual decrease of TOC after surfactant addition cannot be explained by the mechanism observed by others (Ramirez et al., 2012; Wang et al., 2014), who showed that surfactants can solubilise extracellular polymetric substances (EPS) from biofilms due to their detergent character. This would increase the TOC after surfactant addition and not decrease as we have seen in our experiment, which may be explained by the fact that the biomass in our experiment is suspended and not growing as a fixed biofilm. It has been speculated that exo-polysaccharides produced by methanotrophs (as storage compounds) may decrease mass transfer of methane to the microbes resulting in reduced methane performance in conventional biofilters (Ramirez et al., 2012) . Instead, the TOC in our experiment seems to follow the same trend as the TN concentration in the aqueous phase, where an increasing TN concentration resulted in an increased TOC (**Figure 9-14**). Interestingly, an increasing TN concentration was not only correlated with an increase in TOC in the liquid but also with a decrease in the total biomass concentration. Higher nitrogen concentrations may trigger the release of EPS from the microbes, resulting in an increased suspended organic carbon (TOC) in the aqueous phase. While EPS is produced to serve as carbon storage during periods of reduced nitrogen availability, EPS may be released when nitrogen becomes available again. A reducing TOC concentration in the recirculation aqueous phase in a CBR could possibly be an indicator for a potential looming nitrogen limitation. This is not proven in this study and future studies would therefore be required to elucidate this.

The nitrogen concentration in our experiment was maintained between 40 and 100 mg N L^{-1}. This concentration was not limiting for microbial activity as mass transfer experiments proved that the system was operating under mass transfer limiting condition both at the beginning, when total N was ~ 80 mg N L^{-1}, and at the end, when the total N was ~ 40 mg N L^{-1} as discussed in the previous section on sudden methane load increase. This nitrogen concentration was much lower than recommended values in laminar bioreactors such as biofilters and biotrickling filter, where the biomass is mostly growing as a fixed film on a carrier material rather than suspended in the liquid as is in our CBR. For example, Estrada and co-workers. (2014) showed that a total nitrogen concentration of 100 mg N L^{-1} should be maintained in a biotrickling filter treating methane. Similarly, Girard and co-workers (2011) proved that 100 mg L^{-1} was required for proper methane treating biofilter operation, while Veillette and co-workers (2011) observed optimal total nitrogen concentration at 500 mg N L^{-1} in a biofilter treating methane.

Methane-treating reactors operated with biomass growing in a fixed biofilm may require higher nitrogen concentration in the liquid phase as they are more impacted by the liquid flow patron and packing configuration. The nutrient solution added to a laminar system may have to be higher to reach the active biomass, as the relatively stagnant liquid film and any EPS substances on the biofilm act as barriers. This may especially be valid when the nitrogen concentration in the biomass is relatively low, inducing the formation of EPS by the methanotrophs as a stress response. A thicker EPS film increases the methane mass transfer barrier, thus reducing performance as has been observed by others when total nitrogen was reduced (Estrada et al., 2014; Girard et al., 2011).

In summary, the minimum nitrogen concentration required appear to be much lower in the CBR during our experiment treating methane than what has been reported to be required in conventional biological gas treatment system treating methane. The bioavailability of the nitrogen seems like to be higher in the CBR probably because of the biomass being suspended rather than fixed in a biofilm. In addition, a reducing TOC in the recirculation aqueous phase in a CBR may possibly be an indicator for a potential looming nitrogen limitation.

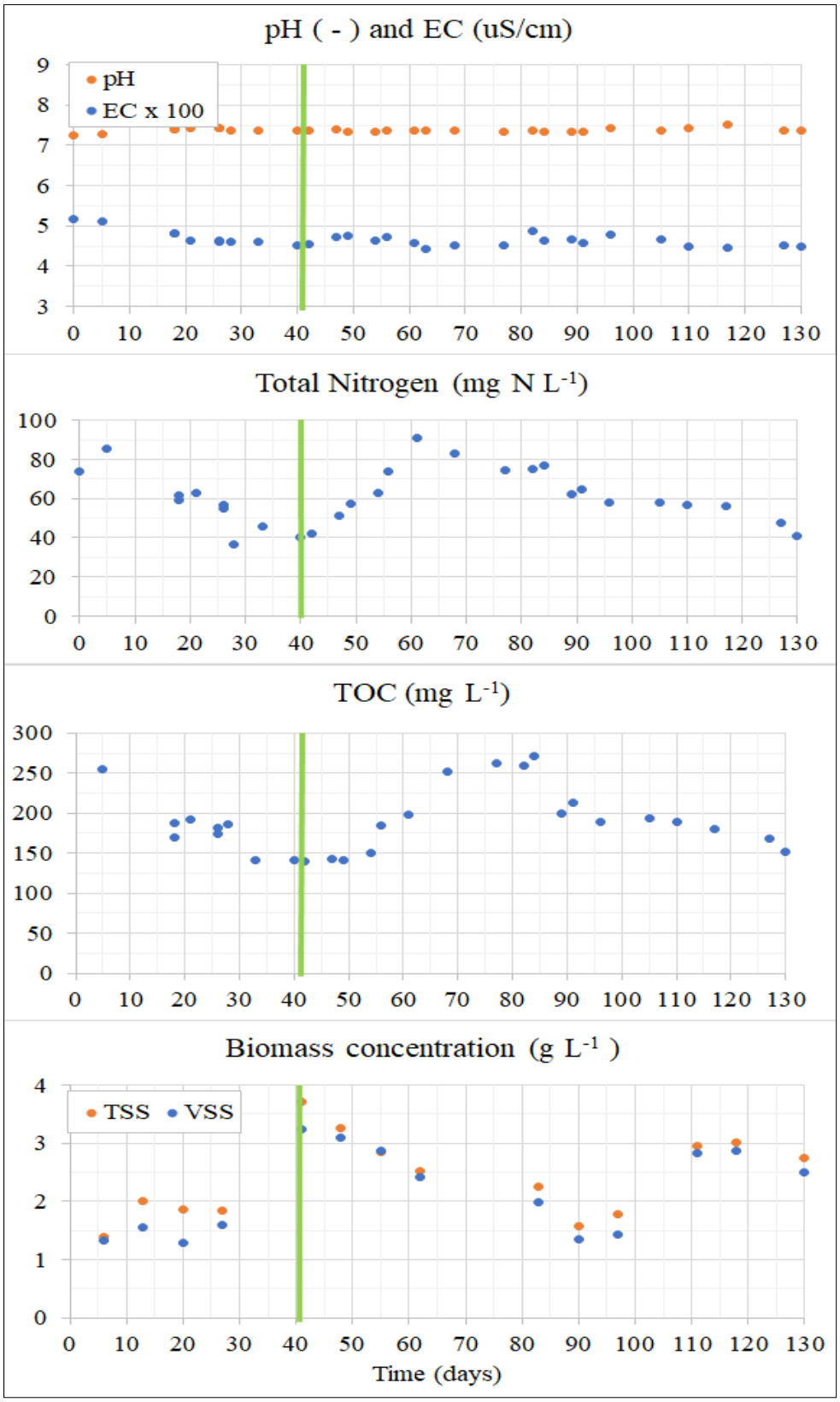


Figure 9-14 Time course of the results of the aqueous phase analyses during the last 130 days of Experiment C with the green line indicating the addition of nitrogen (40 mg N L^{-1} in the form of sodium nitrate).

Elevated Surfactant Concentrations

During the last few days of Experiment C the surfactant concentration was further increased from the 160 mg BRIJ 58 L^{-1} previous added to determine how a sudden increase of surfactant concentration would reduce methane removal in the CBR. Additional BRIJ 58 surfactant was added according to the following schedule: 80 mg L^{-1} on day 305, 160 mg L^{-1} on day 306, and 320 mg L^{-1} on day 307. The results showed that the methane RE dropped from 51% to 44, 38 and 37% after the addition of 80, 160 and 320 mg L^{-1}, respectively (**Figure 9-15**). Excessive foam formation was observed after the second addition (day 306), which is indicative of major microbial cell lysis. These observations are in line with the observations conducted in the Methane Bioavailability Test (**Section 8-3** in Chapter 8), where BRIJ 58 at a concentration of 112 mg L^{-1} significantly enhanced methane bioavailability and methane EC, but it did not at the higher BRIJ 58 concentration of 224 mg L^{-1}, almost certainly due to microbial inhibition.

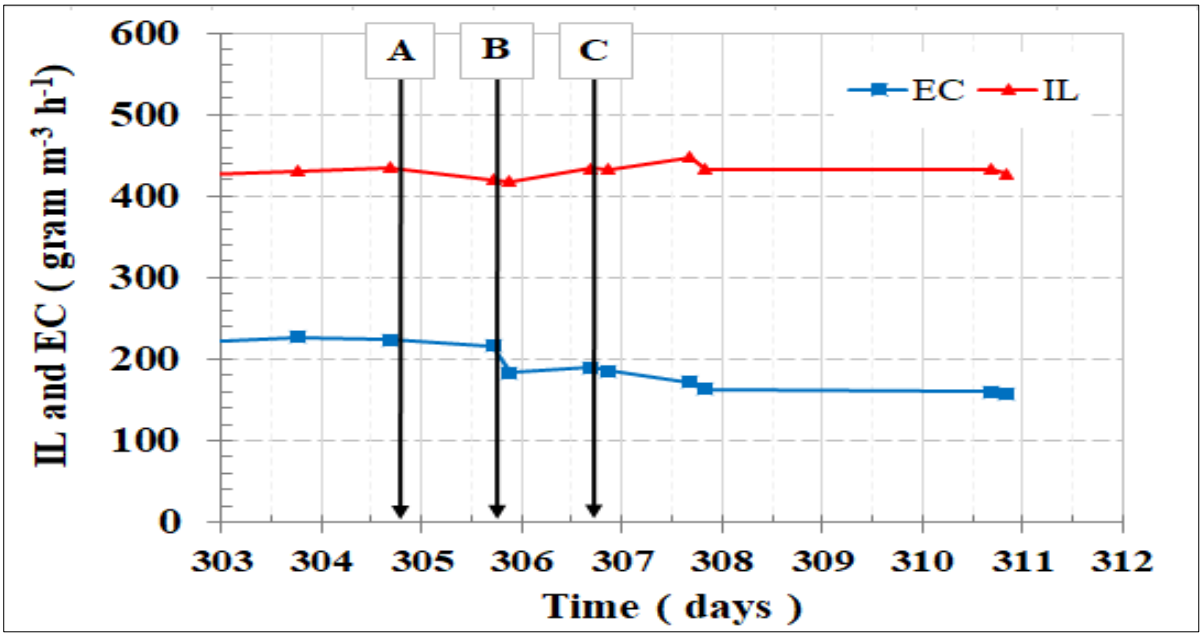


Figure 9-15. Effect of additional BRIJ 58 on the methane Elimination Capacity (EC) at the relatively constant Inlet Load (IL) during the final phase of the experiment with **(A)** the additional 80 mg BRIJ 58 L^{-1}, **(B)** the additional 160 mg BRIJ 58 L^{-1}, and **(C)** the additional 320 mg BRIJ 58 L^{-1}.

Biomass Control

No accumulation of biomass on the walls of the capillary glass channels was observed during the entire period of more than 300-days operation of the CBR. This observation is consistent with the observations during previous experiments as part of this Thesis study (see Sections 5.3 and 6.3 Results and Discussion *Microbial Characterization)* and other long-term studies where no biofilm attachment was observed inside the capillaries (Lopez de Leon et al., 2020). This section explores the factors that may explain this.

Biofilm formation would start with the adhesion of bacteria cells on a surface which may be influence by factors including the characteristics of the surface, the bacterial cell wall,

and the liquid flowing along the surface (Saur et al., 2017; Wang et al., 2018). The surface characteristics may involve material surface roughness and surface hydrophobicity, the bacterial cell wall characteristics may involve cell hydrophobicity and filamentous appendages such as pili and fimbriae, while the liquid characteristic may involve the fluid hydrodynamic forces. Multiple studies have shown that hydrodynamic forces, particularly the shear stress of the liquid on a surface, is the key parameter factor on biofilm formation in terms of the initial adhesion, the biofilm firmness, as well as the composition of the bacterial community (Habouzit et al., 2011; Lecuyer et al., 2011; Park et al., 2011; Rochex et al., 2008).

The shear stress in capillary channels can be estimated assuming that the liquid slugs behave as a fully developed laminar flow in a cylindrical tube, which is characterized by the following velocity distribution:

$$u_z(r) = 2\ U_s \times (1-(r / R)^2) \qquad \text{(Equation 9-6)}$$

where U_s is the superficial liquid slug velocity (m s^{-1}), and R the radius of the capillary tube. The liquid surrounding the gas bubbles follows the hydrodynamic of a falling liquid film (Thulasidas et al., 1995). The gas bubbles are surrounded by a liquid film which has a thickness (δ) of R - R_b, being R_b the radius of the bubble, where the velocity distribution in a cylindrical falling film of thickness δ is (Equation 9-7):

$$u_z(r) = - (g \times \rho) / 4\ \mu \times (R^2 - r^2) – (g \times \rho) / 2\ \mu \times (R – \delta)^2 \ln (r / R)$$

where g is the gravitational constant, μ the liquid viscosity (N s^2 m^{-2} or Pa s), and ρ the liquid density (kg m^{-3}). The shear stress at the walls of the capillary channel will be equal to:

$$\tau_{rz} = - \mu \times (du_z / dr)_{r=R} \qquad \text{(Equation 9-8)}$$

This expression, for the liquid slugs leads to:

$$\tau_{rz} = \mu \times 4 \times (U_s / R) \qquad \text{(Equation 9-9)}$$

and for the regions around the bubbles:

$$\tau_{rz}= - \rho \times g \times R / 2\ (1 - ((R – \delta) /R)^2) \qquad \text{(Equation 9-10)}$$

The negative sense indicates that the force points downwards. The film thickness can be estimated using the correlation proposed by Liu et al. (2005). The shear stress in the capillary channel along the liquid slug would increase with the liquid velocity and the liquid viscosity as illustrated in **Figure 9-16** below.

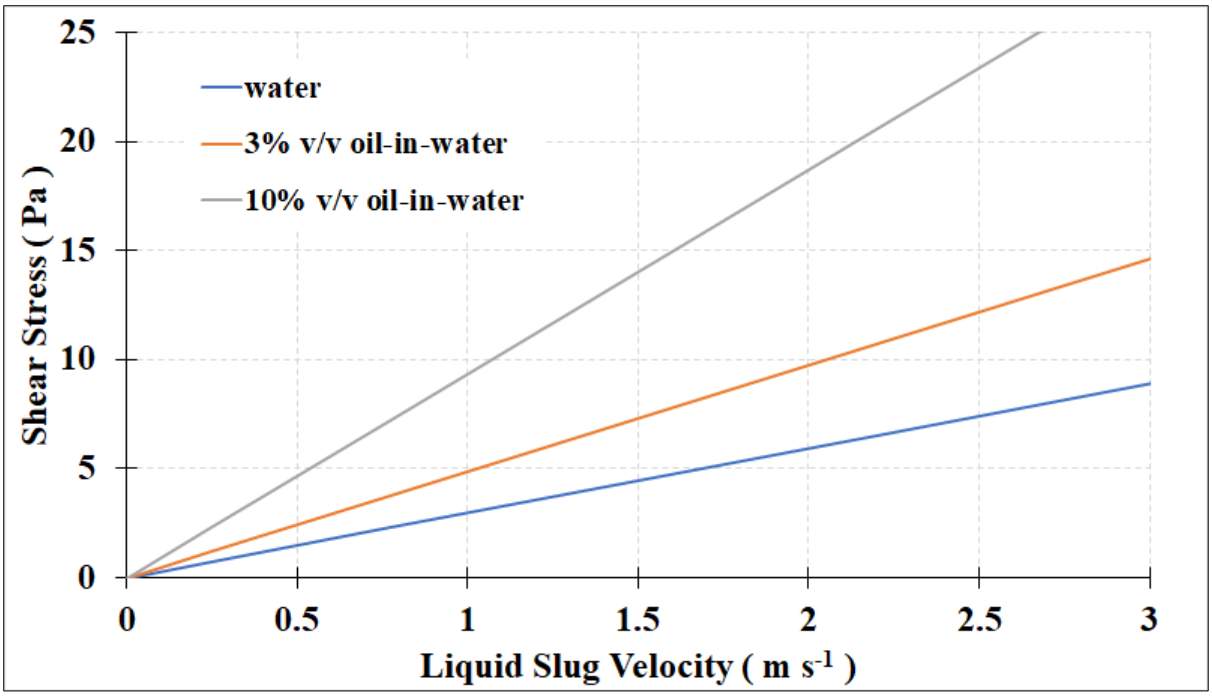


Figure 9-16 The wall shear stress in the liquid slug in the 2.4 mm capillary channel as a function of liquid superficial velocity for water (viscosity 0.89 mPa s) and two oil-in-water emulsions (oil viscosity 20 cSt = 20 mPa s).

Saur and coworkers (2017) showed in a Couette-Taylor reactor that the shear stress of the liquid on a surface wall can strongly impacts the initial bacterial adhesion. Their study showed that an increasing shear stress up to 3.7 Pa initially stimulated adhesion in their experimental set-up (likely due to the increased liquid transport facilitating the access of bacteria to the wall surface), while a higher shear force of 7.3 Pa reduced biofilm formation (likely due to the increased detachment forces). However, biofilm formation was not prevented at 7.3 Pa, which is consistent with other studies where high shear forces (6 to 20 Pa) alone could not prevent biofilm formation (Simões et al., 2022; Lecuyer et al., 2011).

Our long-term experiments using a 2.4 mm capillary channel and liquid velocities between 0.15 and 0.84 m s^{-1} for 238 days (Experiment B) or liquid velocities between 1.3 and 2.5 m s^{-1} for 305 days (Experiment C) did not show accumulation of biomass nor any signs of biofilm formation on the capillary channel walls. The shear stress in our experiments can be expected to be in a similar range (see **Figure 9-16**) as the shear stress estimated in the experiments of Saur and coworkers, and therefore the wall shear stress generated by the liquid slugs alone cannot explain the absence of biofilm formation on the capillary channel wall in our experiments.

Other explanations may be the difference in wall material (glass in our experiment versus plastic in Saur and coworkers' experiment) and/or the different experimental set up (capillary reactor with small diameter capillary channels versus a Couette-Taylor reactor consisting of two concentric glass cylinders, a rotating inner cylinder and a non-rotating outer cylinder). Saur and co-workers operated the Couette-Taylor reactor with a 28 mm gap between the cylinders under conditions that the Taylor vortex inside the liquid would not be present,

while our capillary reactor with the 2.4 mm channels was operated in a way that the Taylor vortex would be expected. The presence of the Taylor flow containing a recirculating liquid vortex could be the critical factor preventing the accumulation of biomass on the inner walls of the channels. Moreover, the segmented gas-liquid flow in the capillary channels cause shear stress alteration induced by the liquid slugs (positive shear stress) and gas bubbles (negative shear stress) as illustrated in **Figure 9-17**. In an up-flow configuration where the bubble train flows upward against gravity, the shear force is upward when the liquid slug passes but downwards when the gas bubble with falling film passes any point on the capillary channel wall. The segmented (Taylor) flow regime contains gas bubbles that are broken up by segmented liquid drops, thus creating a pulsating shear stress possibly contributing to limiting biomass adhesion. Further studies would be required to better understand the contribution of these factors involved in preventing accumulation of biomass on the walls of the capillary channels.

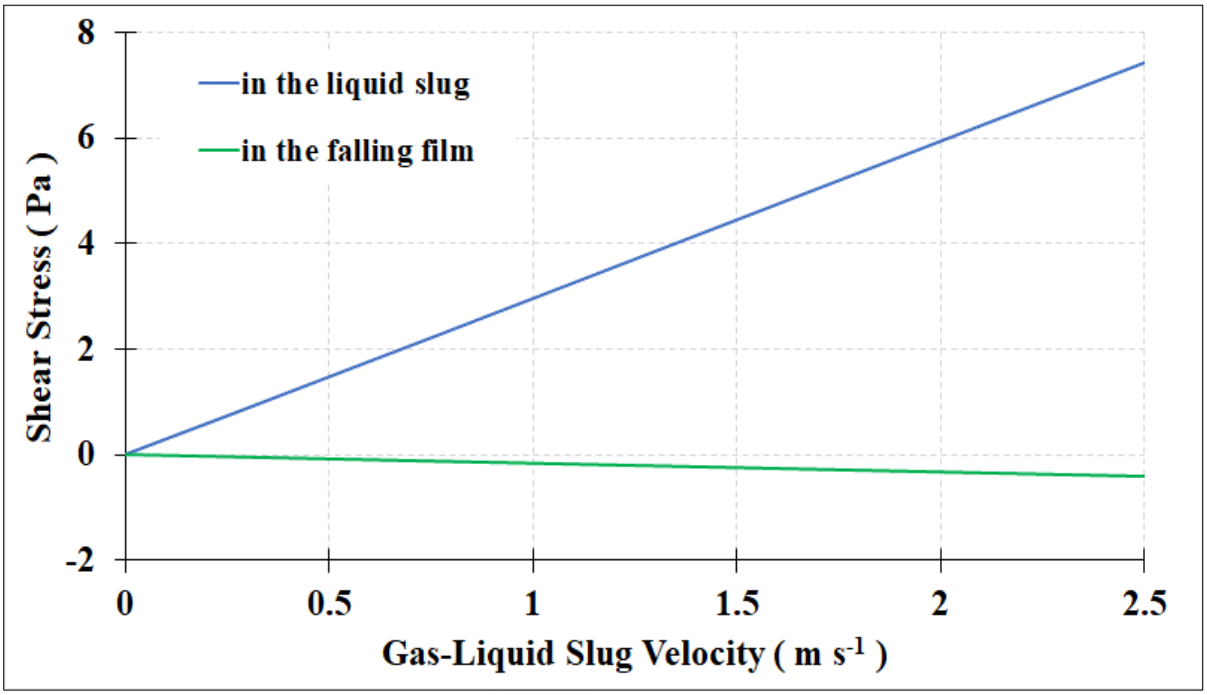


Figure 9-17 The wall shear stress in the liquid slug and in the falling film along gas bubble in the 2.4 mm capillary channel under segmented flow conditions as a function of gas-liquid superficial velocity for water.

Pressure Loss Evaluation

The energy required for the operation of a CBR would be mainly determined by the pressure loss when the gas-liquid slugs flow through the capillary channels. The total pressure loss per length unit in a capillary channel with gas-liquid segmented flow is caused by several frictions. As previously discussed in Chapter 5, total pressure loss for small capillary channels is caused by (1) the wall friction of the liquid slug, (2) the static head of the liquid in the capillary channel (in case of vertical channel configuration), and (3) the wall friction of the gas

bubble. The liquid wall friction can be estimated using the Hagen-Poiseuille equation (Equation 9-11), while the static head can be calculated using the volume and density of the liquid slugs (Equation 9-12).

$$dP_{LWF} / L = 32 \mu \times u_L / d^2 \quad \text{(Equation 9-11)}$$

$$dP_{LSH} / L = \rho \times g \quad \text{(Equation 9-12)}$$

where dP_{LWF} stands for the pressure loss in a capillary caused by liquid wall friction (Pa), L the length of the capillary channel (m), μ the viscosity (Pa s), u_L the superficial velocity of the liquid slug (m s^{-1}), d the diameter of the capillary channel (m), ρ the liquid density (kg m^{-3}), and g the gravitational constant (m s^{-2}).

The wall friction of the gas bubbles was determined experimentally and reported in **Section 5.3** *Pressure Loss* (Chapter 5), where three glass channels diameters were used with an internal diameter of 2.4, 3.4 and 5.0 mm, respectively, all 1.5 m in length. The airflow was measured using a rotameter and the pressure drop was determined using a U-shaped water gauge.

Based on the measured pressure loss by the gas (air bubble) and the calculated pressure loss by the liquid (liquid slug), the total pressure loss per meter capillary channel can be estimated. The overall pressure drop is mainly influenced by the internal diameter of the capillary channel, the slug velocity through the capillary channel, as well as the gas-to-liquid ratio as illustrated in **Figures 9-18**. The pressure loss in:

- a 5.0 mm channel is 262 Pa at slug velocity of 0.5 m s^{-1} and G/L of 9, while 2,476 Pa at slug velocity of 2.5 m s^{-1} and G/L of 1,
- a 4.2 mm channel is 228 Pa at slug velocity of 0.5 m s^{-1} and G/L of 9, while 2,764 Pa at slug velocity of 2.5 m s^{-1} and G/L of 1,
- a 3.4 mm channel is 269 Pa at slug velocity of 0.5 m s^{-1} and G/L of 9, while 3,803 Pa at slug velocity of 2.5 m s^{-1} and G/L of 1, and
- a 2.4 mm channel is 297 Pa at slug velocity of 0.5 m s^{-1} and G/L of 9, while 6,426 Pa at slug velocity of 2.5 m s^{-1} and G/L of 1.

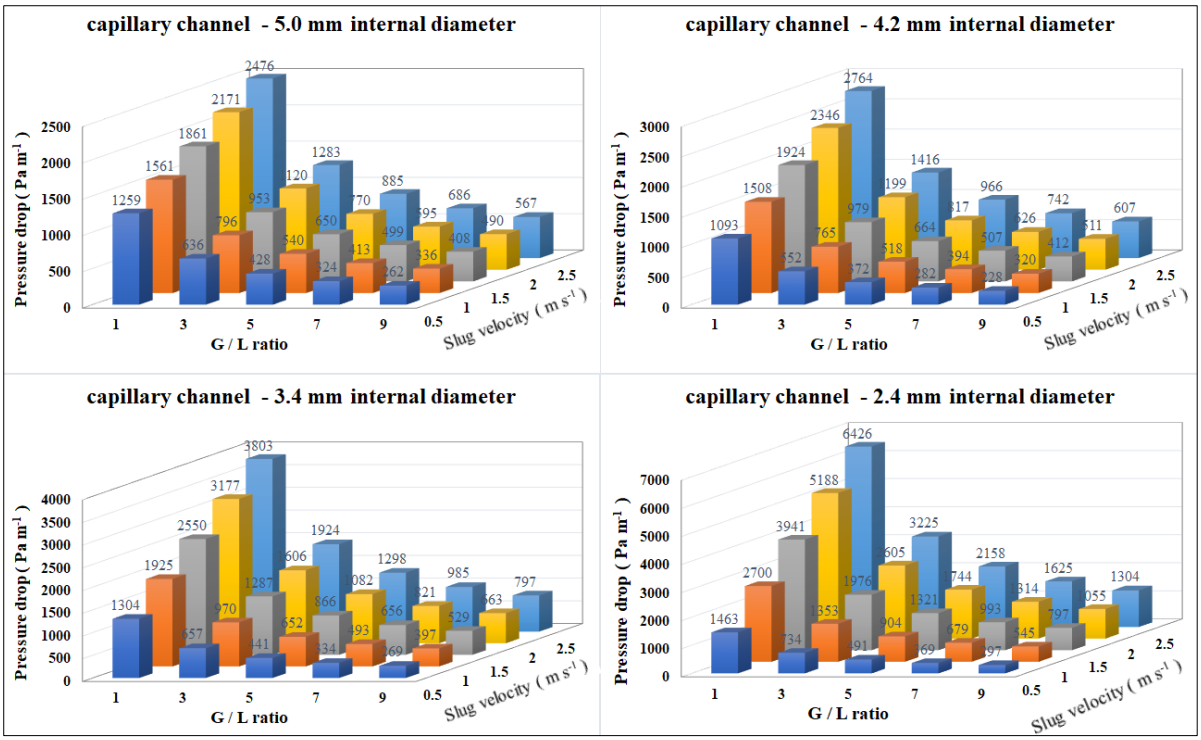


Figure 9-18: The pressure drop as a function of the gas-to-liquid ratio and the slug face velocity for the following capillary channel different in diameter: 5.0 mm (top left), 4.2 mm (top right), 3.4 mm (bottom left), and 2.4 mm (bottom right).

The contribution of (1) the wall friction of the liquid slug, (2) the static head of the liquid in the capillary channel, and (3) the wall friction of the gas bubble differs quite a lot depending on the diameter of the capillary channel, the gas-to-liquid ratio, and the slug velocity. **Figure 9-18** shows the pressure drop caused by gas wall friction, liquid wall friction, and liquid static head for three gas-to-liquid ratios (1 , 5 and 9) and two slug velocities: a relatively low slug velocity of 0.5 m s^{-1} (left graphics) and a relatively high slug velocity of 2.5 m s^{-1} (right graphics) for the following capillary channels different in diameter: 5.0 mm (top), 4.2 mm (upper middle), 3.4 mm (bottom middle), and 2.4 mm (bottom).

It can be concluded that the liquid static head dominates at the relatively low slug velocity and the larger channel diameters, while the liquid wall friction dominates at the relatively high slug velocities and especially at smaller channel diameters. Note that the liquid wall friction and the liquid static head are proportional to liquid hold-up, and thus the gas-liquid ratio. In addition, it can be concluded that the gas wall friction forces are in general negligeable but can't be ignored for the larger channel diameters at the higher G/L ratio as illustrated in **Figure 9-19**. The sum of the liquid wall friction and liquid static head may be used to predict pressure drops reasonably well, but the gas wall friction would need to be considered for the larger channel diameters (>3.5 mm) with a high gas-to-liquid ratio (> 5) flow regime.

However, there are other forces that should be considered and may be important depending on the configuration and the operating conditions of the CBR system. First, the entrance pressure losses generated by the inlet side of the capillary channel, where gas and liquid are mixed to form the gas-liquid bubble train needs to be taken into account. This is

especially important for multi-channel reactors where the gas needs to be mixed with the liquid. The method of gas injection and mixing can greatly impact the overall pressure loss and thus energy consumption of CBRs as e.g., a gas-liquid mixing zone of only 10 cm could create 100 mm static head by the liquid generating ~1,000 Pascal of additional pressure drop. Further research on gas-liquid zones for multi-channel capillary bioreactors would therefore be valuable.

Secondly, the Laplace pressure, which is the pressure difference caused by the surface tension of the gas-liquid interface, governs also the pressure drop in Taylor flow reactors. The Laplace pressure is for example used to determine the pressure difference in gas bubbles different in size, where the internal gaseous pressure increased as the gas bubble size decreases. The Laplace pressure increases with smaller capillary channel diameter and is proportional to the number of gas bubbles per unit length. Kreutzer et al. (2005) determined that the Laplace pressure may become important for slug length shorter than 10 times the capillary channel diameter. The slug-length may be expressed as the dimensionless slug length (= L_s / d) or as the bubble frequency per length unit (i.e., the number of slugs per meter). The overall pressure drop in a capillary channel under segmented flow regime is therefore dependent on the slug-length (L_s). In this study, the slug length observed in the CBR experiments (1.5 mm and 2.4 mm diameter channels) was typically between 2 and 3 cm, which means a dimensionless slug length between 8 and 15, and thus close to where the Laplace pressure may not be considered negligeable.

The Laplace number may be used to assess the importance of the Laplace pressure in relation to other forces, as the Laplace number (La) is related to the Reynolds number (Re) and the Weber number (We), as shown in Equation 9-13.

$$La = \gamma \times \rho \times L / u^2 \ (= Re^2 \times We^{-1}) \qquad \text{(Equation 9-13)}$$

In addition, Eq. 9-8 shows that any non-aqueous liquid additive (i.e., silicone oil) should have a low viscosity to minimize not only the liquid wall friction (as illustrated in Eq. 9-6), but also to minimize a possible pressure drop caused by the Laplace pressure losses.

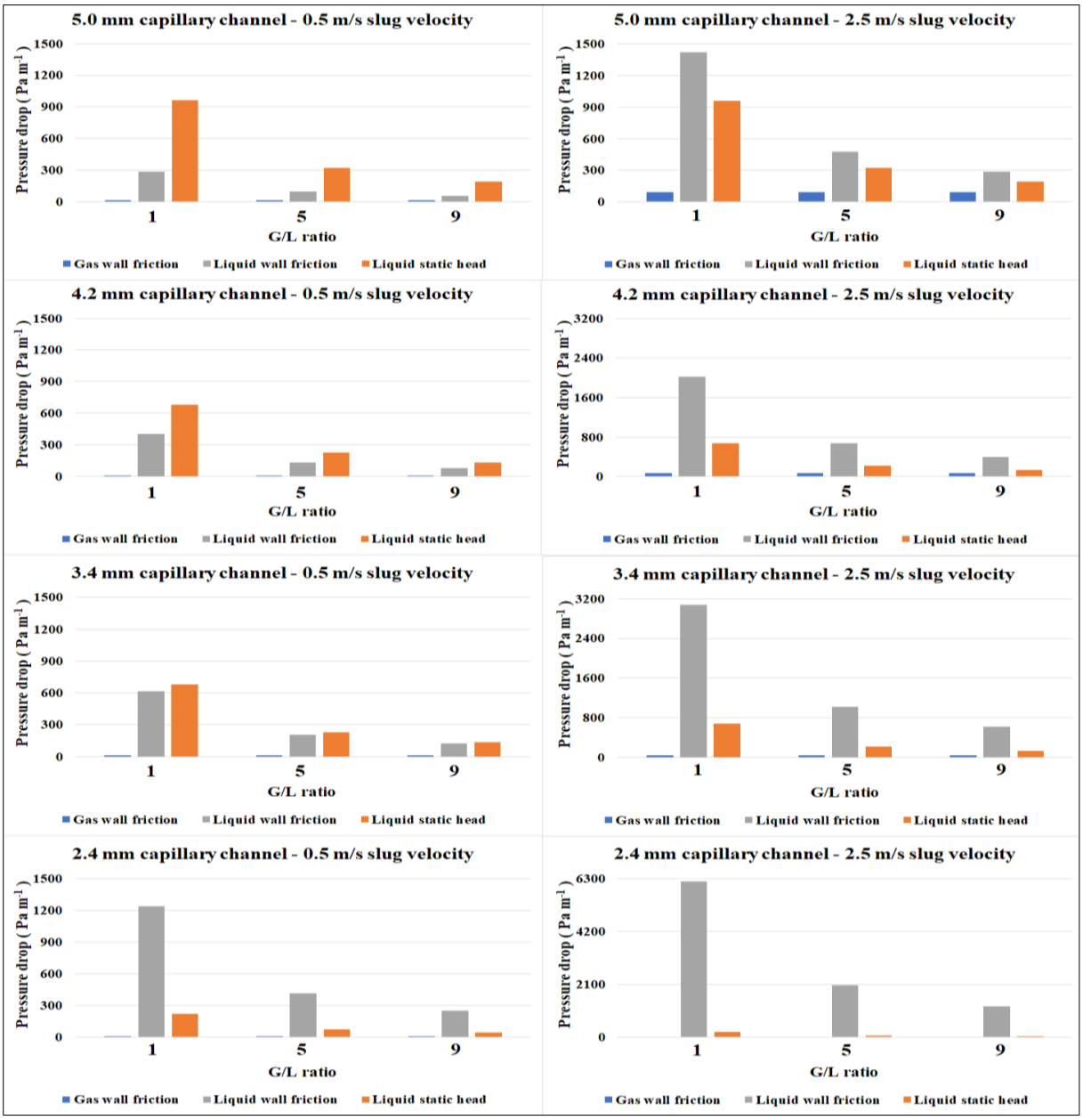


Figure 9-19: The pressure drop caused by gas wall friction (**blue**), liquid wall friction (**grey**), and liquid static head (**red**) as a function of the gas-to-liquid ratio for a relatively low slug face velocity (left graphics) and relatively high gas velocities (right graphics) for the following capillary channel different in diameter: 5.0 mm (top), 4.2 mm (upper middle), 3.4 mm (bottom middle), and 2.4 mm (bottom).

9-4 Conclusions

The removal of gaseous methane was investigated in different capillary bioreactor configurations and evaluated for operating conditions and parameters relevant to input requirements (e.g., energy) and reliable long-term performance. Biotic experiments were

performed in multi-channel capillary bioreactors to study different capillary channels, changes in gas-liquid slug velocities, gas-liquid ratios, methane inlet loading rates, gas contact times, and with/without internal gas recirculation. Although all reactors showed a high methane removal capacity, the addition of only surfactant (Experiment A) or only silicone oil (Experiment B) did not show any enhancement in methane removal efficiency.

The capillary bioreactor containing silicone oil and BRIJ 58 (Experiment C) treated dilute methane the best at an elimination capacity of 231 ± 30 g methane per m^3 internal capillary channel per hour at an efficiency of 52.8 ± 6.1% at an empty channel gas contact time of 23 seconds. The optimised liquid phase consisted of water containing nutrients, silicone oil (20% v/v, 20 cSt), and BRIJ 58 (160 mg L^{-1} = 1.8 CMC). The silicone oil acting as a buffer for methane was confirmed in a test that showed no deterioration in methane removal in the CBR following the methane supply interruption of six days.

The use of surfactants and silicone oil, along with the improved bioavailability of methane, promoted a strong microbial specialization by the end of the operation of the CBR with the most abundant aerobic methanotroph belonging to the genus *Methylosarcina*, with an increase in the relative abundance of *Lacunisphaera*. No accumulation of biomass on the walls of the capillary glass channels was observed during the entire period of more than 300-days operation of the CBR. It appears that a CBR with an optimized liquid phase, when operated with internal gas recirculation and thus decoupling optimal conditions for mass transfer from the gas contact time, may be a useful platform for further exploring the abatement of dilute methane.

No accumulation of biomass on the walls of the capillary glass channels was observed during the entire period of more than 300-days operation of the CBR. Moreover, the minimum nitrogen concentration required appear to be much lower in the CBR during our experiment treating methane than what has been shown to be required in conventional biological gas treatment system treating methane.

The energy required for the operation of a CBR would be mainly determined by the pressure loss when the gas-liquid slugs flow through the capillary channels. It was illustrated that the contribution of (1) the wall friction of the liquid slug, (2) the static head of the liquid in the capillary channel, and (3) the wall friction of the gas bubble differs quite a lot depending on the diameter of the capillary channel, the gas-to-liquid ratio, and the slug velocity. The Laplace pressure increases with smaller capillary channel diameter and is proportional to the number of gas bubbles per unit length and may not be ignored for short slug length in small capillary channels.

PART V

CONCLUSIONS AND OUTLOOK

10. CONCLUSIONS

Microorganisms have natural potential to convert gaseous contaminants into harmless or added value bioproducts. However, bioavailability of contaminants in traditional biological gas treatment systems is often hampered. Bioavailability governs the rate of bioconversions of these gaseous contaminants and may be the result of limited mass transfer to the microorganisms. Contaminants that are hydrophobic, present in low concentration or that can inhibit biodegradation typically result in poor removal rates in traditional biological gas purification systems.

This study obtained an enhanced understanding of bioavailability limitations of especially hydrophobic contaminants at relatively low concentrations for gas treatment bioprocesses. Specifically, methods to enhance the bioavailability of gaseous hydrophobic contaminant have been investigated from an experimental and theoretical point of view, and resulted in the following main conclusions:

- Bioavailability was investigated in capillary channels as gas-liquid contactors under segmented (Taylor) flow conditions that resulted in the effective removal of hydrophobic compounds at a gas contact time of less than 1 second (**Chapter 5**).

- It revealed that the overall mass transfer coefficient (K_La) in the tested capillary channels increased most with the gas superficial velocity ($U_{G/L}$) and increased somewhat with gas volume fraction (ε_G): $K_La = 220\ U_{G/L}^{0.47} / (1 - \varepsilon_G)^{0.18}$ (**Equation 5-4**). At the highest gas flow evaluated, K_La values above 400 h^{-1} were measured for the wide range of gas to liquid ratios between 1.2 to 6.2 (**Chapter 5**).

- The removal efficiency of the model air contaminants different in hydrophobicity and biodegradability (hexane, toluene and α-pinene) was on average 58, 90 and 44%, and up to about 75, 99 and 75%, respectively as a gas contact time in the capillary channel of about 0.5 seconds. This extremely low gas contact time is at least one and closer to two orders of magnitude lower than conventional biological air treatment systems (**Chapter 5**).

- An active contaminant-degrading culture could be sustained in the system treating hexane, toluene and α-pinene and no accumulation of biofilm inside the capillary channels was observed. The bioreactor system showed stable operation for 100-days and was robust against three common upset scenarios, most likely facilitated by the highly diverse bacterial community that was observed (**Chapter 5**).

- Toluene, α-pinene and hexane removals were enhanced up to 99, 98, and 55%, respectively, when 10% (v/v) silicone oil with a viscosity of 20 cSt was dispersed in the recirculating liquid. The addition of silicone oil increased the removal efficiency of α-

pinene from 45 ± 6% to 98 ± 2% over two days, likely due to the silicone oil alleviating biokinetic inhibition by acting as a buffer for the VOCs and their metabolites. For toluene, the removal efficiency gradually increased after silicone oil addition from 81 ± 3% to 99 ± 1% over eight weeks, likely due to microbial adaptation. The removal efficiency of hexane did not increase after silicone oil addition, potentially due to inhibition of hexane or its metabolites as the bioreactor was deliberately operated without replenishment of the recirculation liquid (**Chapter 6**).

- Interestingly, visually all the biomass adhered to the silicone oil phase rather than residing in the water phase (**Chapter 6**).

- The feasibility of a capillary bioreactor as a platform for the biological gaseous co-abatement of CO_2 and hydrophobic VOCs was investigated and confirmed (**Chapter 7**). An instant reduction of the outlet CO_2 concentration compared to the inlet CO_2 concentration was observed after the introduction of microalgae into the capillary bioreactor. A net CO_2 consumption was observed achieving complete carbon sequestration from the removed VOCs with additional CO_2 removed from the inlet ambient air.

- The co-abatement of CO_2 and hydrophobic VOCs in the capillary bioreactor identified several operational requirements, such as pH-neutralization and/or replenishment of the recirculation liquid and the requirement to alleviate the risk of channel blockage due to algae-growth (**Chapter 7**).

- Different bench-scale experiments elucidated that the liquid phase in a capillary bioreactor can be optimized to enhance the bioavailability of dilute methane (**Chapter 8**).

- Synthetic surfactants were investigated to assess their potential to enhance bioavailability and mass transfer, both with and without the presence of silicone oil. Three non-ionic surfactants were selected for their widespread availability and common use in many households or industries. The surfactants BRIJ 58 and SDBS, in contrast to TWEEN 60, both showed to be able to significantly enhance bioavailability of dilute methane at the concentrations tested (**Chapter 8**). The lower apparent gas-liquid partition coefficient of methane and the enhanced cell hydrophobicity of the methane oxidizing consortium appear to be the main mechanisms.

- The surfactant BRIJ 58 was found to enhance the gas-liquid mass transfer in a capillary channel, but the effect was significant only when combined with silicone oil. The enhanced emulsification of the oil by the surfactant appeared to be the main mechanism for this enhancement, rather than the modification of the gas-liquid partial coefficient of methane (**Chapter 8**).

- The amount of silicone oil added impacted mass-transfer significantly when comparing 10% v/v versus 25% v/v, regardless of the oil viscosity. This was explained by the impact of emulsion viscosity on the liquid film thickness surrounding the gas bubbles, which increases the methane carrying capacity of the liquid film each time a gas bubble passes it in the segmented flow in the capillary channel (**Chapter 8**).

- The viscosity of the silicone oil (and thus the overall viscosity of the emulsion) appeared to be critical to maintain optimum turbulent (Taylor) flow conditions, with a lower viscosity better as confirmed in the abiotic methane mass transfer rate experiment (**Chapter 8**).

- It appears that a capillary bioreactor, when operated with internal gas recirculation and thus decoupling optimal conditions for mass transfer from the gas contact time, is a useful platform for further exploring the abatement of hydrophobic gaseous compounds such as dilute methane (**Chapter 9**).

- When the removal of gaseous methane was investigated in different capillary bioreactor configurations (**Chapter 9**) the addition of only surfactant or only silicone oil did not enhance methane removal.

- In contrast, the capillary bioreactor containing silicone oil and the surfactant BRIJ 58 treating dilute methane did enhance methane removal. This bioreactor displayed an average elimination capacity of 231 ± 30 g methane per m^3 internal capillary channel per hour at an efficiency of 52.8 ± 6.1% at an empty channel gas contact time of 23 seconds (**Chapter 9**). This is remarkable since conventional biological methane treatment systema typically requires more than 4 minutes empty bed gas contact time while their elimination capacity is typically less than 80 g methane per m^3 per hour.

- The optimised liquid phase consisted of water containing nutrients, silicone oil (20% v/v, 20 cSt), and BRIJ 58 (160 mg L^{-1} = 1.8 CMC) (**Chapter 9**).

- The silicone oil acting as a buffer for methane was confirmed in a test (**Chapter 9**) that showed no deterioration in methane removal in the capillary bioreactor following the methane supply interruption of six days.

- The use of surfactants and silicone oil, along with the improved bioavailability of methane, promoted a strong microbial specialization by the end of the operation of the capillary bioreactor with the most abundant aerobic methanotroph belonging to the genus *Methylosarcina,* with an increase in the relative abundance of *Lacunisphaera* (**Chapter 9**).

- No accumulation of biomass on the walls of the capillary glass channels was observed during the entire period of more than 300-days operation of the capillary bioreactor (**Chapter 9**). The oscillating shear-stress appeared to be high enough to prevent biomass growth on the inside wall of the glass capillary channels.

- The energy required for the operation of a capillary bioreactor would be mainly determined by the pressure loss when the liquid slugs flow through the capillary channels. It was illustrated that the contribution of (1) the wall friction of the liquid slug, (2) the static head of the liquid in the capillary channel, and (3) the wall friction of the gas bubble differs quite a lot depending on the diameter of the capillary channel, the gas-to-liquid ratio, and the slug velocity. The Laplace pressure increases with smaller capillary channel diameter and is proportional to the number of gas bubbles per unit length and may not be ignored for short slug length in small capillary channels (**Chapter 9**).

In summary, characteristics limiting bioavailability for biological gas treatment have been investigated in general terms, with an emphasis on the underlying principles and technically feasible methods to overcome bioavailability limitations of especially hydrophobic contaminants in a capillary bioreactor when operated under the segmented (Taylor) flow pattern.

11. OUTLOOK AND RECOMMENDATIONS

11.1 General

While the experiments in this study were performed in relation to two gas treatment scenarios (hydrophobic model compounds to improve IAQ and dilute methane to reduce GHG emissions), most of the results could be extrapolated to other gas treatment scenarios. VOCs are a large group of organic chemicals that include basically any compound of carbon that are emitted from a variety of anthropogenic sources, including chemical manufacturing facilities, refineries, factories, consumer and commercial products.

Adsorption processes (mainly activated carbon filtration) and thermal oxidative processes (incineration) strongly dominate the field of industrial air and gas purification applications but require typically ongoing input of resources making them far less sustainable. Moreover, thermal oxidative processes can lead to health-damaging smog from its NOx-emissions and generate GHG emissions: carbon dioxide, methane slip and potentially nitrous oxide. These traditional treatment methods urgently need to be altered too to make them more sustainable. Many of the physical-chemical applications treat gaseous streams that contain hydrophobic compounds, which currently require biological gas treatment methods to be very large to overcome limitations related to especially bioavailability and therefore restraining its economic feasibility.

Moreover, biological production processes that involve gaseous process streams (gas-phase biorefineries) are often hampered by the bioavailability including mass transfer of the contaminants from the gas to the liquid phase containing the microorganisms converting them into added value bioproducts. This is key for upscaling these processes and achieving fast enough conversion rates to be economically interesting. Improved biological gas treatment methods such as the capillary bioreactors investigated herein can enhance gas-liquid mass transfer and could eliminate current limitations in bioavailability for future biorefineries to be more cost-effective.

However, despite the fact that the study presented herein confirms that capillary bioreactors are promising to expand the application field of biological gas treatment, a specific analysis and exploration for each scenario is commended for an adequate selection, design and operation of any gas treatment method. Future research would be required for a wider use of capillary bioreactors that can overcome bioavailability limitations and should include the quantification of its robustness against transient conditions or common upsets, often considered as ‘unknowns’ and therefore perceived as an operational risk limiting its widespread use.

11.2 Capillary Bioreactor Technology Further Development

Capillary reactors have been extensively investigated within the context of chemical reaction engineering and as such are increasingly being used in industrial processes due to their unique hydrodynamic characteristics. Most of this research and applications are dealing with micro capillary channels (0.2 mm > d < 10 um) or nano capillary channels (d < 10 um), while capillary bioreactor with suspended biomass would require larger capillary channels (> 2 mm), which would generate the condition to prevent blockages of the capillary channels by biomass aggregates as found and discussed herein this study. Future research in the specific field of capillary bioreactors should therefore focus on micro-channels (2-4 mm) for the following aspects:

1) A further **systematic evaluation of the key parameters that are interdependent** and somewhat specific for different gaseous streams and overall treatment objectives. Based on this study, the key target parameters to be further investigated are:
    - Gas-liquid **segmented flow stability** (for optimum bioconversion capacity)
    - Gas-liquid **maximal mass transfer** (for optimum bioconversion capacity)
    - Overall **system pressure loss** (for minimum energy requirement)

2) The **evaluation of its life-cycle sustainability in terms of design and operation** to especially minimize its pressure losses (**energy use**) and to ensure long-term stable operation (eliminate operator intensive measures, for example related to removing **biomass** potentially accumulating on the capillary channel wall reducing overall reactor performance).

3) The **gas-liquid mixing methods at the inlet side** of the capillary channels to better control the bubble frequency per unit length, to minimise the residence time distribution among the channels, and to minimise the entrance pressure losses generated by the inlet side of the capillary channel, where gas and liquid are mixed to form the gas-liquid bubble train.

The parameters are interdependent as sketched in **Figure 11-1** and somewhat specific for different gaseous streams, which makes process optimization complex. This is especially relevant when not only performance in terms of bioconversion capacity (mainly relevant for capital costs) are essential, but also optimization in terms of minimizing resources such as energy (mainly relevant for operating costs) and in terms of operability (often a key decision factor when selecting technologies). Some of the design inputs relevant for further optimisation and upscaling are discussed below.

Channel diameter: Chemical engineering studies have been carried out over especially the last decade with structures containing channels diameter up to about 1 mm (e.g., monolith or honeycomb structures). The study herein proved that using channels of 2.4 mm performed well for liquids containing microorganisms without plugging the channels, while preventing

biomass growth on the internal channel's wall likely due to the relatively high oscillating shear forces. Smaller diameter channels (1.7 mm) showed increased risk of plugging (see Experiment A, **Section 9.3** in Chapter 9). Larger diameter channels would not necessarily reduce mass transfer rate as demonstrated in our theoretical analyses (Bordel et al., 2024) up to a diameter threshold where capillary is lost. For water-air gas-liquid capillary reactor, this threshold is ~ 5 mm, while this study has proven that nutrients and biomass slightly reduce the window of capillarity for different gas-liquid velocities and different gas-liquid ratios. The optimum channel diameter for a capillary bioreactor is anticipated to be quite similar for different applications, when only water with nutrients and biomass is used and is expected to be in the range of 2.0 to 4.0 mm. Nevertheless, the addition of a second non-aqueous liquid phase, such as silicone oil, would reduce the upper range (meaning < 4.0 mm) depending on especially the amount and the viscosity of the non-aqueous phase.

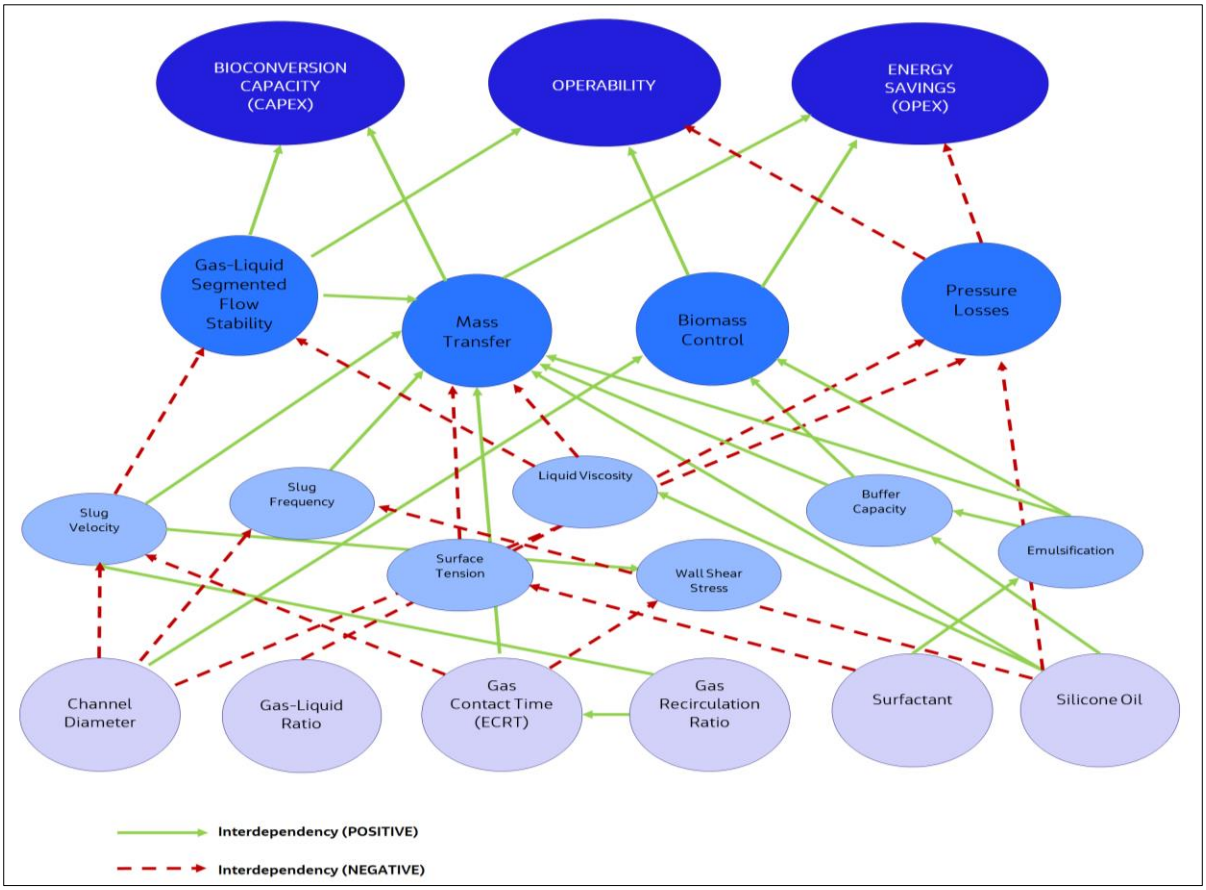


Figure 11-1 Schematic presentation of the interdependent relations between capillary bioreactor designs inputs (bottom) and relevant economic functionality outputs (top).

Mass transfer: The mass transfer from the gas to the liquid phase can occur from the gas bubble into the liquid slug via the bubble caps and into the liquid film surrounding the gas bubble. In our theoretical analysis we showed that the contribution via the liquid film surrounding the gas bubble was at least one of magnitude larger than the contribution via the bubble caps for a capillary reactor containing gaseous methane and water (Bordel et al., 2024).

This is consistent with data in literature e.g., illustrated by Dietrich and co-workers (2013) as shown below for oxygen transfer into water in a capillary channel.

This means that further research should probably focus on how to maximise the use of the liquid film either by shortening the gas bubble length (to prevent full saturation before the gas bubble has passed the liquid film), or by enhancing the carrying capacity for the target contaminant (e.g., through adding a non-aqueous liquid phase such as silicone oil and/or through increasing film thickness via increased gas-liquid velocity or increased liquid viscosity). Alternatively, a porous wall between the channels could also be further explored, as proposed and investigated by Bakker and co-workers (2005).

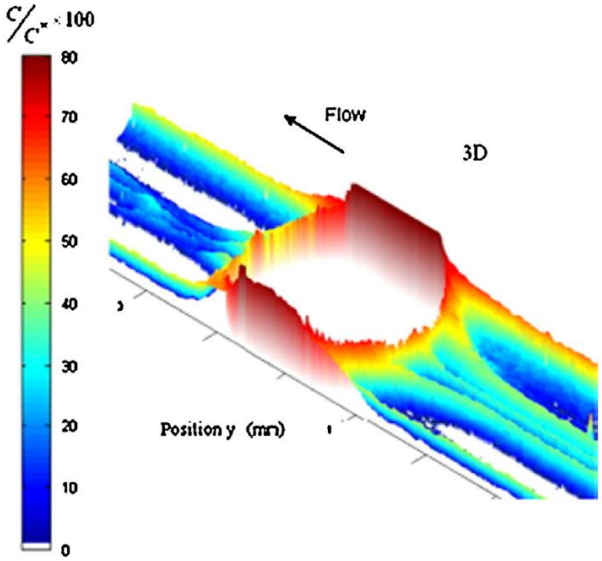


Figure 11-2 Computational Fluid Dynamics (CFD) visualisation of oxygen concentrations around a phase gas bubble in a capillary channel under segmented (Taylor) flow (courtesy of Dietrich et al., 2013).

The optimal turbulent flow condition in a capillary channel is independent of the contaminant (type and concentration). Nevertheless, the optimal overall reactor mass transfer rate from the gas phase to bulk of the liquid, containing the microorganisms catalysing the conversion of the contaminant, may require a different length of the capillary channel to utilise the maximum carrying capacity of the liquid inside the channel. When the liquid inside the capillary channel is saturated (has become in equilibrium with the gas phase inside the channel), mass transfer would cease, and the contaminants must be removed first (empty the bucket as soon as it is full).

Slug Frequency: The length of the gas bubble (L_b) and the length of the liquid slug (L_s) are critical for the mass transfer as confirmed in this research (e.g., **Section 8.3** in Chapter 8). A shorter total unit length ($L_u = L_b + L_s$), which means an increase in slug frequency per unit length, may increase mass transfer as it reduces the risk that the liquid film surrounding the gas bubble gets saturated, limiting further mass transfer as discussed elsewhere (Bordel et al., 2024). Predicting or modelling the slug frequency formation is problematic, with some

empirical or semi-empirical correlation being used to predict the liquid slug and the gas bubble lengths. These correlations were based on dimensionless numbers containing liquid properties, but specific to the experimental set-up and conditions tested for channels diameters less than 1 mm (Haase et al., 2016). Improved prediction and control of the slug frequency, which is directly linked to the mixing methods at the inlet side of the capillary channels, would be critical for further optimisation and upscaling.

Silicone oil fraction: The addition of up 10% v/v silicone oil has proven to promote bioavailability by either enhancing mass transfer mainly in combination with a surfactant (**Figure 8-8**, Section 8.3 in Chapter 8) or by providing a buffer to contaminants and/or its metabolites (**Figure 6-2**, Section 6.3 in Chapter 6). However, increasing the silicone oil fraction from 10 to 25% v/v made the total unit length become significantly longer (and thus reducing the slug frequency). In the abiotic methane mass-transfer experiments in a single channel, the average total unit length (L_u) increased from about 1 cm to more than 3 cm (**Figure 8-8**, Section 8.3 in Chapter 8). The optimum faction of silicone oil seems to be ~ 10% v/v when 20 cSt oil is used and the capillary reactor is operated at a slug velocity of 2 m s^{-1}, but that optimum will be dependent especially on the oil viscosity, the slug velocity and the surface tension as expressed in the Ca number (**Equation 8-5**) to maintain gas-liquid segmented flow stability.

Liquid viscosity: Increasing the liquid viscosity of the oil-in-water emulsion increases the liquid film thickness as explained elsewhere (Ausillous and Quéré, 2000), which increases the contaminant carrying capacity of the liquid film each time a gas bubble passes it in the segmented flow in the capillary channel. The liquid film thickness flowing around gas bubbles is critical for gas-liquid mass transfer in a capillary channel under segmented (Taylor) flow regime. However, an increased viscosity reduces the window of gas and liquid flow rates where required flow (Taylor) regime for optimal mass transfer can be maintained (**Figure 6-1**, Section 6.3 in Chapter 6). Maintaining a low liquid viscosity is therefore important to maintain segmented (Taylor) flow regime when adding a second non-aqueous liquid phase such as silicone oil. An oil viscosity of 20 cSt or lower is therefore recommended in future research of capillary bioreactors.

Gas-liquid mixing zone: The gas-liquid mixing methods at the inlet side of the capillary channels influences the bubble frequency per unit length and the entrance pressure losses generated by the inlet side of the capillary channel where gas and liquid are mixed to form the gas-liquid bubble train. This is especially important for multi-channel reactors where the gas needs to be mixed with the liquid. The method of gas injection and mixing can greatly impact the overall pressure loss and thus energy consumption as e.g., a mixing zone containing gas-to-liquid ratio of 1 (50% liquid) of only 20 cm could create ~100 mm static head by the liquid generating ~1,000 Pascal of additional pressure drop. Further research on minimizing pressure losses at the gas-liquid mixing zone would therefore be important.

Predicting how the gas-liquid mixing will exactly influence the slug length is unfortunately difficult. The gas liquid distribution at the inlet of the capillary channels requires further study and should also be focused on controlling the slug frequency. The slug length may not only impact the mass transfer rate (as discussed in **Chapter 8**) but may also impact the overall pressure loss and thus energy consumption (as discussed in **Chapter 9**).

In this study we tested two types of gas-liquid mixing: using a perforated membrane and using coarse bubble aeration into the liquid containing a floating random packing material. The first method was applied in the experiments discussed in Chapters 5 till 7 and Experiment A and B in Chapter 9, while the second method was applied in Experiment C discussed in Chapters 8 and 9. The second method provided similar slug lengths as the first method but requiring much less pressure drop and had the benefit that no liquid was pushed back into the gas reservoir upon temporarily stopping the air supply. No detailed comparisons between the two methods were undertaken and no further refinements of the methods were tested. Further research on gas-liquid mixing zones for multi-channel capillary bioreactors would therefore be beneficial.

Residence time distribution in multi-channels: The residence time distribution has not been investigated herein but would need to be quantified to further optimize the performance in terms of mass transfer and scaling up a capillary reactor. Residence time distribution in multi-channel capillary reactors has been investigated, revealing that large differences in residence time distribution curves can exist when compared to a single capillary channel (Kreutzer et al., 2005; Lei et al., 2020). Relatively simple tracer studies could be undertaken using a gaseous tracer or a colored dye liquid tracer, but other techniques such as MRI tomography and optical fiber probes have been used as well. These methods could assist in optimizing the operating conditions and optimizing the gas-liquid mixing zone. Moreover, these methods can be used to help quantify the effect of internal gas recirculation or stacked sections of multiple channels with cross-channel connections for redistribution in between each section of multiple channels when this is considered.

Pressure Losses: The energy required for the operation of a CBR would be mainly determined by the pressure loss when the liquid slugs flow through the capillary channels. It was illustrated (**Figure 9.19**, Section 9.3 in Chapter 9) that the contribution of (1) the wall friction of the liquid slug, (2) the static head of the liquid in the capillary channel, and (3) the wall friction of the gas bubble differs quite a lot depending on the diameter of the capillary channel, the gas-to-liquid ratio, and the slug velocity. In addition, the Laplace pressure increases with smaller capillary channel diameter and is proportional to the number of gas bubbles per unit length and may not be ignored for short slug length in relatively small capillary channels. Since energy requirement is a key factor determining economic feasibility and sustainability, it therefore should always be considered in any further capillary bioreactor study.

Gas composition: The capillary bioreactor has shown in this study to be capable of effectively treating contaminants in ambient air streams, but not for contaminants in other gas streams such as biogas, syngas or else that could be used as feedstocks in gas-phase biorefineries. This would also be an area of further studies.

In summary: Although the mechanisms of enhancing bioavailability are not fully elucidated and different technical challenges need to be resolved before capillary bioreactors can be further scaled up, several promising strategies to improve mass transfer, while minimizing power consumption and preserving long-term operational stability, have been demonstrated that could mark the future trend. Further understanding of the bioavailability of contaminants (i.e., mass transfer behaviour and buffer capacity) in biological gas treatment systems should improve bioreactor designs, bioreactor operation, and modelling tools to further maximize efficiency and minimize costs. Considering the bleak performance of hydrophobic contaminant removal using conventional biological gas treatment methods it appears that a capillary bioreactor has potential. Capillary bioreactors could expand the application field of biological gas treatment to replace less sustainable conventional physical-chemical gas purification techniques currently dominating the industrial market.

11.3 Hybrid System for Improving Indoor Air Quality

Capillary reactor combined a Botanical Green Wall

Further research should be undertaken to investigate the feasibility that a capillary reactor is combined with an existing botanical green wall for indoor air purification (**Figure 11-3**).

This hybrid system could embrace green building certification schemes as it will:

1. advance existing (mainly aesthetic) green walls,
2. improve IAQ, indoor comfort and overall well-being, and
3. foster heating ventilation and air conditioning (HVAC) energy savings.

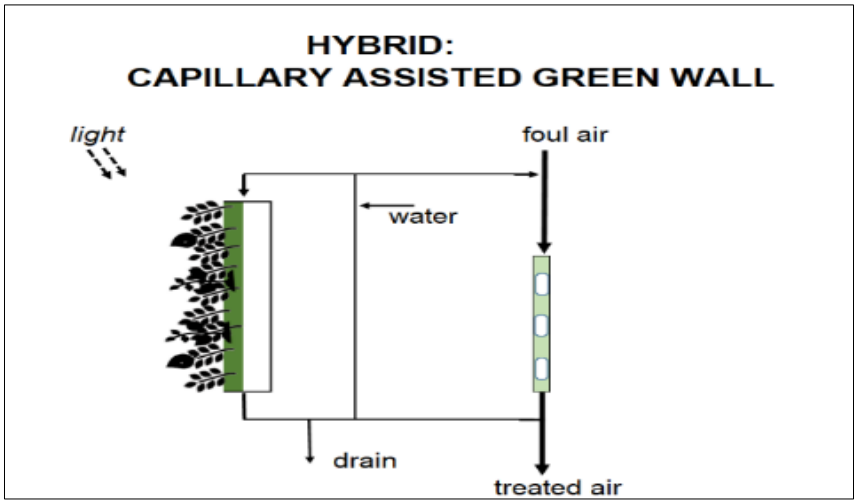


Figure 11-3 Sketch of the concept of a capillary reactor combined with a green wall.

Figure 11-4 An example of a botanic green wall (courtesy of NEDLAW Living Walls).

Besides overcoming mass transfer limitations, the hybrid biological indoor air purification system may also be able to sustain enough microbial activity under conditions of trace pollutant concentrations. Indoor air pollutants may not always have high enough energy and/or carbon content to support cell maintenance and growth, and co-metabolism may be required for an effective pollutant removal. The bioactive zones of plants (i.e. soil, plants roots

and plant leaves) can provide extra energy and carbon substrates to sustain overall microbial eco-system stability, while hydroponic substrates may be used as secondary substrate in plant-based systems for biological indoor air purification systems. A capillary reactor could be combined with an existing vertical green wall so that the process liquid from the capillary reactor is fed to the root zone of the plant in the green wall. The advantage of such a combination is that the benefits of the plant-based green wall such as aesthetics and support of microbial activity (through root exudates produced by photosynthesis that enhances mutual benefit between plant and microbes) are combined with the high mass transfer capacities of a capillary reactor. This hybrid system could be obtained using existing vertical green walls that use a hydroponic substrate with a recirculation water flow, so that one liquid stream is combined in the two systems. The size, materials and labour involved in adding a capillary reactor would be significantly less compared to installing a green wall.

The performance of air treatment systems is usually evaluated by the removal efficiency of pollutants of a single pass through the system (the difference in concentration between inlet and outlet air). Rather than the single pass purification efficiency, the overall purification capacity per volume of indoor space is more important for indoor air purification systems. The clean air delivery rate (CADR) is the reduction in outdoor air intake that can be obtained with an indoor air purifying system, while maintaining low levels of pollutants in the room (Shaughnessy and Sextro, 2006). The CADR can be translated in total energy expenditure to evaluate potential costs savings for HVAC. The concept of CADR was introduced to evaluate various indoor air purification devices (Shaughnessy and Sextro, 2006), where CADR is defined as the volume of purified air delivered per unit of time providing a specific air purifier refreshment capacity α (h^{-1}) for an indoor room:

$$\alpha = CADR / V = RE \times Q / V \qquad \text{(Equation 11-1)}$$

Where V is the volume of the indoor room (m^3), RE is the single-pass removal efficiency of the purifier (%) and Q is the airflow treated by the purifier ($m^3\ h^{-1}$).

Baseline fresh air rate for non-process conditioned spaces of three room-volumes per hour is typically recommended but is dependent of the type of room and its occupancy (AESHRAE, 2019). Calculating the operating effectiveness (CADR/kW) makes it possible to compare ventilation with or without air purifiers. Active green walls integrated in the HVAC system can significantly reduce the intake of fresh outdoor air and have been claimed to save energy up to 60% typically used by conventional HVAC systems (Nedlaw Living Walls, 2020).

Green Building Certification

Biological indoor air purifiers can also provide credits towards Indoor Environmental Quality (IEQ) for green building certification schemes that stimulates to realise sustainable buildings that are healthy, energy-efficient and environmentally friendly. IEQ has a large impact on our typical modern life and requires high indoor air quality to prevent health effects such as dry eyes, headache, tiredness, allergies, respiratory infection and sick building syndrome (SBS) (Burge, 2004). While building professionals and building owners may recognise the

importance of IAQ, they often do not appreciate how routine design and construction decisions can ultimately result in IAQ problems. Sustainable building creates physical structures and uses processes that are environmentally responsible and resource-efficient and consider the full lifecycle of a building.

Green building certification was introduced in Europe and the United States in the early 1990s, including the BRE Environmental Assessment Method certification (BREEAM; in the United Kingdom), Leadership in Energy and Environmental Design certification (LEED; in the United States) and Haute Qualite Environnementale certification (HQE; in France). Since then, more national green building schemes have been generated that have been adapted to local environmental and economic conditions (Wei et al., 2015).

Indoor Comfort and Overall Well-being

In addition to building energy cost savings and improving IEQ, biological indoor air purifying systems can contribute to occupants' mental health in indoor spaces and may directly influence human performance and productivity. IEQ is typically quantified by indoor air pollutant concentrations (e.g., CO_2 concentration) and indoor climate conditions (i.e., temperature, relative humidity and air movement), while occupants' comfort and overall well-being may be quantified in terms of a physical sensation, a persons' mental state or both at the same time.

Physical health has been typically quantified in terms of physiological reactions of blood pressure and perspiration rates. Mental health can be estimated by psychological responses (e.g., verbal scale vote of occupant what he/she considers a feeling of comfort). Kim et al. (2020) showed a statistically significant negative relationship between the indoor climate and CO_2 concentrations and occupants' mental health, which was determined by blood pressure and psychological responses.

In this context, green plants in indoor spaces without specifically being designed to clean indoor air have already been proven to provide valuable improvements on indoor comfort and well-being, resulting in environments that are healthier and aesthetical more pleasant to work and live in. Plants may help evaporate moisture lowering the temperature, produce oxygen through photosynthesis or may help reduce sound levels as an acoustic absorption system. Vegetation has also shown to affect emotions of consumers (Tifferet and Vilnai-Yavetz, 2017). Vegetation brings elements of nature inside a building that may provide spaces that could create an aesthetical pleasant environment and potentially reduce stress. Plant-based systems may improve worker productivity and creativity as well as comfort or perception of their indoor space quality creating a more desirable place to work (Moya et al., 2018).

Maybe the further development and benefits of (biological) indoor air purifying systems should be focussed on the overall human well-being and productivity, as it may be easier to motivate people and companies than air-pollutant-related chronic health benefits that occur decades in the future (Siegel, 2019).

11.2 Dilute Methane Applications

Wastewater and Sludge Treatment Processes

Wastewater collection and treatment processes at industrial and municipal water resource recovery facilities (WRRFs) are emitting GHGs at a sizable contribution to global methane emissions (EEA, 2021; UNFCCC, 2024). An increase amount of the wastewater is treated in centralized wastewater treatment facilities with an increase amount of the produced sludge anaerobically processed to recover methane for energy. Although this creates the opportunity to make wastewater management energy-neutral or even energy-positive (Parravicini et al., 2022), there is a risk of increased fugitive process emissions from these water and associated sludge treatment processes. Reducing methane emissions and oxidise some of the dilute methane emissions may be necessary to achieve that goal. Oxidation of methane to carbon dioxide allows a significant reduction of the GHG emissions as the global warming potential of methane is significantly higher than that of CO_2 (see also **Section 2.3** in Chapter 2). Moreover, the produced carbon dioxide is part of the so-called short-term organic cycle and does therefore not contribute to the greenhouse effect.

The main dilute methane sources at WRRFs are the headworks, secondary digestors, biosolids dewatering and biosolids storage. Since wastewater and sludge processing facilities occupy already biological processes and the integration of dilute methane capture and treatment within existing processes at WRRFs should be further explored. Similarly to as proposed above in using existing botanical green wall to augment with a capillary reactor for indoor air purification, dilute methane capture in a capillary reactor could be combined with the aerobic conversion of dilute methane in existing activated sludge tanks (**Figure 11-5**). Methane oxidizing bacteria are present in activated sludge (see also **Section 9.3** *Microbial Characterisation – Experiment C* in Chapter 9). Return activated sludge could be used as liquid phase to supply the capillary reactor for dilute methane capture that could be discharged in the activated sludge tank for complete methane oxidation. The water and gas phase would need to be recirculated to enhance the removal capacity in the capillary reactor.

Animal housing

Livestock production contributes substantially to the economies of many countries in terms of employment, food production, and export of products. However, the intensive livestock production relates to a number of environmental challenges including the emissions to the air (i.e., mostly ammonia and methane) and the soils and surface waters (i.e., mostly phosphate and nitrogen). Current air treatment methods for emissions from animal houses include acid scrubbing and biotrickling filtration, which can effectively remove ammonia by 96% and 70% on average, respectively (Melse, 2009), when operated properly. Although methane removal in biotrickling filters has been demonstrated, the practical application is limited by the bioavailability of methane in the biotrickling filter systems (Melse et al., 2005).

Currently, enhancing the removal of methane from exhaust air from animal husbandries and manure storages would provide a large potential for their reduction of GHG emissions. As shown in **Table 3-2** (Section 3.3 of Chapter 3) conventional biological gas

treatment systems are seriously hampered by methane bioavailability and require extended gas residence times – often of several minutes – to achieve efficient removal due to the limited bioavailability of methane. Capillary reactors, as second stage after an ammonia acid scrubber or a biotrickling filter, could provide opportunities that also should be explored in future research.

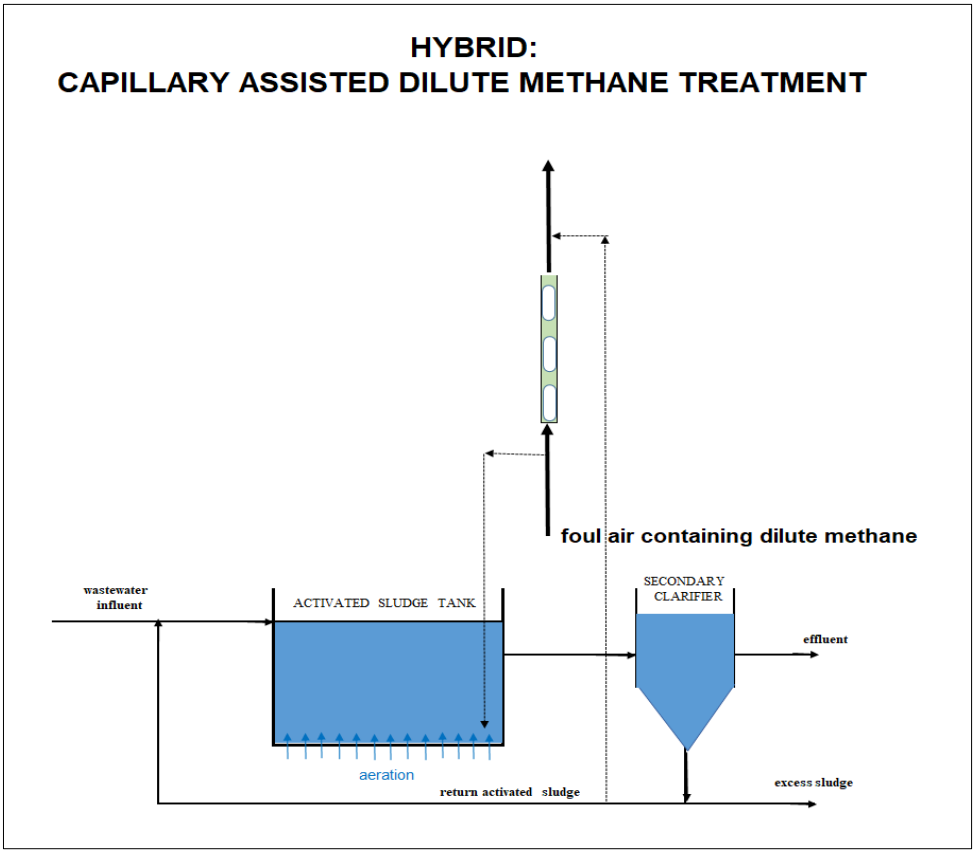


Figure 11-5 Sketch of the concept of a capillary reactor combined with an existing activated sludge tank.

Nomenclature

a	Interfacial area ($m^2\ m^{-3}$)
C	Contaminant concentration ($g\ m^{-3}$)
CBR	Capillary Bioreactor
d	Diameter (m)
D	Gaseous contaminant diffusivity in the liquid ($m^2\ s^{-1}$)
dP	Pressure loss (Pascal)
EBRT	Empty bed gas retention time (s)
EC	Elimination capacity ($g\ m^{-3}$ reactor h^{-1})
ECRT	Empty channel gas retention time (s)
EPS	Extracellular polymetric substances
g	Gravitational constant ($m\ s^{-2}$)
H	Henry coefficient (-)
IAQ	Indoor Air Quality
IL	Inlet Load ($g\ day^{-1}$)
k_La	Volumetric mass transfer coefficient (s^{-1})
K_s	Half-saturation constant (uM)
L	Length (m)
m	Mass (kg)
ppm_v	Part per million by volume
ppb_v	Part per billion by volume
R	Capillary radius (m)
RE	Removal efficiency (%)
rpm	Revolutions per minute
s	Seconds
VIC	Volatile inorganic compound
VOC	Volatile organic compound
TN	Total Nitrogen ($mg\ L^{-1}$)
TOC	Total organic carbon ($mg\ L^{-1}$)
TVOC	Total Volatile organic compounds
TSS	Total Suspended Solids ($mg\ L^{-1}$)
TVS	Total Volatile Solids ($mg\ L^{-1}$)
u	Velocity ($m\ s^{-1}$)
v/v	Volume per volume

Greek letters

γ	Surface tension ($N\ m^{-1}$)
μ	Viscosity (Pa s)
ρ	Density ($kg\ m^{-3}$)
τ	Shear stress
δ_{film}	Liquid film thickness (m)

Dimensionless groups

Ca	Capillary number ($= \mu \times v / \gamma$), the ratio of viscous drag forces to its surface tension forces.
Fr	Froude number ($= u / (g \times L)^{0.5}$), the ratio of the flow inertia to gravity.
La	Laplace number ($= \gamma \times \rho \times L / u^2 = Re^2 \times We^{-1}$), the ratio of surface tension to momentum ($m * u$).
Oh	Ohnesorge number ($= u / (\rho \times \gamma \times L)^{0.5}$), the ratio of viscous forces to inertial + surface tension forces.
Re	Reynolds number ($= r \times U \times d / m$), the ratio of fluid's inertia forces to viscous forces.
We	Weber number ($= \rho_G \times u_{Gs}^2 \times d / \gamma$), the ratio of the fluid's inertia forces to its surface tension forces.

Subscripts

B	bubble
F	film
G	gas
L	liquid
S	slug

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Norbertus Joannes Richardus Kraakman (Bart Kraakman) was born on April 16, 1968 in St. Maartensbrug, the Netherlands. He grew up at a dairy farm with his father (Cees Kraakman) and mother (Vronie Kraakman-Koenis) and his two brothers (Olof and Marc). After finishing his secondary education (HAVO and VWO) at the Rijks Scholen Gemeenschap in Schagen he studied at the Wageningen University, the Netherlands where he qualified with an MSc in Molecular Sciences. Since then, he worked as process engineer and principal process design lead for different industries around the world in projects that involved treatment processes for gas, water and organic solids, from assessments, planning, concept design, detail design through to construction, commissioning and handover, including training/after services to operations staff.

He worked for the last 14 years at Jacobs Engineering (and CH2MHill), as a chartered professional engineer, and lived and worked in Europe, North America, Asia-Pacific and United Kingdom. Before that he held a position as technical director with an equipment manufacturer (Bioway International b.v.) where he was also responsible for Research & Development and led the development of new innovative products which included working with multiple research centres around the world. He has extensive experience in the design, the commissioning, and the performance testing of advanced air treatment facilities (biological, chemical, and physical). He has managed projects related to air quality, ventilation of occupied spaces, foul air treatment, biogas cleaning, micro-aerobic digestion, biosolids bio-drying, wastewater collection system asset management. He also taught air quality and air treatment courses to industry and academics (e.g., NASA, Purdue University, Aalborg University, University of Valladolid, Technical University Delft, Portland University) and had an affiliation from 2010 – 2014 as part time guest faculty member with the Technical University Delft (The Netherlands).

He is passionate about implementing (especially biological) solutions that provide sustainability based on shared values for environmental stewardship and diversity, now and for the generations that follow. Bart is married with Fiona Shadbolt and has four children Yasmin, Miles, Maya and Roy.

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