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BIOFILTRATION DU MÉTHANE ISSU DE SITES D'ENFOUISSEMENT SANITAIRE EN PRÉSENCE DE COMPOSÉS ORGANIQUES VOLATILS

Methane biofiltration from sanitary landfills in the presence of volatile organic compounds

Thèse de doctorat

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In memory of my supervisor Peter Jones

Résumé

Le réchauffement climatique est une préoccupation croissante en raison de l'augmentation des gaz à effet de serre (GES) dans l'atmosphère. Le méthane (CH_4) contribue à 11% des émissions mondiales de GES et les sites d'enfouissement sanitaires (SES) génèrent 17% des émissions anthropiques mondiales de CH_4. Les biotechnologies telles que la biofiltration offrent des solutions durables pour le traitement biologique du CH_4 (à des concentrations inférieures à 5% v/v), bien que la présence d'autres polluants tels que les composés organiques volatils (COVs) dans le gaz des sites d'enfouissement (GSE) doit être prise en compte. La biofiltration du CH_4 dans des mélanges complexes en présence de COVs nécessite des études supplémentaires pour renforcer les connaissances dans ce domaine. Cette étude se concentre sur la biofiltration simultanée du CH_4 en présence de deux composés aromatiques, le xylène (X) et l'éthylbenzène (EB) ; l'effet des changements de paramètres opérationnels tels que le temps de séjour en fût vide (EBRT) et la concentration de CH_4, de X et de l'EB sur les performances de la biofiltration a été étudiée. Tout d'abord, une revue de littérature a porté sur les émissions de GSE, les méthodes conventionnelles de réduction des GSE, l'adéquation des biotechnologies pour l'élimination des GES dans les anciens SES ou les SES de faible taille, ainsi que sur les défis et avantages de la biofiltration des GES. Ensuite, la biofiltration simultanée du CH_4 en présence de X ou de l'EB a été effectuée dans des biofiltres à lit inorganique sous un EBRT de 4.5 minutes pour des concentrations de CH_4 comprises entre 1000 et 10000 ppmv et des concentrations individuelles de COVs comprises entre 200 et 500 ppmv. L'étude a révélé que les faibles concentrations de CH_4 (2000-6000 ppmv) avaient un effet mineur sur la conversion (RE) des COVs, avec une RE moyenne supérieure à 85% pour les COVs (concentration de 200 ppmv). Cependant, pour des concentrations de CH_4 plus élevées, c'est-à-dire 10000 ppmv, une inhibition est apparue à la fois pour les COV et le CH_4, réduisant leurs REs respectives de 80%. Ensuite, un mélange ternaire composé de CH_4, de X et de l'EB a été traité dans un biofiltre à lit inorganique pour des concentrations de CH_4 comprises entre 1000 et 10000 ppmv et des concentrations de COVs variant de 200 à 600 ppmv. L'étude a montré que la RE du CH_4 était de 41% lorsque sa concentration était de 2000 ppmv et que les concentrations de X et EB étaient de 200 ppmv, sous un EBRT de 9 minutes. De même, les REs de X et EB étaient de 58% et 57% respectivement, pour des concentrations identiques mais avec un EBRT plus court de 4,5 minutes. La biodégradation des polluants était située dans différentes sections du biofiltre. La RE du CH_4 était la plus élevée dans la section supérieure, tandis que les REs de X et de l'EB étaient les plus élevées dans la section intermédiaire et n'étaient pas affectées par les concentrations de CH_4. Dans la troisième partie de l'étude, un réseau de neurones artificiels (RNA) a été utilisé pour prédire les performances du biofiltre. Les modèles de RNA ont prédit avec précision les REs dynamiques et pseudo-stationnaires du CH_4 et des COVs. Les résultats suggèrent la nécessité d'une grande base de données pour améliorer les performances des RNAs dans la simulation de la cinétique de la biofiltration complexe du CH_4. Dans l'ensemble, cette étude fournit des résultats prometteurs et des connaissances sur la biofiltration simultanée du CH_4 en présence de COVs et met en évidence l'importance des concentrations de polluants et de l'EBRT. L'utilisation des RNAs pour la prédiction des performances montre un potentiel pour des applications industrielles, ce qui permettrait d'économiser du temps et des coûts liés aux expérimentations.

Mots clés : Biofiltration simultanée, gaz de sites d'enfouissement, xylène, éthylbenzène, inhibition, réseaux de neurones artificiels

Abstract

Global warming is a growing concern due to the increase in greenhouse gases (GHG) in the atmosphere. Methane (CH_4) contributes to 11% of global GHG emissions and landfills generate 17% of global anthropogenic CH_4 emissions. Biotechnologies such as biofiltration offer sustainable solutions for the biotreatment of CH_4 (at concentrations lower than 5% v/v), although the presence of other pollutants such as volatile organic compounds (VOCs) in landfill gas (LFG) and low CH_4 mass transfer issues need to be considered. Biofiltration of CH_4 in complex mixtures with VOCs is yet to be fully understood, with further studies required to strengthen knowledge in this field. This study focuses on the simultaneous biofiltration of CH_4 with two aromatic compounds, xylene (X) and ethylbenzene (EB), by studying the effect of operational parameter changes such as empty bed residence time (EBRT) and concentration of CH_4, X and EB on biofiltration performances. First, a literature review discussing LFG emissions, conventional LFG abatement methods, the suitability of biotechnologies for LFG removal in old and small landfills, and the challenges and advantages of biofiltration for LFG were provided. Secondly, the simultaneous biofiltration of CH_4 in the presence of either X or EB was carried out in inorganic packed bed biofilters (BFs) at an EBRT of 4.5 min at CH_4 concentrations in the range of 1000-10000 ppmv and individual VOC concentrations between 200-500 ppmv. The study found that low concentrations of CH_4 (2000-6000 ppmv) had a minor effect on the removal efficiency (RE) of the VOCs, with average RE remaining above 85% for VOCs at 200 ppmv. However, at higher CH_4 concentrations i.e. 10000 ppmv, inhibition became apparent for both VOCs and CH_4, reducing both their REs by 80%. Thirdly, a ternary mixture consisting of CH_4, X and EB was treated in an inorganic based-bed BF for CH_4 concentrations in the range of 1000-10000 ppmv and VOC concentrations varying from 200 to 600 ppmv. The study found that CH_4-RE was 41% when its concentration was 2000 ppmv and the concentrations of X and EB were 200 ppmv, at an EBRT of 9 min. Similarly, X and EB-REs were 58% and 57% respectively, at the same concentrations but with a shorter EBRT of 4.5 min. The biodegradation of pollutants in the BF was found to be located at different sections. The highest CH_4-RE was in the top section while X and EB-REs were highest in the middle section and were not affected by CH_4 concentrations. In the third part of the study, an artificial neural network (ANNs) was used to predict the BF performance. The ANN models accurately predicted dynamic and pseudo-steady-state CH_4 and VOCs-REs. The findings suggest the need for a large database to enhance ANN performance in simulating complex CH_4 biofiltration kinetics. Overall, this study provides promising results and insights into the simultaneous biofiltration of CH_4 with VOCs, highlighting the significance of pollutant concentrations and EBRT. The use of ANNs for performance prediction shows potential for industrial applications, saving time and costs associated with experimentations.

Key words: Simultaneous biofiltration, landfills gas, xylene, ethylbenzene, inhibition, artificial neural network

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CHAPTER 1. Introduction

Global warming is a threat causing increasing concerns in worldwide community due to its important repercussions in our daily lifestyle. The primary cause of global warming is the increase in greenhouse gases (GHG) concentrations in the atmosphere which absorb the solar radiations thus resulting in the entrapment of heat (Ritchie et al., 2020). Several conventions like COP21 and COP26 were held aiming to reduce the global temperature increase to 2°C within the end of the current century by reducing the GHG emissions from several industrial sectors like oil and gas, agriculture, energy, transportation and landfills (UN, 2022). Among the different GHGs that can be emitted, methane (CH_4) has a global warming potential (GWP) 25 times higher than carbon dioxide (CO_2) (Forster, 2016). The annual worldwide CH_4 emissions are around 580 Mt with 60% being from anthropogenic sources (IEA, 2022). Anthropogenic CH_4 represents 11% of global GHG emissions and accounts for 25% of global temperature increase since the industrial revolution (IPCC, 2022). The atmospheric CH_4 concentrations have increased above 1900 ppbv by 2022 and keep increasing with an approximate rate of 10 ppbv per year (Dlugokencky et al., 2003; IEA, 2022; Nisbet et al., 2019; GML, 2022). The rapid increase in global temperatures has led several countries to agree on a CH_4 emission cut of 30% by the end of 2030 during the COP26 (Buchanan et al., 2022). In Canada, Landfills are the principal method of municipal solid waste treatment and account for around 17% of total anthropogenic CH_4 emissions (Gingerich, 2022). Methane is produced in landfills due to the anaerobic biodegradation of covered organic wastes by methanogenic bacteria. Several other pollutants such as volatile organic compounds (VOCs) and volatile inorganic compounds (VICs) are also produced which increases the harmful effect of landfill gas (LFG) (Themelis and Ulloa, 2007a).

Methane concentration in LFG can vary between 40 and 60% v/v (L. Fjelsted et al., 2020). It can be recovered for energy production after a pre-treatment aiming to remove contaminants such as hydrogen sulfide (H_2S) if CH_4 concentration is higher than 50% v/v or being eliminated using flaring, adsorption, thermal and catalytic oxidation (Ciuła et al., 2018). However, for small or old landfills, the concentration of CH_4 in LFG usually does not exceed 5% v/v, and since LFG flow rate is less than 50 m^3/h, the recovery is no longer profitable and CH_4 should therefore be eliminated (Nikiema et al., 2007a).

Biotechnologies offer a more suitable and sustainable solution (compared to conventional LFG treatment technics) for the treatment of gaseous emissions containing CH_4 at concentrations <5% v/v. Biotechnologies can achieve relatively high CH_4 removal efficiencies (REs) with low investment and operating cost while being relatively easy to operate with absence of hazardous by-product emissions (Delhoménie and Heitz, 2005). However, the performance of biotechnologies is easily influenced by several operating parameters like pollutant concentrations, gas flow rate, temperature, humidity, etc.

The most common bioprocess for air treatment is biofiltration which consists of passing the polluted gas through a bed packed with an organic or inorganic material on which the fixed microorganisms are responsible for transforming pollutants such as CH_4, VOCs and VICs to biomass, CO_2, water (H_2O), etc. (Helen La et al., 2018a).

The main concern with the biofiltration of LFG emissions is the feasibility of CH_4 co-biodegradation in presence of other pollutants like VOCs. The interaction effect between several components in the biofiltration of a mixture is likely to cause an inhibition that would reduce the RE of the mixture (Albanna et al., 2010).

The individual biofiltration of CH_4 and several other VOCs like xylene (X) and ethylbenzene (EB) has already been reported in literature (Álvarez-Hornos et al., 2008; Amin et al., 2014; Gallastegui et al., 2017a; Helen La et al., 2018a) but only a few authors investigated the biofiltration of CH_4 in complex mixtures with VOCs and VICs. The biofiltration of CH_4 in a binary or ternary mixture with aromatic compounds like X and EB is yet to be reported to the author's best knowledge. Previous studies on the biofiltration of CH_4 in presence of styrene (B. Khabiri et al., 2020) or toluene (Ménard et al., 2014) have shown that the VOCs inhibited CH_4 biodegradation and caused a decrease in CH_4 biodegradation. High concentrations of CH_4 also inhibited the biofiltration of VOCs and reduced their REs (Ménard et al., 2012a). The effect of changes in pollutant concentrations on the performance of the biofilter (BF) is an aspect that has not been fully understood in the biofiltration of mixtures and further studies are therefore required to strengthen our knowledge in that field.

The purpose of this research is to address the requirements of a BF designed to remove LFG. It aims to investigate various factors that affect the bioelimination of different pollutants found in LFG. However, achieving a high CH_4-RE (over 60%) is challenging due to the sensitivity of the bioprocesses to factors such as pollutant concentration and the characteristics of the packing-bed. The general objective of this study was to investigate the simultaneous biofiltration of CH_4 and VOCs (X and/or EB) in binary and ternary mixtures using BFs packed with inorganic packing materials. This study aimed to achieve a better understanding of the interaction effects between CH_4, X, and EB under different concentrations and the absence or presence of either CH_4 or X and EB.

The first objective was to study the biofiltration of a binary mixture of CH_4 with either X or EB under different concentrations for a period of 281 days in a BF packed with an inorganic bed. The second objective was to increase the complexity of the mixture by investigating the biofiltration of a ternary mixture of CH_4, X and EB and varying their concentrations and EBRT for a better comprehension of the interaction effects between the pollutant as well as the determination of the optimal EBRT for the highest removal efficiencies of all pollutants. The BFs were operated without initial inoculation in order to take advantage of indigenous microorganism strains present in the BF environment (tap water, air, etc.). The third objective was to use an empirical technic which is an artificial neural network (ANN) for the modeling of the simultaneous biofiltration of CH_4 X and EB (pseudo-steady state and dynamic).

This thesis is composed of 6 chapters including a literature review and 3 research papers.

Chapter 1 is the introduction where current situation regarding LFG biofiltration, problematic, originality of the study, hypothesis and general objectives are presented.

Chapter 2 presents a literature review of the biofiltration of CH_4 and VOCs in LFG. Several CH_4 abatement technics are presented as well as the major biotechnologies used for that purpose. The principal advantages and challenges that are present in the biofiltration of LFG are discussed.

Chapters 3 and 4 are dedicated to the biofiltration of CH_4, X and EB in binary and ternary mixtures, respectively. Chapter 3 describes steady state performances of the biofiltration of binary mixtures of either CH_4 and X or CH_4 and EB under different concentrations of CH_4 and the VOCs while a more complex mixture containing CH_4, X and EB under different concentrations and EBRTs was studied in Chapter 4. The interaction effect between the 3 pollutants were studied and investigated.

Chapter 5 presents the use of an ANN for the modeling of dynamic and stead-state CH_4 biofiltration as a single pollutant in addition to the steady-state simultaneous biofiltration of CH_4 in presence of other VOCs. The precision of predictive results by an ANN was assessed by comparing simulation results to experimental results performed during this study.

Chapter 6 presents the conclusion where the general findings of the research are presented and future perspectives are mentioned.

1.1. Introduction en français

Le réchauffement climatique est une menace croissante qui suscite de plus en plus d'inquiétudes dans la communauté mondiale en raison de ses répercussions importantes sur le mode de vie quotidien. La principale cause du réchauffement climatique est l'augmentation des concentrations de gaz à effet de serre (GES) dans l'atmosphère. Plusieurs conventions telles que la COP21 et la COP26 ont été organisées dans le but de limiter l'augmentation de la température mondiale à 2°C d'ici la fin du siècle en réduisant les émissions de GES provenant de plusieurs secteurs industriels tels que le pétrole et le gaz, l'agriculture, l'énergie, les transports et les décharges. Parmi les différents GES qui peuvent être émis, le méthane (CH_4) a un potentiel de réchauffement global (PRG) 25 fois supérieur à celui du dioxyde de carbone (CO_2). Les émissions mondiales annuelles de CH_4 sont d'environ 580 Mt, dont 60% sont d'origine anthropique. Le CH_4 d'origine anthropique représente 11% des émissions mondiales de GES et contribue à 25% de l'augmentation de la température mondiale depuis la révolution industrielle. Les concentrations atmosphériques de CH_4 ont dépassé 1900 ppbv en 2022 et continuent d'augmenter à un rythme d'environ 10 ppbv par an. L'augmentation rapide des températures mondiales a conduit plusieurs pays à s'engager à réduire les émissions de CH_4 de 30% d'ici la fin de 2030 lors de la COP26. Au Canada, les sites d’enfouissement sanitaire (SES) représentent environ 17% des émissions anthropiques totales de CH_4. Le CH_4 est produit dans les SES en raison de la biodégradation anaérobie des déchets organiques par des bactéries méthanogènes. Plusieurs autres polluants tels que les composés organiques volatils (COVs) et les composés inorganiques volatils (CIVs) sont également produits, ce qui augmente les effets nocifs du gaz des décharges.

La concentration de CH_4 dans le gaz des SES peut varier entre 40 et 60% v/v. Il peut être récupéré pour la production d'énergie après un prétraitement visant à éliminer les contaminants tels que le sulfure d'hydrogène (H_2S) si la concentration de CH_4 est supérieure à 50% v/v, ou être éliminé par torchage, adsorption, oxydation thermique et catalytique. Cependant, pour les anciens SES ou les SES de faible taille, la concentration de CH_4 dans le gaz des SES ne dépasse généralement pas 5% en volume ; étant donné que le débit volumique du gaz des SESs est inférieur à 50 $m^3.h^{-1}$, la récupération n'est plus rentable et le CH_4 doit donc être éliminé.

Les biotechnologies offrent une solution plus adaptée et durable (par rapport aux techniques de traitements classiques du gaz des décharges) pour le traitement des émissions gazeuses contenant du CH_4 à des concentrations inférieures à 5% en volume. Les biotechnologies peuvent permettre d’atteindre des REs de CH_4 relativement élevées avec des investissements et des coûts d'exploitation réduits, tout en étant relativement faciles à utiliser ; elles ne présentent aucune émission de sous-produits dangereux. Cependant, les performances des biotechnologies sont facilement influencées par plusieurs paramètres de fonctionnement tels que les concentrations de polluants, le débit de gaz, la température, l'humidité, etc.

Le procédé biologique le plus courant pour le traitement de l'air est la biofiltration, qui consiste à faire passer le gaz pollué à travers un lit constitué d'un matériau organique ou inorganique sur lequel des micro-organismes fixés sont responsables de la transformation des polluants tels que le CH_4, les COVs et les CIVs en biomasse, CO_2, eau (H_2O), etc. La principale préoccupation concernant la biofiltration des émissions de gaz des SES est la faisabilité de la co-biodégradation du CH_4 en présence d'autres polluants tels que les COVs. Les effets d'interaction entre plusieurs composants dans la biofiltration d'un mélange est susceptible de provoquer une inhibition qui réduirait l'efficacité de réduction du mélange.

La biofiltration individuelle du CH_4 et de plusieurs autres COVs tels que le xylène (X) et l'éthylbenzène (EB) a déjà été décrite dans la littérature, mais seuls quelques auteurs ont étudié la biofiltration du CH_4 dans des mélanges complexes en présence de COVs et de CIVs.

L'objectif de cette recherche est de répondre aux exigences d'un biofiltre (BF) conçu pour éliminer le gaz des SES. Elle vise à étudier les différents facteurs qui affectent l'élimination biologique des 3 polluants présents dans le gaz des décharges. Toutefois, atteindre une conversion élevée du CH_4 (supérieure à 60%) est un défi en raison de la sensibilité du bioprocédé à des facteurs tels que la concentration de polluants et les caractéristiques du garnissage du BF. L'objectif général de cette étude était d'étudier la biofiltration simultanée du CH_4 et de 2 COVs (X et/ou EB) dans des mélanges binaires et ternaires en utilisant des BFs garnis de matériaux inorganiques. Cette étude visait à mieux comprendre les effets d'interaction entre le CH_4, le X et l'EB sous différentes concentrations et en l'absence ou en présence de CH_4, de X et d'EB.

Le premier objectif était d'étudier la biofiltration d'un mélange binaire de CH_4 avec soit du X soit de l'EB pour différentes concentrations des composés pendant une période de 281 jours dans un biofiltre garni d'un lit inorganique. Le deuxième objectif était d'augmenter la complexité du mélange par l'ajout d'un polluant (mélange ternaire de CH_4, X et EB) et en faisant varier leurs concentrations et le temps de séjour en fût vide (EBRT) lors de la biofiltration avec un lit inorganique pour une meilleure compréhension des effets d'interaction entre les polluants ainsi que pour la détermination du EBRT optimal pour obtenir les conversions les plus élevées pour tous les polluants. Le troisième objectif était d'utiliser une technique empirique, un réseau neuronal artificiel (RNA), pour la modélisation de la biofiltration simultanée du CH_4, de X et de l'EB (état pseudo-stationnaire et dynamique).

Cette thèse est composée de 6 chapitres comprenant une revue de la littérature et 3 articles scientifiques.

Le chapitre 1 est l'introduction, où la situation actuelle concernant la biofiltration du gaz des SES, la problématique, l'originalité de l'étude, les hypothèses et les objectifs généraux sont présentés.

Le chapitre 2 présente une revue de la littérature sur la biofiltration du CH_4 et des COVs dans le gaz des SES. Plusieurs techniques de réduction du CH_4 sont présentées, ainsi que les principales biotechnologies utilisées à cette fin. Les principaux avantages et défis de la biofiltration du gaz des décharges sont discutés.

Les chapitres 3 et 4 sont consacrés à la biofiltration du CH_4, du X et de l'EB dans des mélanges binaires et ternaires, respectivement. Le chapitre 3 décrit les performances à l'état stationnaire de la biofiltration de mélanges binaires de CH_4 et de X ou de CH_4 et d'EB pour différentes concentrations de CH_4 et de COVs, tandis qu'un mélange plus complexe contenant du CH_4, du X et de l'EB pour différentes concentrations et temps de séjour du lit a été étudié dans le chapitre 4. L'effet d'interaction entre les 3 polluants a été étudié et investigué.

Le chapitre 5 présente l'utilisation d'un RNA pour la modélisation de la biofiltration dynamique et à l'état stationnaire du CH_4 en tant que polluant unique, ainsi que la biofiltration simultanée à l'état stationnaire du CH_4 en présence d'autres COVs (X et EB). La précision des résultats prédictifs par un ANN a été évaluée en comparant les résultats de simulation aux résultats expérimentaux obtenus au cours de cette étude.

Le chapitre 6 présente les conclusions, où les principales découvertes de la recherche sont présentées et les perspectives futures sont mentionnées.

CHAPTER 2. Exploring the potential of biofiltration for mitigating harmful gaseous emissions from small or old landfills: A review

Avant propos:

Ce document est une version préliminaire de l'article "Exploring the potential of biofiltration for mitigating harmful gaseous emissions from small or old landfills: A review" soumis au journal "Biodegradation" en août 2023.

TITRE: Investigation du potentiel de la biofiltration pour atténuer les émissions gazeuses nocives de petits ou anciens sites d'enfouissement sanitaire : Une revue de littérature

Title: Exploring the potential of biofiltration for mitigating harmful gaseous emissions from small or old landfills: A review

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Contribution of the document: This paper presents a comprehensive literature review exploring the feasibility, advantages, and challenges associated with LFG biofiltration. The primary focus of this study is on the biofiltration of CH_4 in the presence of VOCs such as X and EB, which are commonly found in landfills. Therefore, this review paper is relevant, as it discusses the simultaneous biofiltration of CH_4 in presence of other pollutants like VOCs and VICs. Moreover, the review paper addresses various operational conditions that can significantly impact the biofiltration of LFG.

2.1. Résumé

Les sites d'enfouissement sanitaire (SES) sont largement utilisés comme moyen principal d'élimination des déchets solides. Cependant, cette pratique génère aussi un gaz de sites d'enfouissement sanitaire (LFG) qui contient du méthane (CH_4), un puissant gaz à effet de serre (GES), ainsi que divers composés organiques volatils (COVs) et composés inorganiques volatils (CIVs). Ces émissions provenant des sites d'enfouissement sanitaire contribuent à environ 25 % du CH_4 atmosphérique total, soulignant le besoin impératif de valoriser ou de traiter le LFG avant son émission dans l'atmosphère. Cette revue vise d'abord à présenter les sites d'enfouissement sanitaire, l'élimination ou la valorisation du LFG, les techniques conventionnelles de traitement couramment utilisées pour le traitement du LFG, telles que les torches et l'oxydation thermique. De plus, elle explore les approches biotechnologiques en tant qu'alternatives techniquement et économiquement plus réalisables pour atténuer les émissions de LFG, en particulier dans le cas des sites d'enfouissement sanitaire de petite taille et anciens où les concentrations de CH_4 sont souvent inférieures à 3% v/v. Enfin, cette revue met en évidence les biofiltres comme la solution biotechnologique la plus appropriée pour le traitement du LFG et aborde plusieurs avantages et défis liés à leur mise en œuvre dans l'environnement des sites d'enfouissement sanitaire.

Mots-clés: Gaz de sites d'enfouissement sanitaire, Biofiltre, Biotechnologies, Méthane, Composés organiques volatils.

2.2. Abstract

Landfills are widely employed as the primary means of solid waste disposal. However, this practice generates landfill gas (LFG) which contains methane (CH_4), a potent greenhouse gas (GHG), as well as various volatile organic compounds (VOCs) and volatile inorganic compounds (VICs). These emissions from landfills contribute to approximately 25% of the total atmospheric CH_4, indicating the imperative need to valorize or treat LFG prior to its release into the atmosphere. This review first aims to outline landfills, waste disposal and valorization, conventional gas treatment techniques commonly employed for LFG treatment, such as flares and thermal oxidation. Furthermore, it explores biotechnological approaches as more technically and economically feasible alternatives for mitigating LFG emissions, especially in the case of small and aged landfills where CH_4 concentrations are often below 3% v/v. Finally, this review highlights biofilters as the most suitable biotechnological solution for LFG treatment and discusses several advantages and challenges associated with their implementation in the landfill environment.

Keywords: Landfill gas, Biofilter, Biotechnologies, Methane, Volatile organic compounds

2.3. Introduction

Municipal waste production currently stands at over 2.1 billion metric tons yearly worldwide. According to the United Nations (UN, 2022), The world's population is expected to exceed 9.8 billion people by 2050 with each person producing 0.7 kg of solid waste daily, resulting in a 40% increase in the total amount of waste generated (The World Bank, 2022). Seventy (70) % of the world's solid wastes are disposed in landfills, however, only 8% of the sanitary landfills are equipped with gas collection systems (The World Bank, 2022). Landfills are a widely used technic for waste disposal due to their simplicity, lower capital and operating costs compared to other methods such as incineration and composting (Purmessur and Surroop, 2019). For example, the operating costs of an incinerator and a landfill in North America are around 140 and 60 US$. metric ton^{-1}, respectively (Kaza et al., 2018).

With a global warming potential (GWP) roughly 21–25 times more than carbon dioxide (CO_2), methane (CH_4) is the second most impactful greenhouse gas (GHG) (Alvarez et al., 2018). In this regard, the Canadian government aimed to reduce CH_4 emissions by 30% compared to the emission levels of 2020 by 2030 (Environment Canada, 2020). Landfills are the third global CH_4 emitters after enteric fermentation and the oil and gas industries (Saunois et al., 2020). Landfills account for 25% of total CH_4 in the atmosphere, leading to an atmospheric CH_4 concentration higher than 1900 ppbv in 2022 (EEA, 2022). Methane and CO_2 released by Canadian landfills represent up to 24% of all the national GHG emissions (Environment Canada, 2022). Less than half of the collected landfill gas (LFG) in Canada is used as an energy source. However, limitations associated with the concentration of CH_4 dropping below 3-5% v/v prevent the widespread use of conventional valorization techniques, making them economically and practically unfeasible (usually after a few decades of landfill operation). The other half is either eliminated or released directly into the atmosphere (Environment Canada, 2022). For example, in Canada, almost 63% of the annual 1400 kt (metric) of CH_4 from landfills are emitted to the atmosphere while only 37% can be recovered.

After being disposed in landfills, the organic wastes undergo an anaerobic decomposition from which LFG and a liquid leachate are produced. Apart from GHGs, LFG also contains volatile organic compounds (VOCs) such as benzene (B), toluene (T), ethylbenzene (EB), xylene (X), styrene (ST) and volatile inorganic compounds (VICs) like hydrogen sulfide (H_2S) and ammonia (NH_3) with odorous and hazardous properties for human health and the environment (Harčárová et al., 2020; Duan et al., 2021b; Purmessur and Surroop, 2019; Wu and Ma, 2016).

With the increasing concerns about air pollution, several air treatment techniques like physicochemical and biological methods are used to reduce the harmful and odorous effects of LFG (Gospodarek et al., 2019). An appropriate solution is to valorize LFG into heat and electricity in large-scale landfills (Yechiel and Shevah, 2016). However, CH_4 concentration could reach values below 3% v/v and cannot be used for valorization. The conventional technics for the elimination of such LFG could be costly and would require additional energy which would increase the carbon footprint of the process. Biotechnologies for the treatment of effluents containing low concentrations of CH_4, VOCs and VICs are economically and technically feasible solutions (Rossi et al., 2020).

The conventional biofiltration of CH_4, VOCs and VICs as a typical biotechnique has been already reviewed by several authors like Delhoménie and Heitz, (2005), Malhautier et al., (2005), Mudliar et al., (2010) and La et al., (2018). But a review discussing the advances and key findings in recent works that could improve the elimination of CH_4 from LFG is still required. Some authors like Ménard et al., (2012) abd Nikiema et al., (2007) reviewed the biofiltration of CH_4 or VOCs from LFG, but with less emphasis on simultaneous biofiltration of the mixture of CH_4 and VOCs/VICs. An updated review about the use of biotechnologies for LFG biodegradation considering the particular advantages and drawbacks of landfills is yet to be discussed to the best knowledge of the authors.

The present review paper will first discuss LFG emissions and traditional LFG abatement and valorisation technics. Secondly, biotechnologies will be introduced as a more suitable option for the removal of LFG, particularly for old and small landfills, and lastly, the different advantages and challenges around the biofiltration of LFG will be discussed.

2.4. Landfill gas production

Sanitary landfills are sites where solid wastes are compacted and covered in an underground unit in order to prevent the by-products and effluents from polluting the environment in addition to creating the necessary anaerobic condition for waste biodegradation. After a landfill is filled to its maximum storage capacity, a layer of soil, gravel or a substitute material is deposited on the top as a cover. The cover prevents biogas and odours from leaking into the atmosphere and encourages the site's revegetation (Kaza et al., 2018). Sanitary landfills are the oldest and most commonly used municipal solid waste (MSW) treatment technique due to their affordability (Spigolon et al., 2018).

Landfills include effluent collection systems. Impermeable liners are placed at the bottom to avoid landfill effluents such as leachates from infiltrating and damaging soil and underground water sources (Teng et al., 2021). An LFG collection system composed of pipes and gas wells is used to trap the gaseous effluent before being further treated/eliminated. Figure 2.1 presents a typical LFG collection system. If not properly monitored, landfills can cause several health and environmental issues such as odour problems in the neighbouring areas, water pollution, vegetation damage due to soil contamination and GHG emissions like CO_2 and CH_4 (Tenodi et al., 2020). Gas and liquid effluents treatment processes in landfill generally continue for periods reaching up to several decades (up to 100 years) after the closure of the site in order to avoid releasing of pollutants to the environment (toxic gases and GHGs in LFG and heavy metals such as mercury (Hg) in the leachate) (Themelis and Ulloa, 2007b).

The process of LFG production involves a series of diverse biological reactions that mainly generates CH_4, CO_2 and multitude of trace gases. The major stages of LFG production are described as the following by (Khalil et al., 2014):

- Phase I: Hydrolysis

Solid organic matters are converted into soluble compounds in the first step of the degradation process by the action of enzymes released by hydrolytic bacteria (Shrestha et al., 2017). Aerobic bacteria use oxygen (O_2) and water (H_2O) to break down proteins, carbohydrates, and lipids in the waste, producing mainly glucose and CO_2. Phase I ends with the consumption of all O_2 present inside the landfill which can take from days to months depending on waste disposal conditions (Khalil et al., 2014).

- Phase II: Acidogenesis

The resulting glucose from Phase I is converted into lactic, acetic, and formic acids, hydrogen (H_2), alcohols as well as CO_2 under the anerobic conditions resulting from Phase I. The pH becomes acidic and drops below 5. Examples of reactions occurring during Phase II are the following:

$C_6H_{12}O_6 \Rightarrow$ butyric acid (C_3H_7COOH) + $2H_2$ +$2CO_2$

$C_6H_{12}O_6 \Rightarrow$ 2 ethanol (C_2H_5OH) + $2CO_2$

- Phase III: Acetogenesis

The organic acids such as C_3H_7COOH and other intermediates such as C_2H_5OH from the acidogenesis Phase (Phase II) are converted into acetic acid (CH_3COOH), H_2 and CO_2. Examples of acetic acid formation reactions are the following:

$C_3H_7COOH + 2H_2O \Rightarrow 2CH_3COOH + 2H_2$

$C_2H_5OH + H_2O \Rightarrow CH_3COOH + 2H_2$

- Phase IV: Methanogenesis

The products and intermediates of Phase III are anaerobically converted by methanogenic bacteria to CH_4 and CO_2 in addition to traces of carbon monoxide (CO), nitrogen oxide (NO), H_2S and aromatic VOCs like X and EB. The acidogenesis and acetogenesis Phases generally last for several months, thus the methanogenesis Phase is reached within less than a year (Khalil et al., 2014). The main reactions occurring during the methanogenesis Phase are the following:

$CH_3COOH \Rightarrow CH_4 + CO_2$

$CO_2 + 4H_2 \Rightarrow CH_4 + 2H_2O$

An LFG containing CH_4 concentrations from 40 to 60% v/v is produced for up to 20 years. Methane generation can last up to 50 years after the closure of a landfill (Popov, 2005). Yechiel and Shevah (2016) estimated that 1.5 billion tons of MSW would generate around 75 billion m^3 of CH_4 in landfills. The amount and concentration of CH_4 in LFG is highly dependant on the type of organic wastes, moisture content along with the decomposition environment and the climate conditions (Vu et al., 2017). The most important operating parameters affecting CH_4 generation is the composition of the disposed waste. The CH_4 generation potential of food wastes is in the range of 300-500 m^3 of CH_4 per metric ton of food waste while the generation potential for other wastes like yard and wood wastes is less than 200 m^3 of CH_4 per metric ton of yard/wood waste (Krause et al., 2016). However, the actual CH_4 generation could be lower than the estimated value due to changes in the conditions inside the landfill (temperature, humidity, etc.). For instance, 1 metric ton of wastes composed of 60% w/w organic matter and 40% w/w moisture content generates around 50-140 m^3 of CH_4 compared to a theoretical estimation of 200 m^3 (Themelis and Ulloa, 2007b).

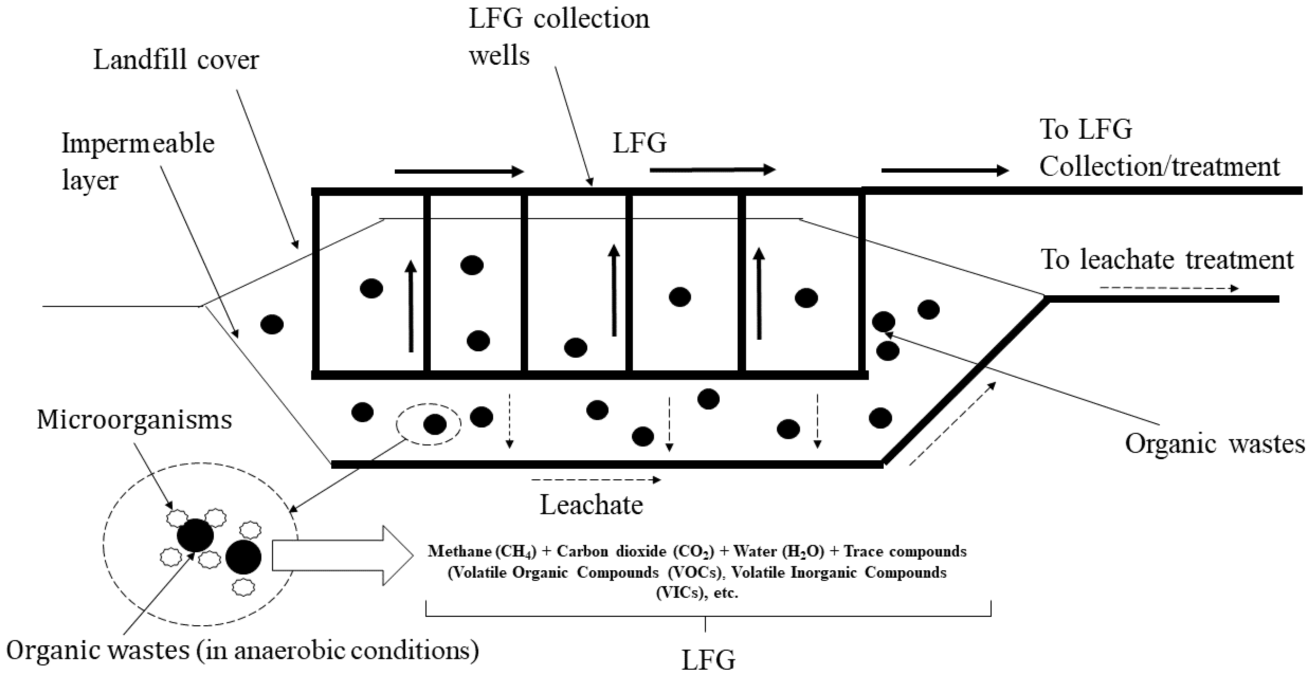

Figure 2.1: Landfill gas (LFG) and leachate collection system

Methanogenic bacterial activity (Phase IV) is highly sensitive to temperature changes. Temperatures around 35-40 °C (at an atmospheric pressure) are usually adequate for LFG production (Purmessur and Surroop, 2019). Cold temperatures limit bacterial activity, which often drops significantly at temperatures below 10 °C. The concentration of O_2 is also critical in LFG production as it determines the type of reaction taking place inside the landfill (CH_4 generation in Phase IV requires anaerobic conditions) (Purmessur and Surroop, 2019). The humidity is particularly important for LFG generation as it provides a transport media for microorganisms (MOs) to access the organic wastes and to proceed to the biodegradation. Humidity is also necessary for Phase I and Phase III of LFG production. Humidity can also act as cooling factor inside the landfill which can hinder MOs from producing CH_4 as MOs are sensitive to temperature decrease (Chakma and Mathur, 2017).

The concentration of CH_4 in LFG changes over time and once the methanogenesis stage is completed due to the depletion of the organic matter or the penetration of O_2 inside the landfill, it decreases from 50 to less than 3% v/v (Manasaki et al., 2021). However, LFG with low CH_4 concentration (below 3% v/v) could still be emitted for several decades lasting up to 100 years (Manasaki et al., 2021; Mønster et al., 2019).

The major chemical groups present in LFG are usually aromatics, sulfur compounds, traces of nitrogen (N) like NH_3, oxygen compounds like alcohols (e.g., ethanol) (Duan et al., 2021b). Sulfur compounds like H_2S and dimethyl sulfide (DMS) are generated from wastes containing sulphates. These compounds are responsible for odour problems related to LFG (Chen et al., 2017). Hydrogen sulfide is emitted principally at the methanogenesis stage as a result of decomposition of sulfurous compounds such as proteins (Jürgensen et al., 2018) and is the dominant sulfur compound constituting 90% v/v of sulfurous pollutants in LFG (Moreno et al., 2014).

Aromatic presence in LFG is usually a result of direct aromatic volatilization of pollutants like B, T, EB and X (BTEX) from wastes like cosmetics, paper, plastics, solvents and petroleum products (Mustafa et al., 2017). These BTEX are the VOCs with the highest concentrations in LFG reaching up to a total concentration of 1000 ppmv in some cases (Duan et al., 2021a). Oxygen compounds like methanol, ethanol, acetone, etc. are usually side products from the reactions in the hydrolysis stages of waste decomposition in addition to products from acidogenesis and acetogenesis Phases. Alcohols such as ethanol could reach concentrations up to 60 ppmv (Duan et al., 2021b). The concentrations of the major problematic components reported in LFG studies conducted in different countries are presented in Table 2.1. Table 2.1 shows that H_2S and aromatic VOCs such as BTEX mixtures are commonly found in LFGs from different landfills at different places in the world.

Table 2.1: Trace compounds concentrations in LFG for different landfills worldwide

Concentration of compounds (mg.m^{-3})	(Duan et al., 2014) (1994-2014) China	(Zhang et al., 2012) China	(González et al., 2013) (1993-2008) Spain	(Tassi et al., 2009) (1976-2009) Italy	(Takuwa et al., 2009) (1970-2007) Japan	(Araiza-Aguilar and Rojas-Valencia, 2019) (2009-2019) Mexico	Duan et al., (2021) (1967-2005) Denmark
Benzene	3.10^{-3} – 62.10^{-3}	67.10^{-3} – 612.10^{-3}	8.10^{-3} – 15.10^{-3}	55-80	0-61	0 – 38.10^{-3}	5–161
Toluene	5.10^{-3} – 166.10^{-3}		58.10^{-3} – 80.10^{-3}	462-652	0-27	$2.15.10^{-3}$ – 770.10^{-3}	13–161
Ethylbenzene	4.10^{-3} – 134.10^{-3}		$1.7.10^{-3}$ – 4.10^{-3}	57-247	0-33		7–73
o, p, m-xylene	166.10^{-3} – 375.10^{-3}		5.10^{-3} – 14.10^{-3}	678-854	0-22	$6.6.10^{-3}$ – 237.10^{-3}	30–270
H_2S	0 – 867.10^{-3}		<800.10^{-3}		17-170	7.10^{-4} – $1.94.10^{-3}$	50–276
DMS	0 – 102.10^{-3}						
Total volatile compounds		1.08 – 5.26					

The rate of LFG generation could be estimated and modeled through empirical zero, first and second order models, although second order models appeared to be the most reliable (Amini et al., 2012). The problem with LFG estimation models is that they consider the MSW as a homogenous medium with similar properties (temperature, humidity, etc.) at all points of the landfill which is usually far from the real conditions (Majdinasab et al., 2017). Prediction of LFG generation remains an important challenge for the waste management industry as it allows the assessment of gaseous emissions from landfills, the impact of LFG on the environment and the correct strategies to be performed to mitigate the gaseous effluent (Chakma and Mathur, 2017).

2.5. Landfill gas valorization

Landfill gas can be used as a cheap fuel for power generation in furnaces and heaters or as pipeline quality natural gas after specific treatment (Omar and Rohani, 2015) as it is proceeded in Quebec (Canada) (Programme Biogaz, 2022). The use of CH_4 in LFG as an energy source can be a solution to problems related to GHG emissions and explosion hazards. Furthermore, since MSWs are continuously produced, LFG can be considered as a renewable and sustainable source of energy (Coskuner et al., 2020). Nevertheless, the high heating value of LFG is half (an average value of 540 kJ. m^{-3}) compared to natural gas (Zhou et al., 2014). Improving the heating value of LFG could be achieved by increasing CH_4 concentration while removing CO_2 and other impurities using the process of pressure swing adsorption (PSA). Gong et al., (2019) reported that VOCs (T, X, EB and cyclohexane) caused adsorbent (zeolite) failure during the PSA of LFG due to their irreversible adsorption. Energy recovery from LFG can be also proceeded by energy storage through conversion to methanol or biodiesel (Winslow et al., 2019).

The choice of the appropriate valorization technic depends on the quality and amount of LFG. Internal combustion engines are the most used techniques for energy production due to economic reasons. Gas turbines can be used for LFG valorization since they can provide a power output of over 3 MW when CH_4 concentration is around 50% v/v at a flowrate over 1800 $m^3.h^{-1}$ (EPA, 2011). However, internal combustion engines present a major drawback considering the environmental aspect as the NO_x and CO emissions generated from the combustion engine can reach up to 60 µg (NO_x or CO).kJ^{-1} (Fiore et al., 2020). The presence of large amount of CO_2 in LFG is another technical drawback for its use as energy source since it decreases the efficiency and stability of combustion process (Jung et al., 2021). Prior to valorization, LFG treatment can be limited to solid particles and liquid droplets removal or can be extended to adsorption in case of high H_2S concentrations (higher than 7 $mg.m^{-3}$) (Latosov et al., 2017). Other contaminants such as VOCs will also need to be removed before valorization as they would cause the emissions of toxic by-products such as formaldehyde (CH_2O) (Dobslaw et al., 2019).

Landfill gas valorization is only possible during the initial 10-20 years of a landfill's operation. This is because the majority of the high-concentration CH_4 in LFG is produced during the early stages of a landfill's lifespan. However, as time progresses, the concentration of CH_4 decreases to levels below 3-5% v/v. This leads to a significant reduction in the quality of LFG, making its valorization unprofitable. Despite the decrease in CH_4 concentration, landfills can still generate low-concentration LFG for several decades, even after the landfill is closed. To effectively control and mitigate LFG emissions throughout the entire lifespan of a landfill, an LFG control/mitigation strategy must be established relying on efficient and low-cost processes to significantly reduce the carbon footprint (Andriani and Atmaja, 2019).

2.6. Physico-chemical LFG elimination technologies

The conventional LFG elimination technics use high temperatures (>800 ˚C) or catalysts to mitigate the unwanted pollutants such as CH_4, VOCs and VICs through generating less troublesome compounds like CO_2 (a lower GHG effect than CH_4) and H_2O.

When compared to phase transfer technologies, LFG elimination techniques like thermal oxidation and flaring typically provide effluents that do not need additional treatment. Landfill gas mitigation processes can also include bioprocesses like biofilter (BF), biotrickling filter (BTF), and bioscrubber (BS), which will be covered in more details in section 5.

2.6.1 Flaring

Flaring is a combustion process that aims to control gaseous emissions by piping them into an elevated location and burning them using a burner. An auxiliary fuel and air to improve mixing are used to achieve up to 98% removal efficiency (RE) of total pollutants. However, it has been reported that field flare sites in Canada have efficiencies as low as 66−84% (Caulton et al., 2014). Flares are designed to be high enough so that undesirable by-products are carried by air far from the unit (Rahimpour et al., 2012).

The combustion of the effluent will result in converting pollutants such as VOCs and CH_4 to CO_2 and H_2O in addition to other harmful compounds such as CO, CH_2O, NO_X, sulfur oxides (SO_X) (if the gaseous emissions contain S), dioxins, furans, polycyclic aromatic hydrocarbons, etc. (Davoli et al., 2010).

When LFG contains CH_4 at concentrations below approximately 35-40% v/v, flaring can be considered as a solution for LFG elimination. However, when CH_4 content drops to 20% v/v, maintaining combustion becomes challenging and an additional fuel is required which increases the operating costs, GHG and other pollutants emissions. Consequently, it is not recommended to use flaring when CH_4 concentration in LFG is below 20% v/v (Lombardi et al., 2016). As a measure for persuading industries to move from flaring to more eco-friendly and green vent gas elimination technics, the provincial governments in Canada have imposed taxes on flares. For example, in Alberta, flaring costs 0.05 $\$.kg^{-1}$ $CO_{2\ eq}$ in 2022 and will increase up to 0.16 $\$.kg^{-1}$ $CO_{2\ eq}$ by 2030 (Galli et al., 2021).

2.6.2. Thermal oxidation

Thermal oxidation systems consist of the combustion of LFG at high temperatures (800-1000˚C). The process can achieve CH_4 and VOC REs up to 99% at residence times between 0.5 to 1 s (pressure can vary from 1 atm to up to 10 atm) (Gao and Gou, 2019; Hashemi et al., 2016), with the capacity of treating feeds from 500-50000 $m^3.h^{-1}$ and pollutant concentration range from 100 to 2000 ppmv for a unit lifetime around 15 years (EPA, 2011).

The process has two types of energy recovery systems: regenerative and recuperative. For both types, heat is recovered from exhaust stream to preheat the inlet gas before entering the combustion zone. Multiple beds permit regenerative systems to achieve up to 95% recovery of the thermal-energy to produce steam or electricity (Kvist and Aryal, 2019). Recuperative thermal-oxidation systems can recover up to 70% of the energy produced by LFG combustion using a shell-tube heat exchanger system. The process has the drawback of secondary emissions like NO_x and SO_x (if N and S compounds are present in the LFG) which means that the effluents would require further treatments like absorption.

The process can be used to effectively eliminate all pollutants present in LFG, but the high operating cost of 120 $US\$.m^{-3}$ (2019) linked to the high temperature of the process makes the process less competitive compared to other existing techniques like flaring and biotechnologies (Tomatis et al., 2019).

2.6.3. Catalytic oxidation

Similarly, to thermal oxidation, catalytic oxidation is a process where pollutants such as CH_4, VOCs and VICs are oxidized to CO_2 and H_2O. Metal oxides and noble metals such as platinum (Pt) and palladium (Pd) are the main catalysts used for the oxidation of CH_4, VOCs and VICs. Noble metal catalysts have been proven to possess a higher activity than metal oxide catalysts. Conversions up to 99% of hexane, B and T over Pt/Al_2O_3 monoliths were obtained at temperatures near 300˚C (Guo et al., 2021). The use of a catalyst allows the process to eliminate LFG just as efficiently as thermal oxidation for a considerably lower temperature (300 - 450˚C

at atmospheric pressure with a residence time of a few seconds (Gélin and Primet, 2002)), substantially reducing the energy demands (Jafarinejad, 2017).
The costs for the catalyst have to be considered as it can be deactivated by coking, thermal degradation or poisoning depending on the treated pollutants and catalyst replacement or regeneration is usually required (Kamal et al., 2016).

2.7. Biotechnologies

Biological treatment offers numerous benefits in comparison to physico-chemical treatment techniques. This biotechnology operates under ambient temperature and pressure conditions, without generating troublesome compounds such as NOx and SOx (Fulazzaky et al., 2014). The main biological treatment processes include biofiltration, biotrickling filtration, and bioscrubbing. Recently, hybrid techniques consisting of a combination of biotechnologies (or biotechnologies with other technics like absorption or ultraviolet (UV) treatment) have been developed (Malakar et al., 2017a). Biological methods to treat air have been used for over 60 years in several industries such as food processing plants, sewage treatment plants and landfills. The common point between the different biotechnologies is the use of MOs to break down pollutants. As polluted air is passed through the medium, the MOs consume the pollutants and convert them into harmless byproducts (Sonil et al., 2012). The biodegradation principles for the three bioprocesses is relatively similar; however, there are differences in the design, liquid phase and possible applications (Oyarzun et al., 2019). The most important bioreactors used for the elimination of CH_4, VOCs and VICs are described in the following section.

2.7.1. Biotrickling filter

Biotrickling filter (BTF) is distinguished from other bioreactors by a continuous irrigation with a liquid phase (Mudliar et al., 2010). According to Barbusinski et al., (2017), the biofilm surrounding the packing absorbs the pollutants, which are subsequently adsorbed into the packing media and biodegraded by MOs living in the biofilm. The liquid phase of the system provides various benefits, such as enabling precise control over operational parameters like pH and distributing the nutrients evenly throughout the packing bed (Rybarczyk et al., 2019a). Figure 2.2 presents the flow diagram of a BTF.

Hydrophobic components such as CH_4 and the majority of aromatic VOCs face strong mass transfer limitations in BTFs due to the continuously recirculated liquid phase that forms an additional barrier to pass from gas to liquid phase (Zhang et al., 2019). The mass transfer limitations could be overcome with the addition of a surfactant or the use of two-phase partitioning bioreactors (TPPBs) (Rybarczyk et al., 2019a). In a recent study by Yousefinejad et al., (2019), the addition of silicone oil (5% v/v of the aqueous liquid phase) allowed a superior performance (62% RE without silicone oil compared to 78% in presence of silicone oil) for T biodegradation at a T concentration of 24.7 g.m^{-3} and an empty bed residence time (EBRT) of 1 min.

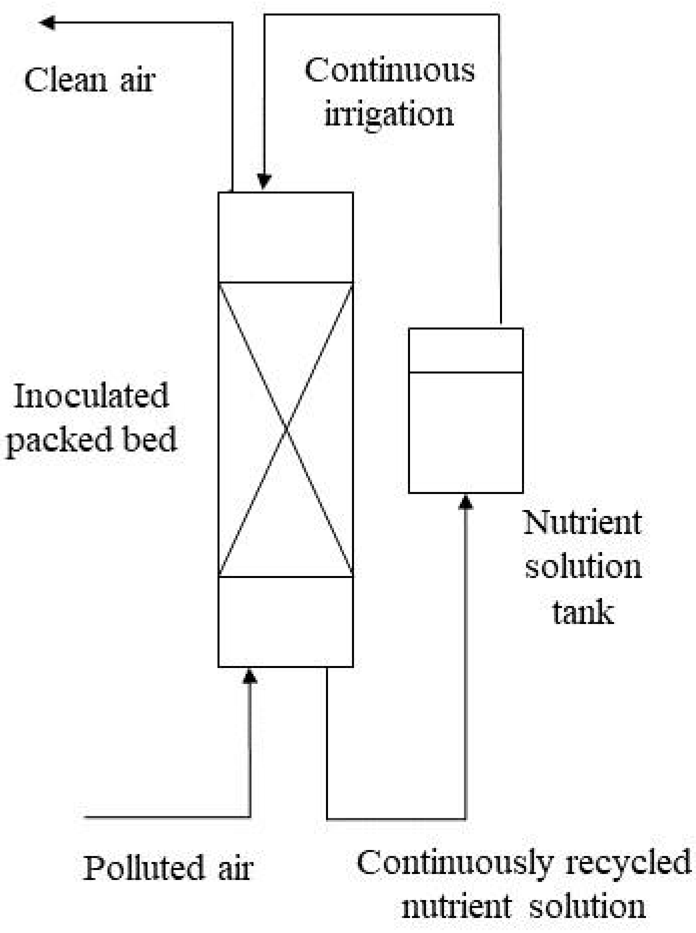

Figure 2.2: A schematic of a biotrickling filter process

Biotrickling filters are particularly effective in eliminating sulfur compounds such as H_2S, DMS and hydrophilic compounds such as alcohols emitted from landfills (Morotti et al., 2011). An experiment where 2 BTFs (a vertical counter-current BTF and a horizontal cross-current BTF) were used to treat a wastewater treatment plant (WTP) effluent containing H_2S (concentration of 10 mg.m^{-3}), NH_3 (concentration of 15 mg.m^{-3}) and VOCs (B, T, X and ST with concentrations of 31, 3, 2, 28 mg.m^{-3}, respectively) at an EBRT of 59s. The BTF study conducted under counter-current conditions exhibited certain benefits, including rapid start-up (7 days for the counter-current BTF compared to 10 days for the cross-current BTF) and greater resilience against shock loading. An average RE higher than 90% was obtained with the counter-current BTF compared to approximately 50% for the cross-current BTF. The study found that counter-current flow condition was the most effective for promoting optimal bacterial performance (Yang et al., 2017). Liao et al., (2018) investigated the elimination of a quaternary mixture of VOCs (B, T, X and ST) in a BTF at a total inlet load (IL) in the range of 40-141 g.m^{-3}.h^{-1} and at an EBRT of 30s. A total VOCs-RE of 63% was obtained. The authors observed that the biodegradation of B was the most inhibited by the mixture followed by X, ST and T.

Biotrickling filters were also used to target single components present in LFG. However, CH_4 is a particularly difficult component to be eliminated with BTFs due to the poor solubility of CH_4 in water (25 g.m^{-3} at 25 ˚C and 1 atm (Staudinger and Roberts, 1996)) given that BTFs mainly rely on the transfer of pollutants from gas phase to the liquid phase. Lebrero et al., (2016) investigated the addition of silicone oil at a 25% v/v ratio to the liquid phase and obtained a CH_4-RE of 40% at an EBRT of 4 min and ILs in the range of 410-440 g.m^{-3}.h^{-1}.

Although several studies on the use of BTFs for single pollutants can be found in the literature (Cáceres et al., 2017; Qian et al., 2018; Wang et al., 2015), the biodegradation of mixtures of LFG components remains insufficient to fully understand the behavior of BTFs during the treatment of LFG. Furthermore, since studies have shown that removal of CH_4 (a principal component of LFG) is difficult to achieve in BTFs, the use of BTF is not recommended for LFG treatment unless a solution to overcome the mass transfer limitations of CH_4 is applied.

2.7.2. Bioscrubber

Bioscrubbers were used for the first time back in the 1970's in German foundries to treat amines, phenol, CH_2O and alcohols present in gaseous effluents (Barbusinski et al., 2017a). According to Figure 2.3, BS is an association of a continuously stirred bioreactor and a scrubber column. The pollutants are absorbed into the scrubbing liquid (usually water) as the inlet gas passes through the absorption unit. The scrubbed (clean) gas is then released into the atmosphere while the liquid containing the pollutants is fed to a bioreactor where suspended MOs biodegrade the pollutants into H_2O, CO_2, biomass and acids depending on the pollutants in the inlet gas (Liu et al., 2019). The continuously stirred bioreactor contains a suspended consortium of MOs strains and the appropriate nutrients for their growth. Most BSs are usually inoculated with a nearby WTP's activated sludge (Barbusinski et al., 2017a).

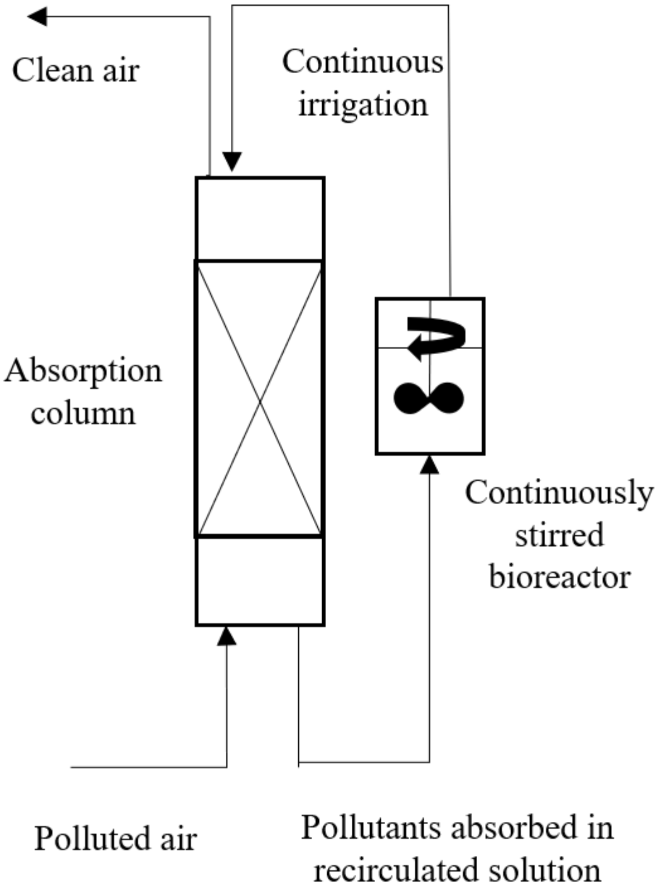

Figure 2.3: A schematic of a bioscrubber process

Due to the process relaying primarily on pollutant absorption to liquid phase before transferring the pollutant to the continuously stirred bioreactor, the process is unsuitable for LFG biodegradation due to the poor solubility of CH_4 and several VOCs like the majority of aromatics. Tilahun et al., (2018) studied the purification of a simulated biogas (H_2S (1% v/v),

CO_2 (39% v/v) and CH_4 (60% v/v)), which was close to LFG composition over the first years of a landfill. The authors obtained over 98% H_2S-RE at an EBRT of 20 min; however, the BS could not eliminate CH_4. Liu et al., (2017) used a BS to treat a gaseous effluent containing CH_4 at a CH_4-IL of 75 $g.m^{-3}.h^{-1}$ corresponding to a concentration of 260 ppmv. The authors reported that no CH_4 elimination could be observed. The inability of BS to biodegrade CH_4 was linked to its low solubility in water in addition to the low EBRTs (1-18 s) used in the experiment.

Bioscrubbers can therefore be a good solution to purify LFG from H_2S, NH_3 along with other hydrophilic compounds when CH_4 concentrations are high enough for valorization (>50% v/v). In this case, BS can eliminate the pollutants without decreasing CH_4 concentration (Quijano et al., 2021).

2.7.3. Biocover

A biocover can be described as an open air bioreactor that is spread across a whole landfill surface (Cossu and Stegmann, 2018). Biocovers consist of 2 layers that LFG passively penetrates. First, a porous layer of gravel ensures a homogeneous distribution of gas, and secondly, a layer consisting of a biologically active bed like compost or peat allows MOs such as methanotrophs to develop and consume CH_4 and other landfill pollutants (Cossu and Stegmann, 2018). Figure 2.4 presents the diagram of a typical biocover system.

Several studies obtained high CH_4-REs using pilot scale biocovers. For instance, Scheutz et al., (2017) used a pilot scale biocover at Av Miljo landfill in Danemark. The biocover had an area of 500 m^2. A layer of gravel (0.3-0.5 m) was used to ensure a homogeneous gas distribution while an upper biological layer of compost (0.8-0.9 m) enabled the bioelimination of CH_4. Methane concentrations in LFG were in the range of 3 – 12 % v/v and CH_4-REs varied between 81 and 100 %. Pecorini et al., (2020) used an alternative form of biocovers called “biowindows”. Biowindows consist of biocovers in specific areas of a landfill (usually spots of high CH_4 emissions), thus reducing the biocover material costs (Duan et al., 2022). A series of 7 full scale biowindows (with an area of 4 m^2 each) was used to treat an LFG from a landfill (capacity of 631000 m^3) containing CH_4 at an average concentration of 33 % v/v in addition to traces of VOCs (BTEX, methanol, ethanol, etc.,) and VICs (like H_2S.). In each biowindow, a layer of 0.4 m of gravel was deployed to improve the gas distribution while a layer of 1.2 m of compost ensured the biodegradation of pollutants. Pollutants REs of 88, 80 and 93% were obtained for CH_4, VOCs and VICs, respectively (Pecorini et al., 2020). Several issues such as the large area that needs to be covered, maintenance expenses and operating conditions control remain obstacles for the use of biocovers (Pecorini et al., 2020).

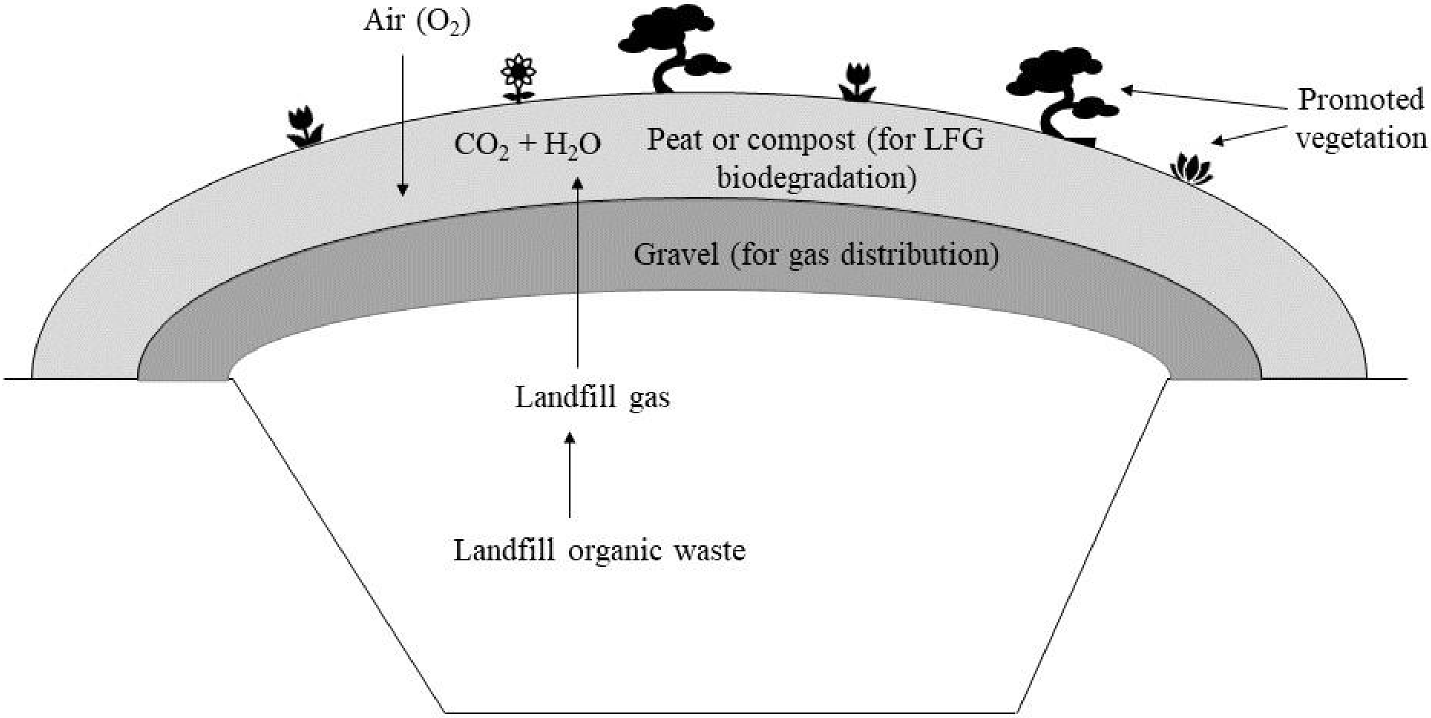

Figure 2.4:A schematic of a landfill biocover (based on Duan et al., (2022))

Biocover performances are affected by several factors such as the limited O_2 supply to the deep parts of the biological cover, formation of preferential flows which leads to high loads of CH_4 at some parts of the biocover and the inability to control certain operating parameters due to climate conditions (Duan et al., 2022).

2.7.4. Biofilter

The first researcher who developed the concept of biofiltration was Bach, a German scientist in 1923. Since then, BFs have become a common air treatment technic in several sectors like WTP, food industry, pulp and paper industry and landfills (Sheoran et al., 2022).

A BF is a 3-phase bioreactor where the packing media acts as a fixed bed for the biocatalyst which are the MOs. The liquid phase consists of a biofilm that surrounds the packing media particles (Cheng et al., 2016). Figure 2.5 presents a schematic of a typical BF. The polluted gaseous effluents require humidification (via a humidification column) before being injected to the BF. Sprinklers can also be added at the top of the BF spraying the appropriate amount of water (Rybarczyk et al., 2018). Humidity is an important parameter for high biofiltration performances and is a key factor for the formation of the biofilm (Danila et al., 2022). The inlet gas may be diluted with air to reduce risks of reaching explosive concentrations of pollutants like CH_4 and to ovoid inhibition by high CH_4 concentrations (Fjelsted et al., 2020).

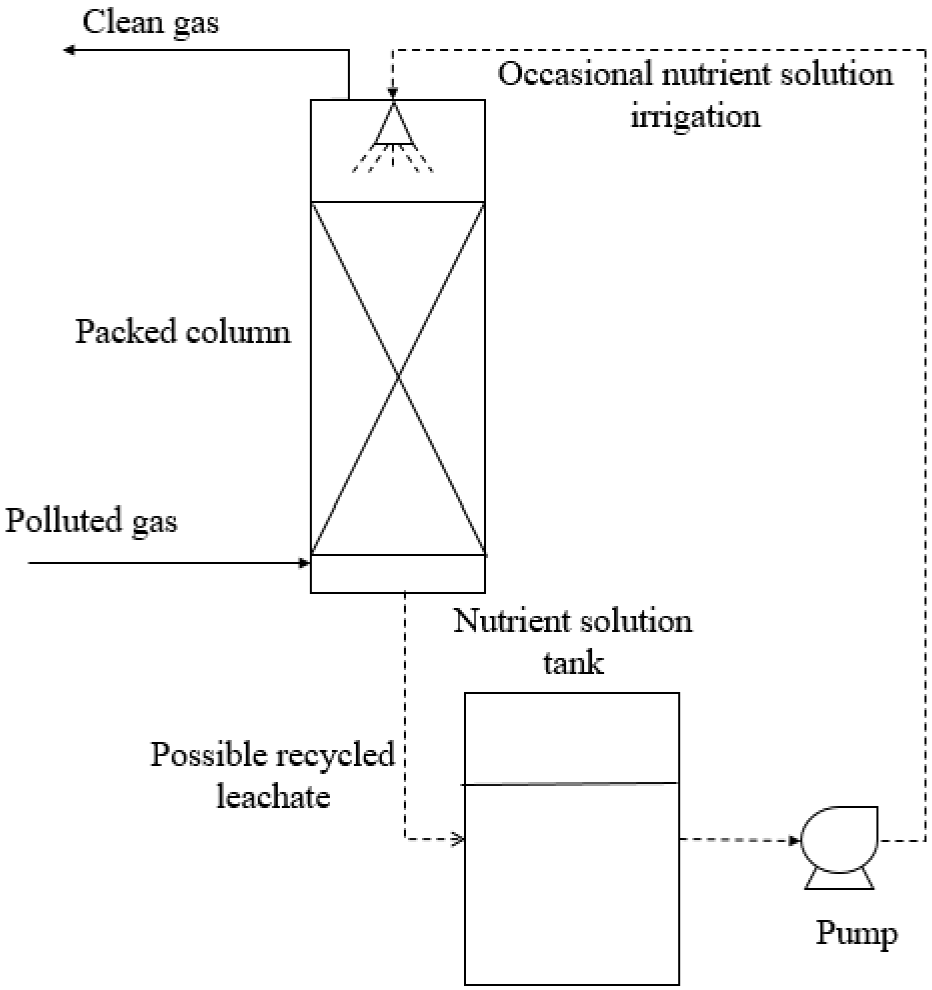

Figure 2.5:A schematic of a biofilter process

When the humidified polluted gas passes through the packing media (in an upflow or downflow direction), pollutants are absorbed to the liquid phase. Mass transfer limitation is a key factor to be considered in the biofiltration as several pollutants in LFG such as CH_4 are hydrophobic.

Several parameters like EBRT, pollutant concentration and packing media characteristics need to be adjusted to ensure the transfer of pollutants to the biofilm (Cheng et al., 2016).

In the biofilm, MOs consume the absorbed pollutants as an energy source for growth and proliferation. The pollutants are converted into CO_2, H_2O, biomass and inorganic acids like hydrochloric acid (HCl) and sulfuric acid (H_2SO_4) if the gaseous effluent contains chlorinated compounds or S compounds (Gospodarek et al., 2019; Rybarczyk et al., 2019a). In this step, the performances of BFs are limited by the biological kinetics (Iranpour et al., 2005). Increasing pollutant concentration in the biofilm beyond MOs threshold would not improve the biodegradation and my even inhibit the MOs performances (Ferdowsi et al., 2017a).

Biofilters are more suitable than BTFs and BSs for the treatment of LFG due to higher BF performances for CH_4 elimination. Furthermore, BFs can eliminate a wider range of pollutants that are present in LFG than BTFs and BSs. The absence of a continuously trickled liquid phase in BFs also results in lower energy consumption, maintenance costs and liquid wastes compared to BTFs and BSs in addition to easier operation (Malakar et al., 2017b). Furthermore, BFs allow a better control of operating conditions such as inlet gas concentration and flowrate compared to biocovers (Duan et al., 2022). Table 2.2 summarizes a comparison between different gas treatment technologies for LFG treatment.

Table 2.2: Comparison between different LFG eliminating technologies in terms of suitability.

Technology	Flaring	Thermal oxidation	Catalytic oxidation	Biotrickling filter	Biofitler	Bioscrubber
Capital cost	+	+	-	+++	+++	+++
Operating cost	-	-	+	++	+++	++
By-Products	-	-	-	+++	+++	+++
Footprint	++	++	++	+++	+	+++
CH_4 elimination	++	+++	+++	-	+++	-
VOC elimination	++	+++	+++	+++	+++	+++

+++: highly recommended

++: recommended

+: average

-: not recommended

2.8. Advantages and inconveniences of LFG biofiltration

Biofiltration implementation for the removal of LFG in landfills can face several environmental limitations, which could impede the effectiveness of biofiltration and result in a decline in the REs of LFG pollutants. Nevertheless, landfills may also offer opportunities and resources that can be utilized to enhance the biofiltration process and reduce operational costs. The next sections outline the advantages and disadvantages that can be anticipated in the biofiltration of LFG.

2.8.1. Advantages in the biofiltration of LFG

2.8.1.1. Landfill soil as a filter bed

The filter bed is an important part of the BF. The pores of the filter bed act as a support to the biofilm which surrounds the packing particles where MOs develop, grow and consume the pollutants present in the biofilm. Choosing the right packing media is necessary to achieve satisfactory long-term biodegradation performance (Kumar et al., 2019) and an important parameter when determining the capital cost of the process (Alinezhad et al., 2019). The soil recovered from landfills is rich in organic matter (up to 24% w/w), inorganic matter (N, S, phosphorus (P) and potassium (K), etc.), with porosity in the range of 0.5 to 0.73 (Schirmer et al., 2022; Song and Lee, 2010). These characteristics indicate that landfill soil can offer several advantages when used as packing media for BFs. Another advantage when using landfill soil as packing media is the presence of indigenous MO communities. The microbial populations present in the landfill soil is already adapted to the specific conditions in landfills, such as pH, temperature, and moisture content, and can be more effective at degrading pollutants in the LFG than non-indigenous MOs (Aicha et al., 2013). Methanotrophs are the principal MOs group responsible for CH_4 biodegradation and have been reported to be widely present in landfill soil (Khider et al., 2021). The enzyme used by methanotrophs for CH_4 oxidation (CH_4 monooxygenase) can metabolize CH_4 and a vast variety of VOCs like aromatics, alkanes, alkenes and esters (Hanson and Hanson, 1996). Scheutz and Kjeldsen, (2003) used landfill soil in a BF as support media to treat CH_4 at an IL of 11 $g.m^{-3}.h^{-1}$ and an EBRT of 45 min. The authors obtained a CH_4-RE of 88% without the need of providing external nutrients to the BF. Similarly, Pratt et al., (2012) used a mixture of landfill soil and perlite (volumetric ratio of 1:1) to treat CH_4 at a CH_4-IL in the range of 16-36 $g.m^{-3}.h^{-1}$ and at an EBRT of 120 min. High CH_4-REs around 100% could be obtained without any nutrient solution supply.

One disadvantage of using organic based beds such as landfill soil materials is their lower structural stability compared to inorganic materials. This makes them more vulnerable to compaction, which can lead to channeling (Huete et al., 2018). Another issue with using organic packed beds such as landfill soil is the degradation of the filter materials over time leading to increased pressure drop, clogging and channeling within the BF (Das et al., 2019). The packing bed must, therefore, be replaced frequently to ensure stable BF performances (Cheng et al., 2019).

2.8.1.2. The potential use of landfill leachate as an inoculum and nutrient solution

Recirculation of landfill leachate is a technique that has been developed to respond to the problem of low moisture content in landfills. The technique involves pumping the leachate collected from the bottom of the landfill and recirculating it over the solid organic wastes to maintain the proper moisture level. Recirculation of landfill leachate has several other benefits such as providing nutrients and the appropriate MOs for the anaerobic waste biodegradation (Teng et al., 2021). It can be hypothesized that methanotrophs also benefit from the advantages that landfill leachate offers while still being able to resist its potential toxicity.

Landfill leachate can be used in the same way to provide the necessary moisture content in a BF treating LFG. Moisture content in the filter bed is another key parameter for the performances of a BF as it is determinant for the formation of the biofilm. An adequate moisture content in a BF is reported to be between 40 and 60% of the inlet air volume, although the optimal moisture level varies according to the packing media (Dhamodharan et al., 2019). A low moisture level (below 40% v/v) will lead to dryness of the biofilm, decrease of microbial activity and slow the absorption of pollutants, meanwhile a high moisture content (above 60% v/v) will increase clogging, pressure drop, the formation of anaerobic zones, compaction of the packing bed and will reduce the transfer rate of important components such as O_2, nutrients and the pollutants (Malakar et al., 2017). Frasi et al., (2020) tested the effect of moisture content on CH_4 biofiltration in a compost based-bed BF. A moisture content of 20% v/v was found insufficient for the development of MO communities while an optimal moisture content of 30% v/v allowed to obtain CH_4-REs above 80% at IL in the range of 4-12 $g.m^{-3}.h^{-1}$.

The landfill leachate also contains high concentrations of nutrients such as ammonium (NH_4^+) (6-3000 g.m^{-3}), nitrates (NO_3^-) (10-500 g.m^{-3}), phosphates (PO_4^{3-}) (1000-3000 g.m^{-3}) and sulphates (SO_4^{2-}) (10-1700 g.m^{-3}) which are essential for the growth, reproduction and biodegradation activities of methanotrophs (Wijekoon et al., 2022). Nitrogen is the most important element for MOs after carbon and O_2. It can be supplied using either NH_4^+ or NO_3^- (La et al., 2018). Gómez-Cuervo et al., (2017) studied the effect of choosing NH_4^+ or NO_3^- as N source for CH_4 biofiltration. The authors supplied a BF with NH_4^+ (0.52 g.L^{-1}) and another BF with NO_3^- (0.25 g.L^{-1}). The BFs were packed with a mixture of wood pine bark chips, perlite and compost. The EBRT was 4.4 min and the CH_4 concentrations were the range of 0.17-0.20 % v/v. Higher CH_4-REs (44%) were obtained in the BF supplied with NH_4^+ compared to the BF irrigated with NO_3^- (CH_4-RE of 30%). However, the authors recommended the use of NO_3^- as N source for long-term operations (higher than 200 days) as they observed acidification (pH drops from 6.8 to 3) in the BF supplied with NH_4^+. Other nutrients like P and S are also important for CH_4 degrading MOs but their consumption has not been studied thoroughly compared to N. For instance, Khabiri et al., (2020) reported SO_4^{2+} and PO_4^{3+} consumptions of 77% and 99%, respectively in inorganic packed BFs treating CH_4 concentrations in the range of 1000-10000 ppmv and for an EBRT of 6 min over a period of 283 days. Similarly, Merouani et al., (2023) also reported a high SO_4^{2+} consumption (83%) in an inorganic packed BF treating a mixture of CH_4, X and EB at respective concentrations of 2000-1000, 200 and 200 ppmv at an EBRT of 4.5 min over a period of 242 days. However, PO_4^{3+} consumption was lower than 11%. Therefore, landfill leachate being rich with essential elements like NH_4^+, SO_4^{2-} and PO_4^{3-} suggests that it can be used as a nutrient solution to provide the essential elements to support MO growth and enhance LFG biodegradation.

Another advantage of using landfill leachate is the presence of abundant indigenous MO communities that can serve as inoculum to the BF. In fact, landfill leachate is an ideal source of MOs for BFs as it contains diverse microbial communities that have already adapted to the conditions of landfills. The MOs in landfill leachate are able to survive in a wide range of pH levels, temperatures, and O_2 concentrations, making them well-suited to use in BFs. Furthermore, both type I and type II methanotrophs can be found in landfill leachate (Watzinger et al., 2005). Landfill leachates share similar characteristics with activated sludge from WTPs or other biological treatment process as it contains a diverse community of MOs that are adapted to efficiently remove organic pollutants. The use of activated sludge from WTPs as inoculum for CH_4 biofiltration has been commonly reported in the literature. For example, some authors used activated sludge from WTPs (Fjelsted et al., 2020; Khabiri et al., 2021; Thomasen et al., 2019) or leachates from BFs treating CH_4 to provide an adequate inoculum for BFs treating mixtures of CH_4 with other VOCs such as ST, X and EB (Khabiri et al., 2020; Merouani et al., 2022). Therefore, landfill leachate can be used in a similar way as inoculum for BFs treating LFG.

It should be noted that the effectiveness of using landfill leachate as a growth medium for methanotrophs may depend on various factors, including the composition and concentration of the leachate. One of the main issues with using landfill leachate in an LFG treating BF is the high presence of toxic contaminants that may inhibit or negatively impact the microbial activity in the BF such as lead (Pb) (0.01-0.05 $g.m^{-3}$), mercury (Hg) (0.0003-0.00057 $g.m^{-3}$) and arsenic (As) (0.002-0.05 $g.m^{-3}$) (Xiaoli et al., 2007). In summary, using landfill leachate as an inoculum and as a nutrient solution for biofiltration can be cost-effective and support the growth of indigenous MOs in the BF. However, the variability of contaminants present in leachate may impact the efficiency and consistency of the biofiltration process.

2.8.2. Expected challenges in the biofiltration of LFG

2.8.2.1. Presence of non-CH_4 volatile compounds in LFG

An important challenge confronting the biofiltration of CH_4 in LFG is the presence of other pollutants such as VOCs and VICs (Albanna et al., 2010). Interaction effects resulting from the simultaneous biofiltration of several pollutants increase the complexity of biodegradation mechanisms occurring during the process (Cheng et al., 2016). Moreover, the presence of several types of pollutants in the biofilm also results in changes in the MOs diversity and different species will compete for the nutrients and carbon source (Yang et al., 2018). Gebert et al., (2008) studied the MOs communities for the biodegradation of CH_4 as a single pollutant and in a complex mixture in presence of several VOCs like X, T, B, acetylene, n-hexane, etc. in a BF for LFG removal. The authors found a diverse and more abundant microbial composition dominated by type II methanotrophs in the BF supplied with CH_4 and VOCs compared to the BF where CH_4 was treated as a single pollutant (Gebert et al., 2008). A similar observation was obtained by Lee et al., (2010) in batch tests (serum bottles containing MOs cultures from landfill soil at 30 °C with 180 rpm shaking rate) for the biodegradation of CH_4 in presence of B and T. The presence of VOCs resulted in the dominance of type II methanotrophs like *Methylocystis* and *Methylosinus* while type I methanotrophs (*Methylobacter, Methylomonas* and *Methylomicrobium)* dominated in the biodegradation of CH_4 alone. A possible explanation could be the resistance of type II methanotrophs to VOC inhibition compared to type I. It is worth mentioning that type II is generally more dominant than type I methanotrophs in landfill soil (Khadem et al., 2012). Table 2.2 summarizes the recent studies of CH_4 biofiltration in mixtures with pollutants present in LFG. The table presents data on the BF performances of various pollutant combinations, such as CH_4 with B, T, EB, X, chlorobenzene, etc. under different operating conditions.

Table 2.3: Previous works on the simultaneous biofiltration of CH_4 in mixtures with LFG

Polluant	Packing	Empty bed residence time (EBRT) (min)	Concentration (ppmv)	Removal efficiency (%)	reference
CH_4+toluene	Inert inorganic materials	4.2	CH_4: 2000-9000 toluene: 0-1008	CH_4: 2-48 toluene: 68-100	(Ménard et al., 2012a)
CH_4+chlorobenzene			CH_4: 2000-9000 chlorobenzene: 17-104	CH_4: 2-48 chlorobenzene: 17-100	
CH_4+dimethylsulfide (DMS)	Pumice and activated carbon	18	CH_4: 35500 DMS: 162	CH_4: 82.8 DMS: 100	(Kim et al., 2013)
CH_4+benzene+toluene			CH_4: 30600 benzene: 98 toluene: 90	CH_4: 73.4 benzene: 100 toluene: 100	
CH_4+DMS+benzene+toluene			CH_4: 22500 DMS: 166 benzene: 69 toluene: 88	CH_4: 64 DMS: 100 benzene: 100 toluene: 100	
CH_4+pentane (C_5H_{12})	Vermiculite	13	CH_4: 20000 Pentane: 71000	CH_4: 40% Pentane: N/A	(Vergara-Fernandez et al., 2020a)
CH_4+BTEX	Compost/expanded clay	1680	CH_4: 510000 (50% v/v) BTEX: 45	CH_4: 90 BTEX >99	(Zdeb and Lebiocka, 2016)
CH_4+ethanol	Inert inorganic materials	6	CH_4: 1981 ethanol: 0-2812	CH_4: 31-55 ethanol: 100	(Ferdowsi et al., 2017b)
CH_4+DMS	Perlite/tobermolite	-	CH_4: 7600 DMS: 1700	CH_4: 70 DMS: 60	(Choi et al., 2018)
CH_4+ethanol	Inert inorganic materials	1	CH_4: 0 ethanol: 265	CH_4: 0 ethanol: 100	(Ferdowsi et al., 2019)

		1.3	CH_4: 248 ethanol: 259	CH_4: 0 ethanol: 100	
		1.6	CH_4: 610 ethanol: 212	CH_4: 0 ethanol: 100	
		2.6	CH_4: 1486 ethanol: 172	CH_4: 17 ethanol: 100	
		6	CH_4: 4573 ethanol: 0	CH_4: 28 ethanol: 0	
CH_4+methanol	Inert inorganic materials	1	CH_4: 0 methanol: 382	CH_4: 0 methanol: 100	
		1.3	CH_4: 248 methanol: 372	CH_4: 0 methanol: 100	
		1.6	CH_4: 610 methanol: 305	CH_4: 0 methanol: 100	
		2.6	CH_4: 1486 methanol: 248	CH_4: 15 methanol: 100	
		6	CH_4: 4573 methanol: 0	CH_4: 50 methanol: 0	
CH_4+styrene	Inert inorganic materials	6	CH_4: 1000-9000 styrene: 200-700	CH_4: 43-80 styrene: 62-100	(Khabiri et al., 2020)
CH_4+ethylbenzene	Inert inorganic materials	4.5	CH_4: 2000-10000 ethylbenzene: 200-500	CH_4: 54-64 ethylbenzene: 75-90	(Merouani et al., 2022)
CH_4+xylene			CH_4: 2000-10000 xylene: 200-500	CH_4: 52-59 xylene: 74-90	
CH_4+ethylbenzene+xylene	Inert inorganic materials	4.5	CH_4: 2000-10000 ethylbenzene: 200-500 xylene: 200-600	CH_4: 20-57 ethylbenzene 10-60 xylene: 10-60	(Merouani et al., 2023)
CH_4+NH_3	Compost/perlite	17	CH_4: 5000 NH_3: 500-1000	CH_4: 32-43 NH_3:100	(Valenzuela-Heredia and Aroca, 2023)
CH_4+ H_2S			CH_4: 5000 H_2S: 150-300	CH_4: 42-54 H_2S:100	
CH_4+NH_3+H_2S			CH_4: 5000 NH_3:500 H_2S:300	CH_4: 36-43 NH_3:100 H_2S:100	

The type of interactions that is predicted to occur during the simultaneous biofiltration of CH_4 with other LFG constituents (VOCs and VICs) is generally antagonistic i.e. the pollutants inhibit the biodegradation of CH_4 (Yang et al., 2018). The inhibition occurs due to a competition between CH_4 and pollutants for the active site with the enzyme MMO thus deactivating the CH_4 biodegradation mechanism (Albanna et al., 2010). This phenomenon is called uncompetitive inhibition and is often caused by compounds that are more soluble in the biofilm than CH_4. Other types of inhibition that can occur during the simultaneous biofiltration of CH_4 with VOCs are competitive inhibition (the MOs interact with the VOCs instead of CH_4) and non-competitive inhibition (where VOCs interact with both MOs and the CH_4-MO complex) (Albanna et al., 2010). The enrichment and dominance of a specific population, favored by specific operating conditions, is mainly due to its competitive advantages in terms of growth and substrate affinity (Cabrol and Malhautier, 2011). Several authors observed uncompetitive inhibition in the biodegradation of CH_4 in presence of ST (Khabiri et al., 2020) or trichloroethane (TCM), trichloroethylene (TCE) and dichloromethane (DCM) (Albanna et al., 2010). The presence of toxic by-products resulting from the biodegradation of other pollutants than CH_4 can also hinder CH_4 biodegradation. Biodegradation of aromatic compounds like B, T, X and EB causes the production of phenols and catechol which have an inhibitory effect on CH_4 biodegradation (Lee et al., 2010, 2011).

The type of effect a specific pollutant (such as X or EB) can have on CH_4 changes depending on the concentrations of both compounds. For instance, Merouani et al., (2022) observed in binary mixture of CH_4 and EB that decreasing EB concentrations from 500 to 200 ppmv (corresponding to 0.05 to 0.02 % v/v, respectively) at a CH_4 concentration of 2000 ppmv increased CH_4-RE from 58 to 64%. However, at an EB concentration of 500 ppmv for CH_4 concentrations of 6000 and 10000 ppmv, CH_4-REs were higher (59 and 57%, respectively) than CH_4-REs at an EB concentration of 200 ppmv (51 and 49%, respectively). The authors established a link between a higher CH_4 biodegradation performance and the abundance of EB, which was a stimulating factor for the growth of CH_4-degrading MOs (Merouani et al., 2022). On the other hand, in a ternary mixture of CH_4, EB and X, increasing the individual concentrations of EB and X from 200 to 600 ppmv (corresponding to 0.02 to 0.06 % v/v, respectively) at CH_4 concentrations of 2000 (0.2% v/v), 6000 (0.6% v/v) and 10000 (1% v/v) ppmv increased CH_4-REs from 34 to 39%, from 18 to 24% and from 13 to 23%, respectively. The hypothesis suggested by the authors is that increasing the concentrations of EB and X could have possibly stimulated the development of methanotrophs or other MOs capable of biodegrading CH_4 (Merouani et al., 2023).

2.8.2.2. Variability in LFG composition and flowrate and starvation periods

The composition and flowrate of LFG vary depending on several factors such as the age of the landfill, the type of waste deposited and the environmental conditions. These variables can impact the efficiency of biofiltration as the MOs may not be able to effectively and immediately adapt to the new pollutant concentrations and flowrates. However, short-term CH_4 starvation periods have the potential to boost the resistance of MOs to pollutant concentration change/absence in the long-term operation (more than 200 days) (López et al., 2018). Specifically, a CH_4 deprivation period of 2-3 days was found to facilitate the performance recovery of type I methanotrophs (Ma et al., 2013; López et al., 2018). Moreover, it is noteworthy that a BF regained the initial CH_4-RE (20% for an IL of 100 $g.m^{-3}.h^{-1}$, EBRT of 17 min) within approximately 1.5 hours of CH_4 re-injection (López et al., 2018). This finding suggests that carefully designed and implemented starvation regimes can effectively enhance the robustness of BFs for maintaining the CH_4 biodegradation performance.

Biofilters are suitable for treating CH_4 concentrations below 3% v/v which is convenient for LFG issued from low and old landfills, although some authors successfully treated CH_4 at higher concentrations (Farrokhzadeh et al., 2017; Vergara-Fernandez et al., 2020b). For instance, Fjelsted et al., (2020) obtained a CH_4-RE of 58% at concentrations of 4.4-9.2% v/v in a compost BF for EBRTs in the range of 24-186 min. High CH_4 concentrations (above 1% v/v or 10000 ppmv) usually causes substrate inhibition for MOs responsible for CH_4 biodegradation (Ferdowsi et al., 2016). In order to keep CH_4 concentrations in the suitable range, diluting pollutant concentrations can be achieved by mixing air with CH_4. However, this method increases the required volume of the BF to maintain the necessary EBRT for satisfactory performances, leading to higher capital costs.

Empty bed residence time is a key parameter to ensure the transfer of pollutants to the biofilm as it permits to provide a sufficient contact time between pollutants and the liquid phase (Ferdowsi et al., 2017a). This parameter is proportional to the flowrate and is subject to changes as the flowrate of LFG fluctuates over time. For example, Amaraibi et al., (2022) reported that LFG flowrate in a landfill can vary from 1000 to 6000 $m^3.h^{-1}$ over a period of 6 months while Gebert and Groengroeft, (2006) reported LFG flowrates in the range of 0.7-2 $m^3.h^{-1}$ over a period of 3 months. A precise determination of LFG flowrate is important for the design of a BF for LFG treatment. Methane biofiltration usually requires an EBRT in the range of 4-30 min in order to obtain CH_4-REs higher than 50%, although some authors used EBRTs as high as 1680 min (Berger et al., 2005). The biofiltration of VOCs is usually carried out at EBRTs lower than 3 min and VOC-REs are usually in the range of 70-90% (Malakar et al., 2017). This is due to a higher solubility of VOCs in water in the range of 200-400 $g.m^{-3}$ compared to 24 $g.m^{-3}$ for CH_4 at 25°C and atmospheric pressure (Mackay et al., 2006). Authors who used low EBRTs for CH_4 biofiltration usually obtain low CH_4-REs (Limbri et al., 2014). For instance, Ganendra et al., (2015) obtained a CH_4-RE of 29% at an EBRT of 0.8 min and a CH_4-IL of 39 $g.m^{-3}.h^{-1}$ in a concrete based-bed BF. On the other hand, authors who used a sufficiently long EBRT obtained complete CH_4 biodegradation such as Zdeb and Lebiocka (2016) who treated a mixture of CH_4 (CH_4-IL of 12 $g.m^{-3}.h^{-1}$) and BTEX (BTEX-IL of 0.005 $g.m^{-3}.h^{-1}$) using a compost/expanded clay BF. All pollutants were eliminated with REs above 90% due to a long EBRT (1680 min). In a recent study on the effect of EBRT in a ternary mixture of CH_4 and 2 VOCs (X and EB), Merouani et al., (2023) obtained CH_4-REs of 41% at an EBRT of 9 min compared to 35% at an EBRT of 4.5 min for a CH_4 concentration of 2000 ppmv. However, X (200 ppmv) and EB (200 ppmv)-REs were 30% higher at an EBRT of 4.5 min compared to an EBRT of 9 min.

The study of a suitable EBRT for the biofiltration of a mixture of pollutants such as LFG is necessary as a sufficient time has to be provided for the transfer of poorly soluble pollutants without saturating the biofilm with the hydrophilic compounds.

2.8.2.3. Seasonal variability

Another challenge associated with biofiltration of LFG is the effect of climate conditions on BF performance. The activity and growth of MOs can be substantially influenced by environmental factors such as temperature and rain level in open bed BFs as well as closed bed BFs lacking adequate insulation. For a given region, high fluctuations in temperature can be observed, with winter temperatures dropping to less than 0 °C, while summer temperatures can exceed 40 °C. The manifestation of such extreme temperature variations is attributed to several factors including the region's geographic location and weather patterns (Jain et al., 2021). The optimal temperature range in a BF is 25-40 °C, although optimal range strongly depends on the pollutants to be treated and MOs (Han et al., 2016). Methanotrophic bacteria are usually mesophilic with an optimum biodegradation rate in a temperature range of 25-30 °C, although a few species of thermotolerant methanotrophs can grow at temperatures up to 50 °C (Fjelsted et al., 2020; Houghton et al., 2019). On the other hand, some methanotrophic bacteria could survive in northern taiga, landfill tundra soil and polar lakes at temperatures between 5–7 °C (Hanson and Hanson, 1996). Furthermore, solubility of gases tends to drop with higher temperatures which reduces the availability of pollutants and O_2 to the MOs which holds particular significance for hydrophobic pollutants, including CH_4 and the majority of VOCs (Malakar et al., 2017).

The influence of temperature on BF performances in an open bed compost BF treating LFG has been carried out by Fjelsted et al., (2020). During the first month, the temperature of the filter bed was approximately similar to the one of ambient air. Then, temperature increased up to 50-60 °C and remained constant even when ambient air temperature decreased during the fall period. When ambient air temperature was below zero, the filter bed temperature remained between 46-49 °C. The temperature distribution across the bed was dependent on its depth, decreasing as the distance from the surface increased and approaching the gas inlet. The elevated temperatures could be caused by exothermic phenomena like CH_4 oxidation and compost respiration in addition to the absorption of solar radiations by packing media. Temperatures tend to increase from the bottom to the top (in an up-flow BF). Temperature differences between sections of a BF (closed-bed BF) can be up to 5°C (Fjelsted et al., 2020).

The impact of rainfall on biofiltration can be a challenge if the BF lacks proper insulation from water. Rainfall can affect biofiltration primarily through increasing moisture content, which can potentially reduce the mass transfer of hydrophobic pollutants (e.g., CH_4 and aromatic VOCs) to the liquid phase. Intense precipitation can also decrease BF temperature and cause flooding of the packed bed leading to channeling (Dever et al., 2011). To ensure optimal elimination of LFG under varying climatic conditions, it is necessary to thermally insulate the BF and protect it from water intrusion, ideally by enclosing it in a sealed space. Table 2.4 represents a summary of advantages and inconvenient for the use of biofilters in the treatment of LFG.

Table 2.4: Advantages and inconvenient for the use of biofilters in the treatment of LFG

Advantages	Inconvenient
- Landfill soil as a filter bed - Potential use of landfill leachate as an inoculum and nutrient solution	- Presence of non-CH_4 volatile compounds in LFG - Variability in LFG composition and flowrate and starvation periods - Seasonal variability

2.9. Conclusion and perspectives

The necessity of reducing anthropogenic CH_4 emissions from industrial gaseous effluents is increasingly urgent as global warming is affecting worldwide climate. Several CH_4 emitting sectors like landfills will be obliged to reduce their emissions by up to 30% by 2030. In order to achieve such reductions, landfills need to choose from different CH_4 elimination/valorization technics like thermal/catalytic oxidation, flares, absorption, adsorption, etc to treat or valorize their LFG effluent. However, traditional LFG treatment processes are not suited for LFG where CH_4 emissions are at low concentrations (below 3% v/v) like old and small landfills as it would require additional investment and operating costs. Biofiltration is a more adequate solution as it is a less expensive and easier to handle process that was proven reliable for CH_4 biodegradation compared to traditional LFG mitigation technics.

Numerous studies on the optimal parameters for CH_4 biofiltration were carried out during the last 2 decades. The bioprocess appears to provide satisfactory results when MOs are provided with the appropriate conditions such as a nutrient source (mainly N), packing media, moisture content in the BF, etc. The inhibition that occurs after increasing CH_4 concentrations (usually above 1% v/v or 10000 ppmv) and in presence of VOCs is a phenomenon that requires further understanding especially at the microbial scale.

Landfills possess certain components that can be used to enhance LFG biofiltration. Landfill soil is rich in nutrients for MOs whereas landfill leachate can be utilized as an inoculum, a nutrient solution, and a mean to maintain adequate moisture content within the BF. However, LFG biofiltration also presents several challenges. The influence of weather conditions (temperature fluctuations above 40 °C or below 0 °C) on BF operation and the ongoing fluctuations of LFG concentrations and flow rate are among the examples. Furthermore, CH_4 in landfill emissions is frequently accompanied by the presence of volatile compounds like VOCs and VICs. It is imperative to investigate the interactions that occur during the biofiltration of CH_4 in mixtures, for example, with VOCs like the B, T, EB and X. Although some studies on the simultaneous biofiltration of CH_4 with other landfill pollutants have been published recently, they remain insufficient for a complete comprehension of the mechanisms that take place during that situation.

For future research, another issue that often affect LFG biofiltration is the excess production of biomass. The accumulation of biomass in BFs can have several negative effects on the performances of the biofiltration such as clogging, inhibition of MOs and reduction of the mass transfer of pollutant to the biofilm. A microbial study within BFs treating LFG at different pollutant concentrations is also necessary for a full understanding of LFG biodegradation.

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CHAPTER 3. Biofiltration of methane in presence of ethylbenzene or xylene

Avant propos:

Ce document est une version préliminaire de l'article "Biofiltration of methane in presence of ethylbenzene or xylene" soumis dans le journal "Atmospheric Pollution Research" en juillet 2022; l'article a été accepté en janvier 2022.

TITRE: Biofiltration du méthane en présence de l'éthylbenzène ou du xylène

Title: Biofiltration of methane in presence of ethylbenzene or xylene

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Contribution of the document: This paper is relevant to the first objective of this thesis. The steady-state performances of biofilters of CH_4 in the presence of either ethylbenzene or xylene were evaluated. The paper discusses the effect of VOC presence as well as the effect of pollutant (CH_4 or VOCs) concentration changes on the removal of CH_4 and VOCs.

3.1. Résumé

Les gaz des sites d'enfouissement (LFG) sont des émissions gazeuses contenant plusieurs composés nocifs tels que les composés organiques volatils (COVs) et les composés inorganiques volatils (CIV) ainsi que le méthane (CH_4), un puissant gaz à effet de serre. Dans le cas de petits ou anciens sites d'enfouissement, l'élimination du LFG peut être économiquement difficile par les procédés conventionnels tels que les torchères, et une solution possible est la biofiltration. La biofiltration du CH_4 en présence de 2 COVs a été étudiée, l'éthylbenzène (EB) pour biofiltre 1 (BF1) et le xylène (X) pour biofiltre 2 (BF2). Les 2 biofiltres étaient remplis de lits filtrants inorganiques, un temps de résidence en fut vide (EBRT) de 4.5 min a été utilisé. Les concentrations de CH_4 variaient de 2000 à 10000 ppmv alors que les 2 concentrations pour les COVs étaient de 200 et de 500 ppmv. Dans le cas de l'élimination individuelle des 2 COVs, la période d'acclimatation des micro-organismes à l'EB et au X était d'environ 30 jours, ce qui indiquait une période d'adaptation similaire pour EB et X. L'ajout de CH_4 sous une faible concentration de 2000 ppmv a eu un effet mineur sur la biodégradation des 2 COVs, de sorte que les conversions des 2 COVs sont restées supérieures à 85 %, tandis que les conversions du CH_4 étaient d'environ 56 % dans les 2 biofiltres. Lorsque la concentration du CH_4 a augmenté jusqu'à 10000 ppmv, l'inhibition de la biodégradation est devenue un problème indépendent de la concentration des 2 COVs, et a réduit les conversions des COVs et du CH_4 jusqu'à 80 % de leurs valeurs initiales (proche de 90% et 60% pour les 2 COVs et le CH_4, respectivement). Le type et la concentration du COV ont joué un rôle clé dans l'intensité de l'inhibition. En général, le régime de transfert de masse contrôlait l'élimination des 3 substrats.

Mots-clés: biofiltration, biotechnologies, inhibition, COV, gaz à effet de serre, effet synergique

3.2. Abstract

Landfill gas (LFG) is a gaseous emission containing several harmful compounds such as volatile organic compounds (VOCs) and volatile inorganic compounds (VICs) along with methane (CH_4) which is a powerful greenhouse gas. In case of small or old landfills, disposal of LFG can be economically challenging, and a possible solution is biofiltration. Biofiltration of CH_4 in presence of two VOCs was studied, ethylbenzene (EB) for BF1 and xylene (X) for

BF2. Both biofilters were packed with inorganic packing materials and operated with an empty bed residence time (EBRT) of 4.5 min. Methane concentrations varied from 2000 to 10000 ppmv along with 2 concentrations for VOCs i.e., 200 and 500 ppmv. In the case of individual VOC's removal, the acclimation period of microorganisms to EB and X were close to 30 days, indicating a similar adaptation period for X and EB. The addition of CH_4 under low inlet concentration of 2000 ppmv had minor effect on VOCs biodegradation such that the average VOC removal efficiencies (REs) remained above 85% for VOC inlet concentrations of 200 ppmv while the average CH_4-RE were around 56% in both biofilters. When CH_4 inlet concentration increased up to 10000 ppmv, inhibition became an issue disregard to the VOC concentration, and dropped VOC and CH_4 REs down to 80% of their original values. The type and concentration of the VOC played a key role in the intensity of the inhibition. In general, mass transfer regime was controlling the elimination of the three substrates.

Keywords: biofiltration, biotechnologies, inhibition, VOC, greenhouse gas, synergistic effect

3.3. Introduction

Methane (CH_4) with a global warming potential (GWP) approximatively 21-25 times higher than carbon dioxide (CO_2), is the most important greenhouse gas (GHG) after CO_2 (Padrón et al., 2020). Recent estimations in 2020 indicate that an annual global emission around 570 million metric tonnes of CH_4 has been emitted worldwide from which 60% are from anthropogenic sources such as landfills (IEA, 2020). Methane concentration in the atmosphere is increasing by 0.6% (10 ppbv) each year (Padrón et al., 2020). Atmospheric CH_4 concentration was estimated around 1,875 ppbv in 2019 (Schiermeier, 2020). The current CH_4 emission estimation indicates the possibility of an increase in global temperature above 3°C by the end of this century. A reduction in emissions is therefore required in order to meet the temperature increase limit of 1.5–2°C indicated in Paris Agreement (COP21) (Nisbet et al., 2019).

Landfills are important sources of CH_4 emission due to anaerobic degradation of organic matters producing a biogas called landfill gas (LFG) with CH_4 concentrations up to 60% v/v (Padrón et al., 2020; Pecorini et al., 2020). It is estimated that 68 Mton of CH_4 were globally produced from waste management systems including landfills in 2019 (IEA, 2020). Along with CH_4, other compounds can be found in LFG such as volatile organic compounds (VOCs) and volatile inorganic compounds (VICs) (Nikiema et al., 2007a). Concentration of total VOCs in LFG can vary in the range of 0.04 - 1 $g.m^{-3}$ (Gong et al., 2019b). Among VOCs, aromatic compounds such as xylenes (X) and ethylbenzene (EB) are commonly present in LFGs, which can cause cardiorespiratory diseases and are carcinogenic (Borhani and Noorpoor, 2017; Ran et al., 2018). For example, Sevimoğlu and Tansel, (2013) reported concentrations varying from 10-80 $mg.m^{-3}$ and 20-50 $mg.m^{-3}$ for X and EB, respectively, in LFG.

For CH_4 concentration in LFG exceeding 60% v/v (Nikiema et al., 2007a), LFG can be valorized by combustion for electricity production or heating (Ciuła et al., 2018; Themelis and Ulloa, 2007a). When CH_4 concentration is in the range of 35-60% v/v, valorization may not be economically sustainable and LFG physico-chemical elimination techniques are preferred. Several LFG elimination techniques exist such as incineration, thermal and catalytic oxidation, but the most commonly used mitigation technique is flaring (Ménard et al., 2012c). In case of concentrations below 3% v/v (the case of small-scale landfills or landfills older than 30 years) biotechnologies present several advantages over mentioned conventional techniques for LFG treatment in term of feasibility, environmental aspect and economical sustainability (Malakar et al., 2017; Pecorini et al., 2020).

The most used biotechnology for CH_4 and VOC mitigation is biofiltration. This process relies on microorganisms to act as biocatalysts removing pollutant from the gas and transforming them to CO_2, water (H_2O), biomass, etc. (Delhoménie and Heitz, 2005). The microorganisms are supported in a humidified packed bed (organic and/or inorganic or synthetic) forming a biofilm and are periodically supplied with a nutrient solution (NS) containing essential nutrients (Bahman Khabiri et al., 2020b).

Methane and VOC biofiltration have been intensively studied over the last two decades for LFG treatment purpose. Fjelsted et al., (2020) eliminated 60% of CH_4 from LFG with an inlet load (IL) of 9-66 $g.m^{-3}.h^{-1}$ and empty bed residence time (EBRT) in the range of 0.4-3 h in a compost packed biofilter (BF) in a landfill in Denmark. Lebrero et al., (2016) obtained a removal efficiency (RE) close to 90% at CH_4 IL of 40 $g.m^{-3}.h^{-1}$ for a BF packed with compost and inoculated with a pure strain of *Graphium* sp. Cho et al., (2008) obtained EB-RE of 92% in a rock-compost BF for ILs between 10-40 $g.m^{-3}.h^{-1}$ and EBRT of 62 s. Elmrini et al., (2004) used a peat BF to treat X at ILs around 36 $g.m^{-3}.h^{-1}$ and EBRT of 150 s and obtained X-RE above 96%.

Even though several studies of VOC elimination by biofiltration were reported in the literature, only a few of them treated CH_4 and VOC simultaneously. Khabiri et al., (2020) used an inorganic BF to treat a mixture of CH_4 (IL of 6-70 $g.m^{-3}.h^{-1}$) and styrene (IL of 9-32 $g.m^{-3}.h^{-1}$) at an air flowrate of 0.018 $m^3.h^{-1}$. A complete styrene elimination was observed (RE=100%) while CH_4-RE was between 43-80%. Zdeb and Lebiocka, (2016) used a compost/expanded clay BF to treat a model LFG composed of CH_4 and benzene, toluene, ethylbenzene, xylene (BTEX). Due to long EBRT (28 h), all pollutants were removed with REs above 90%. Although the authors in the abovementioned studies usually indicated a negative effect of VOCs presence on CH_4 elimination, further studies on simultaneous biofiltration of CH_4 and VOCs are required to understand the interactions between the pollutants. Since LFG contains CH_4 along with multiple VOCs and VICs, the studies on LFG biofiltration should consider interactions between CH_4 and VOCs as well as the possible inhibition that can be caused by one component on another.

It is hypothesized that VOCs tend to have an inhibitory effect on CH_4 elimination due to their toxicity and possible competitive inhibition for methanotrophic bacteria (the main microorganisms responsible for CH_4 biodegradation). Methane might also have a negative effect on VOC elimination. Sudden absence or presence of the second pollutant in an ongoing biofiltration process could also affect the BF performance. The use of an inorganic packing material would allow a BF to have stable long-term performance but presents several challenges like the absence of nutrients and indigenous microorganisms; the addition of inoculum and NS are therefore required (H. La et al., 2018b).

The aim of this study was to investigate the simultaneous biofiltration of CH_4 with two VOCs as binary mixtures i.g., CH_4/X and CH_4/EB, in two identical BFs with inorganic packing materials at different concentrations of CH_4 and VOCs. To the authors best knowledge, the elimination of mixtures of CH_4/X and CH_4/EB in BFs have never been studied. The first specific objective was the biofiltration of two individual VOCs (EB and X) under two levels of concentrations. The second specific objective was to study the biofiltration of VOCs with CH_4 addition at different ILs. The interactions between the EB or X in presence of CH_4 at different ILs were investigated. The possible inhibition of the 2 VOCs on CH_4 elimination as well as the effect of high CH_4 concentrations on VOCs elimination were studied.

3.4. Materials and methods

3.4.1. Biofilters experimental set-up

Two (2) upflow BFs (BF1 and BF2) made of plexiglass with a volume of 0.018 m^3 (1 m height and 0.15 m diameter) were used for a period of 278 days (Figure 3.1). The BFs were composed of 3 beds (0.3 m height). The bottom bed was packed with an inorganic material with the following properties: an average diameter of 7.5 mm, a void fraction of 0.55, a water holding capacity of 0.15, a density of 750 $kg.m^{-3}$ and a specific surface area of 470 $m^2.m^{-3}$. The properties of the middle and top beds packed with stone-based inorganic materials were: an average diameter of 5.0 mm, a void fraction of 0.43, a water holding capacity of 0.07, a density of 1200 $kg.m^{-3}$ and a specific surface area of 1250 $m^2.m^{-3}$. The material with the highest void fraction was chosen to be in bottom bed as it is more likely to have biomass accumulation (Ferdowsi et al., 2019). The composition of the materials cannot be indicated for confidentiality reasons.

Methane (Praxair Inc., Canada) flow rate was controlled by a mass flow controller (MFC) (Brooks, USA) and was injected at the bottom of the bioreactor along with humidified air and one VOC (EB for BF1 and X for BF2). Air was humidified by passing through a bubbler humidifier (0.1 m diameter) providing a relative humidity of 90%. Dry air was injected through a VOC bubbler filled with either EB (>99%, Sigma-Aldrich, USA) for BF1 or X (>99%, Fisher chemicals, USA) for BF2. Both humidified and dry air flows were controlled by rotameters (Brooks, USA).

3.4.2. Analytical tools

Gas samples were taken from the inlet and outlet of the BFs. A total hydrocarbon flame ionization analyzer equipped with a single continuous flame ionization detector (FIA 510, HORIBA, Japan) was used to analyze the concentration of CH_4 and VOCs. A CO_2 gas analyzer (ULTRAMAT 22P, SIEMENS, Germany) was used to measure CO_2 concentrations in the BFs inlet and outlet and to monitor CO_2 production. Gas samples from the BFs were extracted by vacuum pumps and directly supplied to the hydrocarbon and CO_2 analyzers.

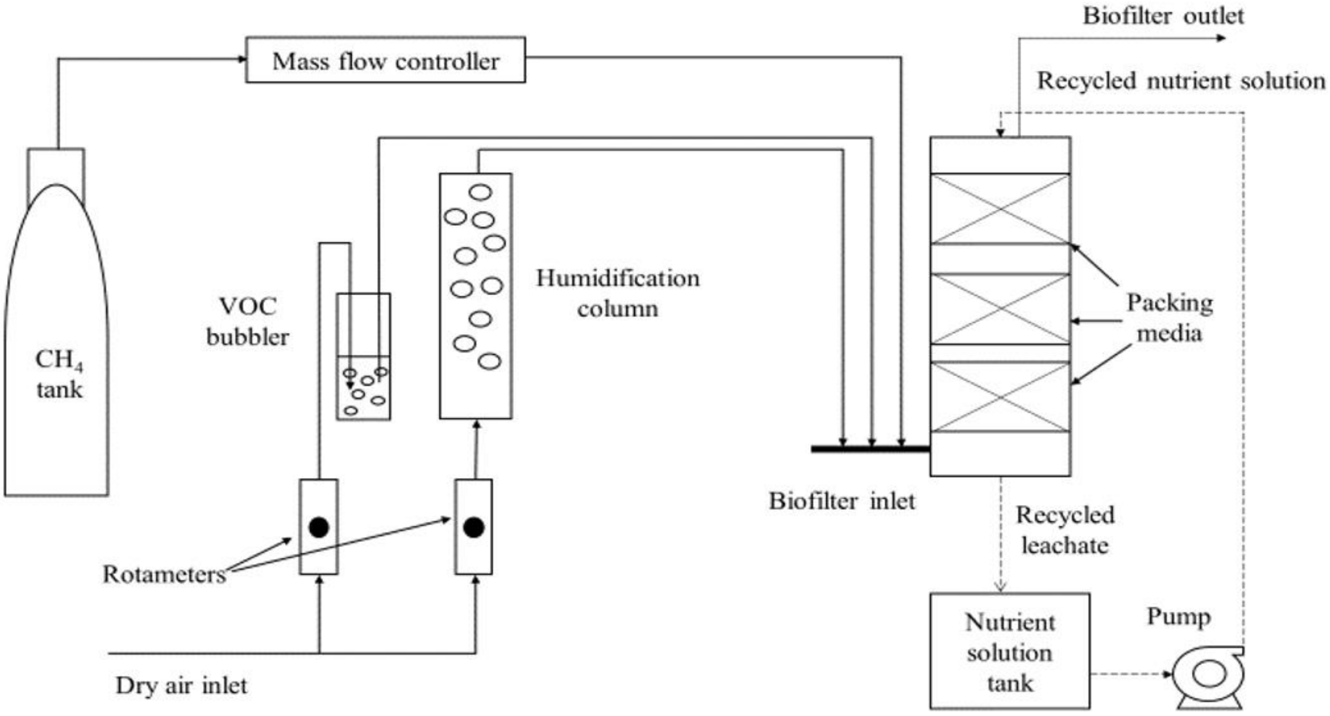

Figure 3.1 : Experimental set-up for biofiltration of CH_4 and VOCs

3.4.3. Performance parameters

The performance parameters used to evaluate the biofiltration process are the following:

- Inlet load: $IL = C_{in}\ Q/V$ [$g.m^{-3}.h^{-1}$] (1)
- Elimination capacity: $EC = (C_{in} - C_{out})\ Q/V$ [$g.m^{-3}.h^{-1}$] (2)
- Removal efficiency: $RE = 100*(C_{in} - C_{out})/C_{in}$ [%] (3)
- CO_2 production rate: $PCO_2 = (C(CO_2)_{out} - C(CO_2)_{in})\ Q/V$ [$g.m^{-3}.h^{-1}$] (4)

Where Q is the gas flow rate ($m^3.h^{-1}$), V is the packed bed volume (m^3) and C_{in} and C_{out} are the inlet and outlet pollutant concentrations, respectively ($g.m^{-3}$). $C(CO_2)_{in}$ and $C(CO_2)_{out}$ are the CO_2 concentrations in the BFs inlet and outlet , respectively ($g.m^{-3}$).

3.4.4. Experimental methods and operating conditions

Five (5) liters of leachate from an active BF treating CH_4 (IL = 60 $g.m^{-3}.h^{-1}$, RE = 76%) were used to inoculate the packing materials that had been thoroughly washed with tap water prior to inoculation. The leachate was recirculated 3 times on the same day from the top to the bottom of the BF in order to ensure homogeneous distribution of microorganisms through the filter bed (Ferdowsi et al., 2016). The addition of NS was started a week later. The components and composition of the NS were the same as the one used by Khabiri et al., (2020). The NS was then recycled in a $20*10^{-3}$ m^3 tank and fed to the BF from the top at a rate of $60*10^{-3}$ $m^3.h^{-1}$ for 2 min every 2 days. The experiments were designed based on 8 consecutive phases and the NS tank was refreshed at the end of each phase. Gas flow rate was kept constant during the whole experiments at 0.24 $m^3.h^{-1}$ corresponding to an empty bed residence time (EBRT) of 4.5 min for both BFs.

Table 3.1: Operating conditions during the experiments

Phase	VOC concentration (ppmv)	CH_4 concentration (ppmv)	Duration (days)
1	200	0	40
2	500	0	40
3	500	2000	47
4	500	6000	25
5	500	10000	50
6	200	2000	30
7	200	6000	24
8	200	10000	30

At the beginning of the experiment, VOCs (EB for BF1 and X for BF2) were injected to the BFs along with humidified air at an IL of 13 $g.m^{-3}.h^{-1}$ (Phase 1) corresponding to inlet concentration of 200 ppmv. After reaching a pseudo-steady state (constant BF performance), VOC IL was increased to 32 $g.m^{-3}.h^{-1}$ corresponding to inlet concentration of 500 ppmv (Phase 2). Once a pseudo-steady state was reached, CH_4 was added to inlet gas at ILs of 19 (Phase 3), 57 (Phase 4), 95 (Phase 5) $g.m^{-3}.h^{-1}$ corresponding to concentrations of 2000, 6000, 10000 ppmv, respectively. The transition from one CH_4 IL to another was only carried out after steady performance was obtained. The IL of VOCs was then returned to 13 $g.m^{-3}.h^{-1}$ and CH_4 ILs were changed again to 19 (Phase 6), 57 (Phase 7), 95 (Phase 8) $g.m^{-3}.h^{-1}$. Carbon dioxide concentrations were measured every 3 days. Table 3.1 presents the different phases of the experiments.

3.5. Results and discussion

3.5.1. Methane and ethylbenzene removal efficiencies for different inlet loads (BF1)

Figure 3.2 presents CH_4-REs and EB-REs for BF1 in different phases of experiments. In Phases 1 and 2, only EB was injected to BF1 and EB-REs of 83±5 and 89±3% were obtained for ILs of 12.0±0.2 $g.m^{-3}.h^{-1}$ (EB concentration of 200 ppmv) and 32.0±0.4 $g.m^{-3}.h^{-1}$ (EB concentration of 500 ppmv), respectively. Ethylbenzene-RE increase can be attributed to the development and growth of microorganisms responsible for EB removal and/or the increase of EB bioavailability in the biofilm phase. Gallastegui et al., (2017) obtained similar EB-RE of 90% during the acclimation period for an IL varying in the range of 4.5 – 16.1 $g.m^{-3}.h^{-1}$ in a black slag packed BF at an EBRT of 3 min.

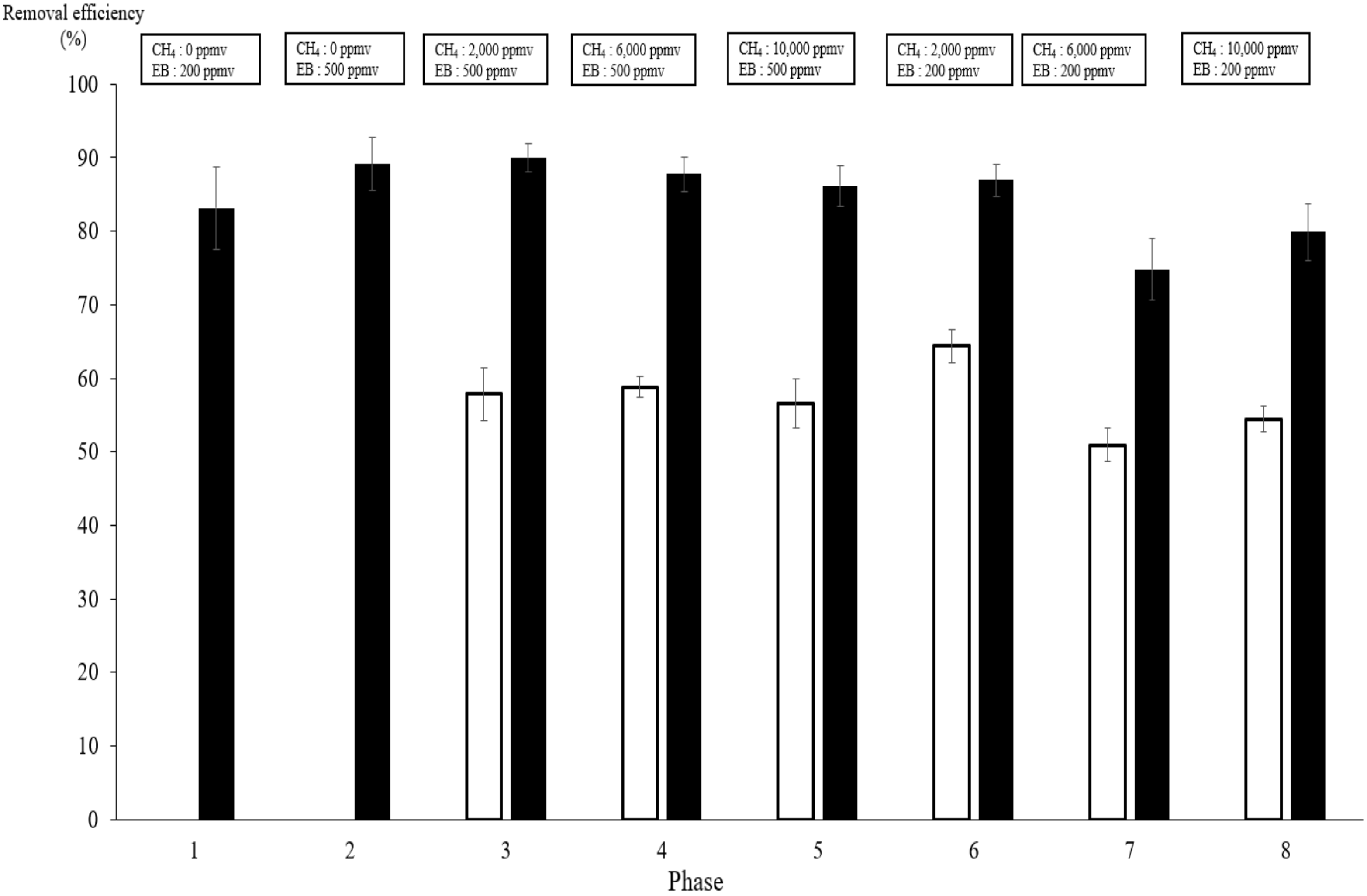

Figure 3.2: Pollutants removal efficiencies for each phase in BF1 (■ for EB-RE and □ for CH_4-RE)

In Phase 3, CH_4 was added to BF1 at an IL of 19.0±0.7 $g.m^{-3}.h^{-1}$ (CH_4 concentration of 2000 ppmv). According to Figure 3.2, CH_4-RE reached 58±4% while EB-RE remained almost constant at 90±2% (EB-IL was kept constant at 32.0±0.4 $g.m^{-3}.h^{-1}$). The neutral effect of CH_4 addition on EB-RE could be due to a co-metabolism mechanism as EB can be biodegraded by methane monooxygenase enzyme (MMO) produced by methanotrophic bacteria. Volatile organic compounds degrading bacteria such as *Pseudomonas* sp. was also reported to be able to consume CH_4 (Buettner et al., 2019). Hernández et al., (2015) obtained a higher CH_4-RE of 62% for an IL of 18 $g.m^{-3}.h^{-1}$ and EBRT of 4.4 min in a tree bark BF. Gómez-Borraz et al., (2017) obtained a CH_4-RE of 62% for an EBRT of 19 min and CH_4-IL of 21 $g.m^{-3}.h^{-1}$ in a compost BF. Khabiri et al., (2020) obtained a CH_4-RE of 64% for CH_4-IL of 20 $g.m^{-3}.h^{-1}$ in the presence of styrene (styrene-IL =32 $g.m^{-3}.h^{-1}$) in a BF packed with inorganic materials with an EBRT of 6 min. Methane-RE (58±4%) in Phase 3 was 8% lower than REs obtained for CH_4-ILs close to 19 $g.m^{-3}.h^{-1}$ in the abovementioned studies due to a possible inhibition for CH_4 biodegradation by EB presence or shorter EBRT of 4.5 min. Lee et al., (2011) reported an inhibitory effect of EB on methanotrophic bacteria in a batch bioreactor as CH_4 oxidation rate dropped from 100 to 80% when EB was added to an enriched CH_4-oxidizing microbial culture from landfill cover soil. Methane was injected at a concentration of 5000 ppmv along with 100-200 ppmv of EB. Incubation was carried out at 30 °C and shaking rate of 180 rpm.

In Phase 4, CH_4-RE and EB-RE were 59±1 and 88±2%, respectively when CH_4-IL was increased to 54.0±2.0 $g.m^{-3}.h^{-1}$ (CH_4 concentration of 6000 ppmv) while EB-IL remained unchanged at 32.0±0.4 $g.m^{-3}.h^{-1}$. Methane-RE and EB-RE did not significantly differ from Phase 3 possibly due to microorganism adaptation to higher CH_4-ILs.

In phase 5, BF1 tolerated the high CH_4 and EB concentrations (10000 ppmv for CH_4 and 500 ppmv for EB) while being fed simultaneously. According to Figure 3.2, CH_4-RE and EB-RE stayed over 57 and 86 % respectively for corresponding CH_4-IL and EB-IL of 96±2.0 and 32±0.4 $g.m^{-3}.h^{-1}$, respectively. Methane-RE (57±3 %) was higher compared to REs reported in the literature despite the short EBRT of 4.5 min and the presence of VOC in this study. Kim et al., (2014) obtained CH_4-RE of 51% for an IL of 99.5 $g.m^{-3}.h^{-1}$ with an EBRT of 20 min (more than 4 times higher than the EBRT used in the present study) in a perlite packed BF. Nikiema and Heitz, (2009) reported that for the same CH_4 concentration (10000 ppmv), an increase of EBRT from 3 to 9 min resulted in an increase of CH_4-RE from 50 to 90%.

For the following phases 6-8, the EB inlet concentration returned to the lowest level of 200 ppmv while CH_4 inlet concentration varied again from 2000 to 10000 ppmv. In other words, groups of phases (3 and 6), (4 and 7), and (5 and 8) were identical in terms of CH_4 inlet concentration but different in terms of EB inlet concentration.

In Phase 6, CH_4-IL and EB-IL decreased to 20.0 ± 0.5 and 12.0 ± 0.5 $g.m^{-3}.h^{-1}$, respectively, which corresponds to the lowest values of CH_4 and EB inlet concentrations tested in this study. A comparison between Phases 3 and 6 shows higher CH_4-RE of 64 ± 2 % in Phase 6 compared to 58 ± 4% in Phase 3 for a similar CH_4-IL and a lower EB-IL (32.0 ± 0.4 $g.m^{-3}.h^{-1}$ and 12.0 ± 0.5 $g.m^{-3}.h^{-1}$ in Phases 3 and 6, respectively). It is worth mentioning that CH_4 was introduced to BF1 in Phase 3 for the first time. Therefore, CH_4 degrading community was probably more developed in Phase 6 compared to Phase 3. Ethylbenzene-RE in Phase 6 (87 ± 2 % for an IL of 12.0 ± 0.5 $g.m^{-3}.h^{-1}$) was mildly lower than in Phase 3 (90 ± 2% for an IL of 32.0 ± 0.4 $g.m^{-3}.h^{-1}$). This might be due to high CH_4-IL during Phase 5 (96.0 ± 2.0 $g.m^{-3}.h^{-1}$) which could have led CH_4 degraders to be dominant as a microbial culture at the end of Phase 5 and beginning of Phase 6. In contrast, due to the presence of EB as a single substrate, the EB degraders were likely dominant at the end of Phase 2 just before the beginning of Phase 3.

In Phase 7, CH_4-IL was increased to 57.0 ± 0.6 $g.m^{-3}.h^{-1}$ while EB-IL was kept at 12.0 ± 0.5 $g.m^{-3}.h^{-1}$; the lowest REs of this study were obtained (51 ± 2 % for CH_4 and 75 ±4% for EB). Methane-RE and EB-RE both dropped since CH_4-IL was 3 times higher than Phase 6 which might cause inhibition for CH_4 and EB degradation. For a similar CH_4-IL (54 ± 2 $g.m^{-3}.h^{-1}$) and a higher EB-IL (32.0 ± 0.4 $g.m^{-3}.h^{-1}$), higher CH_4-RE and EB-IL had been obtained (59 ± 1 and 88 ± 2%, respectively) in Phase 4 compared to Phase 7. The EB-RE drop in Phase 7 compared to Phase 4 could be attributed to the dominance of CH_4 degraders over EB degraders due to of significantly higher CH_4-IL compared to EB-IL. The synergistic effect of high level of EB concentration (500 ppmv) on CH_4 and EB biodegradations in Phase 4 might be the reason for higher CH_4 and EB-REs in Phase 4.

In Phase 8, no significant improvement in the performance of BF1 was observed for an increased CH_4-IL of 99.0±4.2 g.m^{-3}.h^{-1} and constant EB-IL of 12.0±0.5 g.m^{-3}.h^{-1}. Methane-RE and EB-RE were obtained as 54±2 and 80±4%, respectively. Methane and EB REs in Phase 8 were lower than REs in Phase 5 (similar CH_4-IL to Phase 5 but lower EB-IL (12.0±0.5 g.m^{-3}.h^{-1})). A decrease from 57±3 to 54±2 % for CH_4 and from 86±3 to 80±4% for EB were observed in Phase 8 compared to Phase 5.

These results indicated that for high level of CH_4-ILs in the range of 54-99 g.m^{-3}.h^{-1}, the presence of high EB-IL of 32.0±0.4 g.m^{-3}.h^{-1} (Phases 4 and 5) led to higher CH_4-REs compared to the presence of low EB-IL of 12.0±0.5 g.m^{-3}.h^{-1} (Phases 7 and 8). In other words, high level of EB concentration (500 ppmv) under high CH_4 inlet concentration (6000-10000 ppmv) could support synergistic interactions. The main bacterial strain responsible for EB biodegradation *Pseudomonadaceae* was potentially able to eliminate CH_4 as well (Buettner et al., 2019). In this regard, high EB concentrations (500 ppmv) might have favored the development of bacterial communities who contributed to CH_4 biodegradation in addition to the VOC removal.

3.5.2. Simultaneous CH_4 and xylenes biodegradation (BF2) in comparison with BF1

Methane-RE and X-RE for BF2 in 8 phases are presented in Figure 3.3. In phases 1 and 2 in BF2 (Figure 3.3), X-RE increased from 76±5 to 90±6% when X-ILs increased from 12.0±0.2 g.m^{-3}.h^{-1} (X inlet concentration of 200 ppmv) to 32.0±0.5 g.m^{-3}.h^{-1} (X inlet concentration of 500 ppmv). Li et al., (2020) obtained a similar X-RE of 90% for ILs of 20-30 g.m^{-3}.h^{-1} and EBRT of 1.5 min compared to 4.5 min used in the current study. Gallastegui et al., (2017) reported X-RE of 86% for an IL of 16.5 g.m^{-3}.h^{-1} and an EBRT of 3 min.

According to Figures 3.2 and 3.3, both BFs displayed an increasing VOC-RE trend over phases 1 and 2. The percentage of VOC-RE improvement from Phase 1 to Phase 2 were 7 and 18% for BF1 and BF2, respectively.

In Phase 3, CH_4 was added at an IL of 20±1 g.m^{-3}.h^{-1} under X-IL of 32.0±0.5 g.m^{-3}.h^{-1}. A CH_4-RE of 55±9% was obtained which was similar to CH_4-RE in Phase 3 in BF1. The addition of CH_4 to BF2 in Phase 3 had no underlined effect on the VOC removal and X-RE remained above 87%.

During Phase 4 in BF2, CH_4-IL was increased by almost 3 times (54±2 $g.m^{-3}.h^{-1}$) compared to Phase 3 under constant X-IL of 32.0±0.5 $g.m^{-3}.h^{-1}$. Both CH_4-RE and X-RE slightly increased to 57±2 and 90±2%, respectively. Methane-IL increase caused no inhibition since appropriate microorganisms for both X and CH_4 removal were probably developed and adapted to remove larger amounts of pollutants.

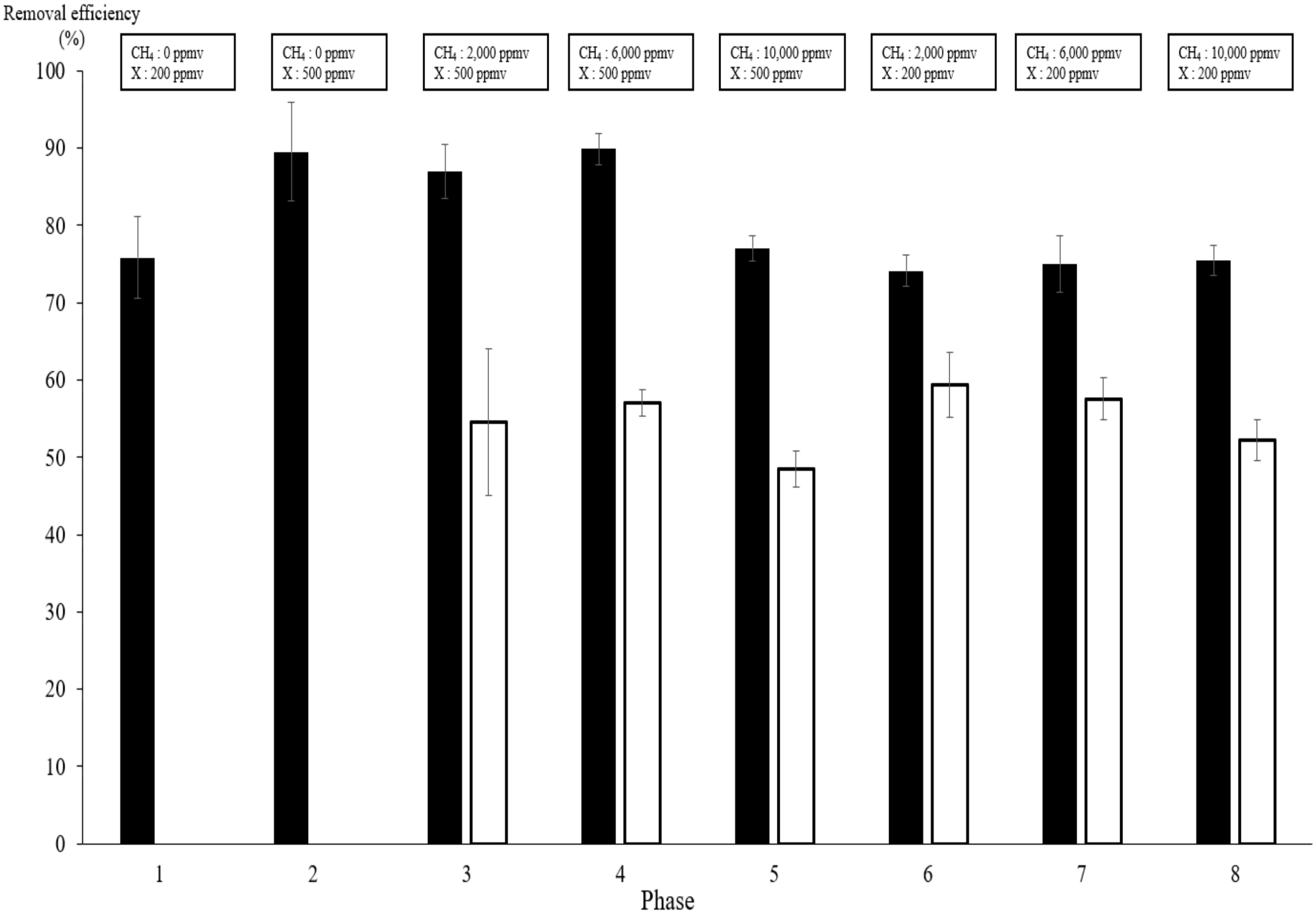

Figure 3.3 : Pollutants removal efficiencies for each phase in BF2 (■ for X-RE and ☐ for CH_4-RE)

In Phase 5, CH_4-IL was increased to 90±4 $g.m^{-3}.h^{-1}$ while X-IL remained unchanged (32.0±0.5 $g.m^{-3}.h^{-1}$). Unlike BF1, the CH_4-IL increase had an inhibitory effect on both CH_4 and X biodegradation as REs decreased from 57±2 (Phase 4) to 49±2% (Phase 5) and from 90±2 (Phase 4) to 77±1% (Phase 5) for CH_4 and X, respectively. Lee et al., (2011) reported that X has more toxicity or inhibition effect on methanotrophs than EB during tests on methanotrophs isolated from a landfill soil.

The addition of CH_4 at increasing ILs did not significantly affect EB conversion as mean EB-RE was 87±4% for Phases 3, 4 and 5. Unlike relatively constant EB-REs in BF1, X-RE slightly decreased from 87 (Phase 3) to 77% in Phase 5 (BF2) possibly due to CH_4 inhibitory effect on X. In general, EB has been reported to be more biodegradable than X (Deeb and Alvarez-Cohen, 1999). For identical CH_4 concentrations, the lower level of VOC concentration (200 ppmv) resulted in lower VOC-RE (Figures 3.2 and 3.3). For instance, EB-RE and X-RE decreased from 88 to 75% and from 90 to 75% respectively, when VOC inlet concentration dropped from 500 to 200 ppmv in Phase 7 compared to Phase 4 under constant CH_4 inlet concentration of 6000 ppmv.

Regarding CH_4 removal, the concentration of accompanying VOC played opposite roles in each BF. In BF2, a 500 ppmv concentration of X resulted in lower CH_4-REs (6% lower) compared to low X concentration of 200 ppmv while the EB concentration had almost a neutral effect on CH_4-RE for CH_4 concentration ranging from 6000 to 10000 ppmv.

3.5.3. Pollutants elimination capacities as a function of their inlet loads

Figure 3.4 (a) presents CH_4 and EB ECs for BF1 as a function of ILs. Maximum CH_4-EC was 54.0 ± 2.9 g.m^{-3}.h^{-1} for a CH_4-IL of 99.0 ± 4.2 g.m^{-3}.h^{-1}. Results were higher than ECs reported for the same CH_4-IL range in inorganic packed BFs. Nikiema and Heitz, (2010) obtained CH_4-EC of 49.5 g.m^{-3}.h^{-1} for CH_4-IL of 90 g.m^{-3}.h^{-1} (EBRT = 4.1 min). Vergara-Fernandez et al., (2020) reported a maximum CH_4-EC of 42.2 g.m^{-3}.h^{-1} for CH_4-ILs in the range of 300-400 g.m^{-3}.h^{-1}. Ethylbenzene-EC increased from 8.0 ± 0.6 to 28 ± 2 g.m^{-3}.h^{-1} (ILs of 12.0 ± 0.2 and 32.0 ± 0.4 g.m^{-3}.h^{-1}). Results were slightly higher than those of Gallastegui et al., (2013) who obtained EB-EC in the range of 8 – 20 g.m^{-3}.h^{-1} for ILs of 10-30 g.m^{-3}.h^{-1} in a black slag BF with EBRTs ranging 100 – 200 s.

Methane and X ECs as a function of ILs in BF2 are presented in Figure 3.4 (b). The highest CH_4-EC obtained (54 ± 4 g.m^{-3}.h^{-1}) for an IL of 101 ± 3 g.m^{-3}.h^{-1} was similar to the highest CH_4-EC in BF1. Xylene-EC increased from 8.0 ± 0.4 to 29.0 ± 2.3 g.m^{-3}.h^{-1} for ILs of 9.0 ± 0.6 to 32.0 ± 0.5 g.m^{-3}.h^{-1}. The values were close to Natarajan et al., (2014) results who obtained X-EC of 9-29 g.m^{-3}.h^{-1} in a tree-bark BF with ILs between 3-40 g.m^{-3}.h^{-1}.

In Figure 3.4, the deviation of CH_4-EC versus CH_4-IL from 100% removal line was an indicator of incomplete conversion of CH_4 in both BF1 and BF2 (RE<100%). A high proportion of EB and X were successfully eliminated and the VOC-EC versus VOC-IL curves showed least deviation from 100% removal line due to higher solubility of VOCs in water

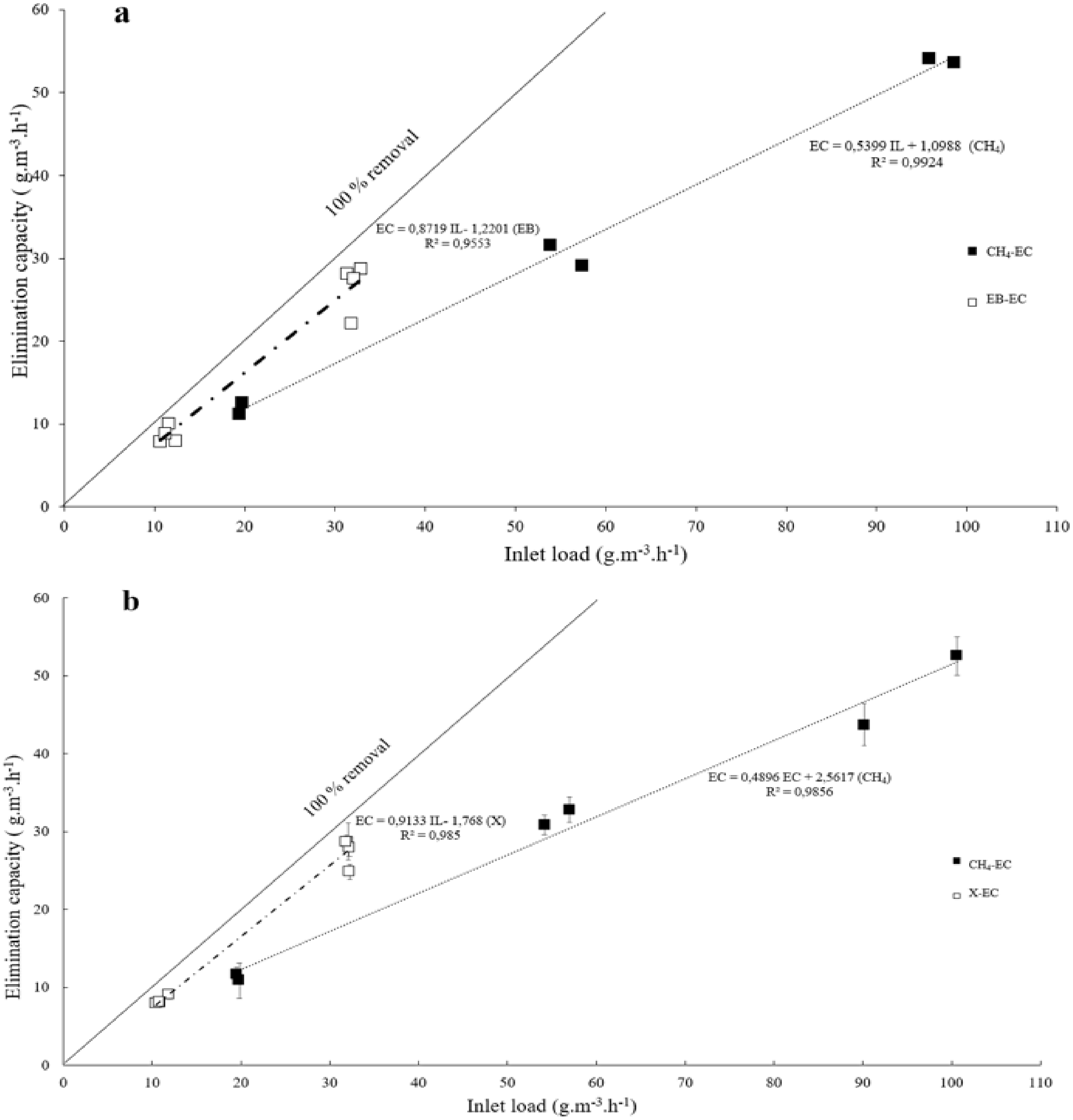

Figure 3.4 : Pollutants elimination capacities as a function of inlet loads for (a) BF1 and (b) BF2 compared to CH_4 (0.022 $g.kg^{-1}$ for CH_4 and 0.150 and 0.106 $g.kg^{-1}$ for EB and

X, respectively at 20 °C) and more biodegradability of VOCs compared to CH_4 (Coquelet et al., 2008; ETB, 2021.).

Elimination capacities as a function of ILs for CH_4 (in both BF1 and BF2) increased by linear trend. Therefore, the highest EC (EC_{max}) for both BFs could not be reached and critical ILs could not be determined (Ferdowsi et al., 2017a). The linear trend of CH_4 elimination versus CH_4-IL in both BF1 and BF2 indicates that CH_4 biodegradation was under mass transfer limitations (Ménard et al., 2014).

3.5.4. Total carbon dioxide production as a function of total elimination capacity

Carbon dioxide production rate (PCO_2) is an indicator of biodegradation activity. The values of EC and PCO_2 can be used to determine the nature of biodegradation reactions (bio-oxidation, biomass production, etc.) occurring within the BF. The mass ratio PCO_2/EC in case of

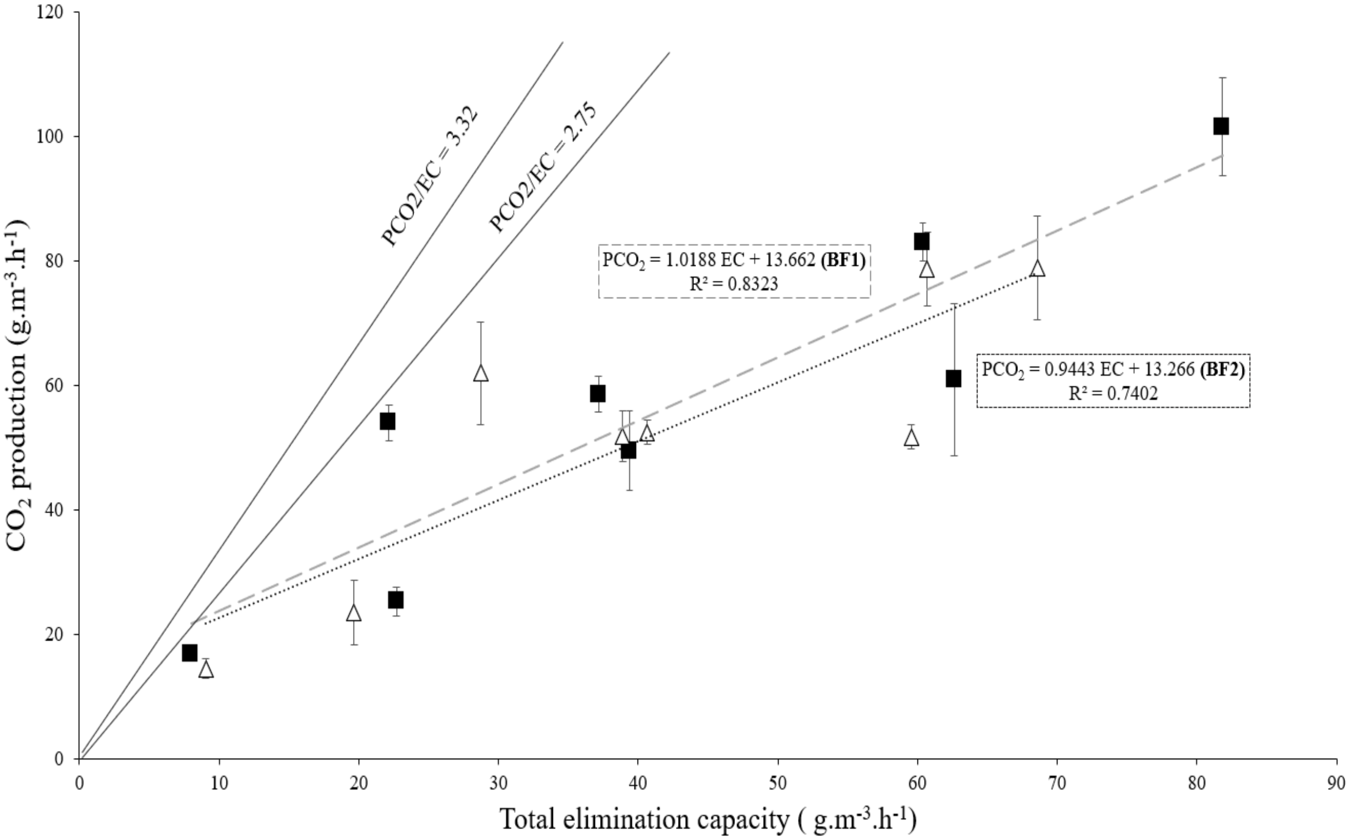

Figure 3.5 : Carbon dioxide production as a function of elimination capacity for BF1 and BF2 (■ for BF1 and △ for BF2)

theoretical oxidation (no oxidation by-products or biomass production) is 2.75 for CH_4 and 3.32 for EB or X as single pollutants. The theoretical PCO_2/EC mass ratio in a BF treating CH_4 and VOC (EB or X) simultaneously, would therefore range between 2.75 and 3.32 depending on CH_4 and VOC concentrations in the mixture (Khabiri et al., 2020).

Figure 3.5 presents PCO_2 as a function of total EC (the summation of CH_4-EC and EB or X-EC) for BF1 and BF2. Carbon dioxide production increased from 17 ± 1 to 102 ± 8 $g.m^{-3}.h^{-1}$ for EC in the range of 8.0 ± 0.6 to 82 ± 6 $g.m^{-3}.h^{-1}$ in BF1 and from 14 ± 2 to 79 ± 8 $g.m^{-3}.h^{-1}$ for EC ranging from 9.0 ± 0.6 to 69 ± 4 $g.m^{-3}.h^{-1}$ in BF2. A higher PCO_2 for BF1 could be attributed to higher EC obtained in BF1 as the mixture EB+CH_4 was easier to biodegrade than X+CH_4.

A linear relation between PCO_2 and EC variation was obtained with slopes of 1.01 and 0.94 for BF1 and BF2, respectively. The slopes show the PCO_2/EC ratios (mass ratio), and the deviation from the theoretical mass ratios (lower than 2.75-3.32) indicates that microorganisms produced biomass and other by-products such as extracellular polymeric substances (EPS), catechol, formaldehyde, etc., along with CO_2. Since the slope for BF1 was 7% higher than for BF2, a higher portion of consumed carbon was converted to CO_2 compared to biomass (Khabiri et al., 2020).

3.5.5. VOC biofiltration dynamic response to concentration increase and CH_4 addition

Figure 3.6 (a) presents the variations of EB-RE as a function of time during Phases 1, 2 and 3. These first 3 phases were selected to investigate VOC elimination as a single pollutant and in a mixture with CH_4 when introduced for the first time. The BF response to VOC concentration increase as well as CH_4 addition were monitored over time. Ethylbenzene-RE was 23% one day after inoculation when EB was injected at an IL of 12.0 ± 0.2 $g.m^{-3}.h^{-1}$. Ethylbenzene-RE gradually increased from day 1 to day 30 (Phase 1) when it reached pseudo-steady state with a RE around 88%. The results indicated that adaptation period was longer than usual for VOCs treatment in BFs. García-Peña et al., (2008) obtained EB-RE close to 90% after about 5 days of inoculation with fungi consortium for EB concentration around 40 $g.m^{-3}$ and an EBRT of 1.7 min in a BF packed with vermiculite. Son and Striebig, (2001) also reported EB-RE of 99% from day 1 of the study in a compost BF for EB-IL of 6 $g.m^{-3}.h^{-1}$ and EBRT of 2 min. The difference in the adaptation period can be due to the absence of indigenous microorganism community in the inorganic packing or lack of EB degraders in the initial inoculum as the inoculum used was leachates from a BF treating only CH_4.

Ethylbenzene-RE dropped sharply to 40% (decreased by 55%) after EB-IL was suddenly increased to 32.0±0.4 $g.m^{-3}.h^{-1}$ (Phase 2). This reduction demonstrated that the increased EB-ILs were beyond the degradation capacity of microorganisms. Volckaert et al., (2013) reported an EB-RE decrease from 95 to 60% when EB-IL was increased from 12 to 50 $g.m^{-3}.h^{-1}$ in BF

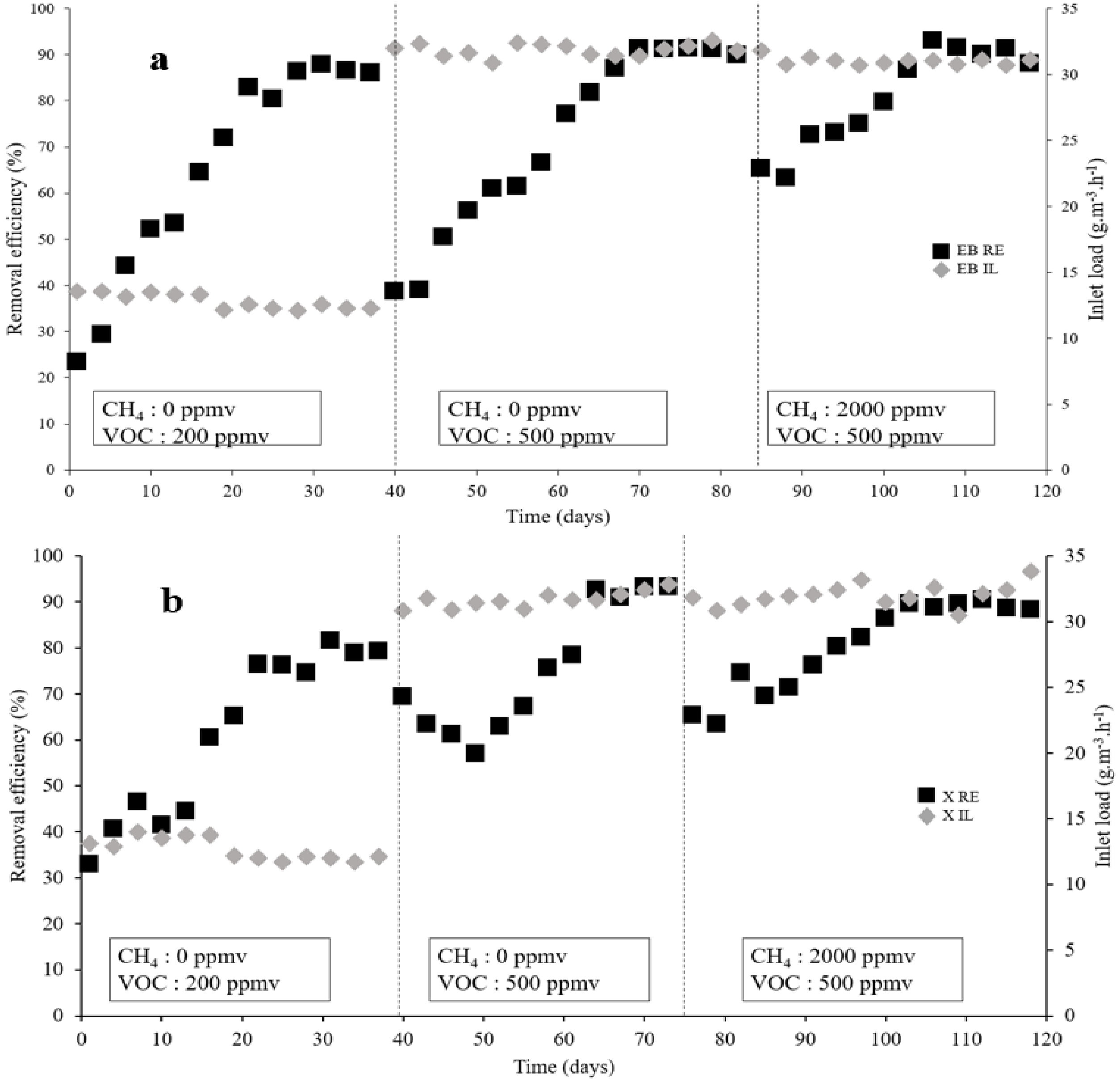

Figure 3.6 : Dynamic response to concentration increase and CH_4 addition (a) BF1 and (b) BF2

packed with macadamia nutshells and with an EBRT of 90s. Microorganisms in BF1 gradually adapted to EB-IL after 30 days and EB-RE returned to 91% like at the end of Phase 1.

According to Figure 3.6 (a) when CH_4 was added at an IL of 19.0 ± 0.7 $g.m^{-3}.h^{-1}$ (Phase 3) at day 76, EB-RE suddenly dropped from 90 to 63% and then gradually increased to 93% after 20 days. Ethylbenzene-RE decrease after CH_4 addition was related to the required adaptation period to the increased substrates load and the presence of a new substrate in biofilm.

Figure 3.6 (b) presents X-RE fluctuations during the first 3 phases in BF2. In Phase 1, when X was injected at an IL of 12.0 ± 0.2 $g.m^{-3}.h^{-1}$, X-RE was 33% from the first day of the operation and gradually increased from day 1 to day 30 to reach a pseudo-steady state at X-RE of approximately 76%. Therefore, the acclimation period for BF1 was similar to BF2. Singh et al., (2017) reported X-RE of 40% (IL = 12 $g.m^{-3}.h^{-1}$) from first day of study and reached a pseudo-steady state condition after 20 days with X-RE of 99% possibly due to a higher EBRT of 58.8 min in a BF packed with wood charcoal.

In Phase 2, X-IL was increased to 32.0 ± 0.5 $g.m^{-3}.h^{-1}$ in day 40 and X-RE gradually decreased to reach 57% in day 49 (27% RE decrease). Then X-RE increased from 57 to 92% after 15 days. According to Figures 3.6 (a) and (b), X-RE decrease after X-IL increase was smooth and less sudden compared to EB-RE. The microorganisms responsible for X removal were likely more resistant to substrate loads instant increase compared to EB. However, EB elimination reached a higher RE possibly due to higher biodegradability of EB compared to X (Natarajan et al., 2017).

At day 65, CH_4 was injected at an IL of 20 ± 1 $g.m^{-3}.h^{-1}$ in Phase 3 when X-RE sharply dropped to 65% and then gradually increased to 89% after approximately 30 days. As explained earlier for BF1, BF2 behaved similarly in terms of RE fluctuation following CH_4 addition as BF1 during Phase 3.

3.6. Conclusion

Two identical biofilters were employed to eliminate either ethylbenzene or xylene as VOC solely and in the presence of CH_4 under the same operating conditions and range of concentration variations. According to the chemical structure similarities between the target VOCs such as number of carbon and aromaticity, the behavior of the biofilters were similar in many aspects. Both biofilters successfully adapted to the single VOCs and REs higher than 90% for VOC-ILs up to 32 g.m^{-3}.h^{-1} were obtained. Also, the addition of CH_4 could be tolerated in both biofilters owing to the initial CH_4-degrading rich inoculum in the original leachate used for inoculation. However, certain substrate characteristics differences such as biodegradability, inhibitory effects and toxicity for microbial cultures resulted in some opposite behaviors in the two biofilters. In the case of binary VOC/CH_4 mixture removal and in contrast to xylene, ethylbenzene concentration (500 ppmv) could partially reduce the inhibitory effect of CH_4 concentration (6000-10000 ppmv). Certain microorganisms for ethylbenzene degradation could contribute simultaneously to CH_4 removal. For CH_4 concentration of 2000 ppmv, both biofilters reached CH_4 REs around 60% under VOC concentration of 200 ppmv. The CO_2 production rate increase when ethylbenzene or xylene were involved in presence of CH_4 confirmed the microbial development and activity during the operation in both biofilters.

3.7. Acknowledgments:

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CHAPTER 4. Biological mitigation of methane in presence of xylene and ethylbenzene in biofilters: Effect of pollutants concentrations and empty bed residence time

Avant propos:

Ce document est une version préliminaire de l'article "Biological mitigation of methane in presence of xylene and ethylbenzene in biofilters: Effect of pollutants concentrations and empty bed residence time" soumis dans le journal "Process Safety and Environmental Protection" en septembre 2022; l'article a été accepté en mai 2023.

TITRE: Élimination biologique du méthane en présence de xylène et d'éthylbenzène dans des biofiltres : effet des concentrations de polluants et du temps de séjour en fût vide

Title: Biological mitigation of methane in presence of xylene and ethylbenzene in biofilters: Effect of pollutants concentrations and empty bed residence time

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Contribution of the document: This paper is relevant to the second objective of this thesis, focusing on the evaluation of steady-state performances of biofilters treating a mixture of CH_4, xylene, and ethylbenzene. The study examines the impact of changes in pollutant concentration and EBRT on the removal of CH_4 and VOCs, while also discussing the distribution of pollutant removal throughout the biofilter and nutrient consumption.

4.1. Résumé

Les émissions de gaz issus des sites d'enfouissement sanitaire provoquent de graves préoccupations environnementales en raison de la présence de méthane (CH_4), un important gaz à effet de serre (GES), ainsi que de plusieurs composés organiques volatils (COVs) nocifs tels que le xylène (X) et l'éthylbenzène (EB). Une série de 9 biofiltres à flux ascendant remplis de lits filtrants inorganiques ont été utilisés pour éliminer le CH_4 en tant que polluant unique, en mélange binaire (X ou EB), ou en mélange ternaire de CH_4, X et EB. L'intervalle de concentrations de CH_4 était situé entre 2000 à 10000 ppmv, tandis que les concentrations individuelles des COVs étaient augmentées de 200 à 600 ppmv pour des temps de séjour en fût vide (EBRT) allant de 2.25 à 9 minutes sur une période de 242 jours. La conversion de CH_4 (CH_4-RE) la plus élevée dans le mélange ternaire était de 41±3% pour une concentration de CH_4 de 2000 ppmv et des concentrations individuelles de COVs de 200 ppmv pour un EBRT de 9 minutes. Les conversions les plus élevées pour X et EB, étaient 58±3% et 57±3% respectivement, ont été obtenus aux mêmes concentrations des composants mais à un EBRT plus court de 4.5 minutes. Près de 40% de la biodégradation du CH_4 s'est produite dans la partie supérieure du bioréacteur, tandis que 50 à 60% de la biodégradation des COVs ont eu lieu dans la section centrale du biofiltre.

Mots clés: Biotechnologie, biodégradation, gaz à effet de serre, COV, interaction, inhibition.

4.2. Abstract

Landfill gas emissions cause serious environmental concerns due to the presence of methane (CH_4), an important greenhouse gas (GHG) and several harmful volatile organic compounds (VOCs) such as xylene (X) and ethylbenzene (EB). A series of 9 up-flow biofilters packed with inorganic materials were used to eliminate CH_4 as a single pollutant, a binary mixture of X and EB or in a ternary mixture of CH_4, X and EB. The CH_4 concentration range was 2000-10000 ppmv while VOCs individual concentrations were increased from 200 to 600 ppmv for empty bed residence times (EBRTs) ranging from 2.25 to 9 min over a period of 242 days. The highest CH_4-RE in the ternary mixture was 41±3% at a CH_4 concentration of 2000 ppmv and VOCs individual concentrations of 200 ppmv at an EBRT of 9 min. Meanwhile, the highest X and EB-REs of 58±3 and 57±3%, respectively, were obtained at the same concentrations of the components but at a shorter EBRT of 4.5 min. Almost 40% of CH_4 biodegradation took place on the top section of the bioreactor while 50-60% of VOCs biodegradation occurred in the middle section.

Key words: Biotechnology, biodegradation, greenhouse gas, VOC, interaction, inhibition

4.3. Introduction

Climate change due to increasing greenhouse gases (GHGs) emissions from anthropogenic sources is a concerning subject that resulted in several regulations aiming to reduce the environmental impact of several sectors such as oil and gas, wastewater treatment, coal mines and landfills (Nisbet et al., 2019). Methane (CH_4) is the second contributor to global warming after carbon dioxide (CO_2) due to its high global warming potential (GWP) approximately 21-25 times higher than CO_2 and the high amounts close to 590 million metric tons emitted worldwide in 2021 (Howarth, 2014; IEA, 2022). Landfills are responsible for 60% of anthropogenic CH_4 emissions in the world (IEA, 2022). The biogas emitted from landfills is produced by the biological anaerobic decomposition of organic wastes and is composed of CH_4, CO_2, nitrogen (N_2), water (H_2O) and traces of volatile organic and inorganic compounds (VOCs and VICs) (Nikiema et al., 2007). In addition to greenhouse emission issues, landfill biogas emissions can also cause health problems as well as unpleasant odors since it contains several VOCs and VICs. Xylene (X) and ethylbenzene (EB) are aromatic compounds commonly present in landfills emissions (LE) at concentrations reaching up to 854 and 247 $mg.m^{-3}$, respectively (Tassi et al., 2009). Both VOCs are reported to be carcinogenic VOCs with cardiorespiratory risks (Borhani and Noorpoor, 2017; Ran et al., 2018; Sevimoğlu and Tansel, 2013).

Flaring or combustion for heat production are commonly used to eliminate or to valorize landfill emissions (LEs) but are not viable solutions in cases of LE with CH_4 concentrations below 3% v/v (small scale landfills or landfills older than 30 years) (Nikiema et al., 2007; Pecorini and Iannelli, 2020). In this regard, biotechnologies such as biofiltration offer a more suitable alternative for LE mitigation compared to combustion or catalytic oxidation as they have a lower environmental impact with a small carbon footprint as well as reduced operating costs (AMBIO, 2022). Biofiltration is the most used biotechnology for the relative simplicity of the process. It consists of transferring pollutants from gas phase to the liquid phase biofilm surrounding a solid packing; the pollutants are then biodegraded by microorganisms producing CO_2, H_2O, biomass, etc. The bioprocess depends on several factors like the pollutant concentration in the inlet gas, empty bed residence time (EBRT), nutrient composition, type of packing, etc. (Ménard et al., 2012).

Due to the complexity of landfill emissions in terms of pollutant concentrations and the simultaneous presence of several compounds alongside CH_4, the biofiltration of ternary mixtures containing CH_4 and VOCs have to be studied for a better understanding of interaction effects that might occur between different pollutants. Although multiple studies on the elimination of VOCs mixtures such as benzene, toluene, ethylbenzene and xylene (BTEX) have been reported (Akmirza et al., 2017; Amin et al., 2017; Strauss et al., 2004), studies aiming to investigate the biofiltration of CH_4 in presence of VOCs remain insufficient to predict the interaction effects between the components. Performances of previous biofiltration studies (2012-2022) on CH_4, X and EB biodegradation as single pollutants or in a mixture are presented in Table 4.1.

The eliminations of CH_4, X or EB as single pollutants in biofilters have been reported in the literature. Jawad et al., (2021) used a compost based-bed biofilter for an EBRT of 3 min and CH_4 inlet load (IL) of 0.015 $g.m^{-3}.h^{-1}$ to obtain a CH_4-removal efficiency (RE) of 72% while Ferdowsi et al., (2016) obtained CH_4-REs up to 87% for an IL of 7 $g.m^{-3}.h^{-1}$ and an empty bed residence time (EBRT) of 6 min in an inorganic packed-bed biofilter. For longer EBRTs of 20 min (Kim et al., (2013), CH_4-IL = 100 $g.m^{-3}.h^{-1}$) and 40 min (Lebrero et al., (2016), CH_4-IL = 20 $g.m^{-3}.h^{-1}$), CH_4-REs of 83% and 95% were achieved, respectively. In case of VOCs, the increase in EBRT from 7 to 45 s resulted in EB-RE elevation from 35 to 71% for EB concentration around 200 ppmv (Qian et al., 2018) while Natarajan et al., (2015) obtained 98% EB-RE for EB-IL of 12.8 $g.m^{-3}.h^{-1}$ and EBRT of 4.7 min. Xylene-REs in the range of 60-90% were obtained for ILs of 9-55 $g.m^{-3}.h^{-1}$ at an EBRT of 2.45 min (Rene et al., 2010). For a relatively high EBRT of 11.7 min, Singh et al., (2017) obtained X-RE between 70-75% for X-ILs of 8.2-11.2 $g.m^{-3}.h^{-1}$. Literature results indicate that biofiltration could be an efficient option for the biodegradation of CH_4, X and EB as single pollutants if the appropriate operating conditions are satisfied.

Table 4. 1: Previous works on biofiltration of methane (CH_4), xylene (X) and ethylbenzene (EB) in the period of 2012-2022

Pollutant	Packing	Empty bed residence time (EBRT) (min)	Inlet load (IL) ($g.m^{-3}.h^{-1}$)	Elimination capacity (EC) ($g.m^{-3}.h^{-1}$)	Removal efficiency (RE) (%)	References
CH_4	Soil-compost	78	83.4	80.9	97	Rose et al., (2012)
	Stones	4.2	68	44.2	65	Avalos Ramirez et al., (2012)
	Stones	4.2	38	16.3	43	Girard et al., (2012)
	Activated carbon-pumice	20	76	62.3	82	Kim et al., (2013)
	Activated carbon, plastic balls and gravel	20	100	83	83	Kim et al., (2014)
	Coal	2.4	139	41.7	30	Limbri et al., (2014)
		1.6	208	41.6	20	
	Wood pine, bark chips, perlite and compost	4.4	17	10.5	62	Hernández et al., (2015)
	Concrete	0.8	39.3	11.5	28.7	Ganendra et al., (2015)
	Perlite-volcanic pumice soil	58	52	30.16	58	Syed et al., (2016)
	Sponge	7.4	20	3	15	Brandt et al., (2016)
	Inorganic-based bed	6	7	6	87	Ferdowsi et al., (2016)
	Compost	20-40	20-41	20-38	93-100	Lebrero et al., (2016)
	Polyurethane	6.5	12.4	3.6	29	Gómez-Cuervo et al., (2017)
	Bark chips-perlite-compost	4	22-55	4.6-9.3	17-21	
	Compost	27-135	66	9.4-54	35-82	Farrokhzadeh et al., (2017)
	Kaldnes rings	17.1	108	21.6	20	López et al., (2018)
	Biochar-lava rock-compost	82.8	36	36	100	La et al., (2018)
	Compost	24-186	542	24.4	58	Fjelsted et al., (2020)
	Vermiculite	13	300-450	48-76	16-17	Vergara-Fernandez et al., (2020)
	Inorganic-based bed	6	13	8	62	Khabiri et al., (2020)
	Mature compost	23	20-25	14-22.5	70-90	Gómez-Borraz et al., (2022)
X	Sawdust-animal manure	0.7-2.3	31.5	29	92	Prenafeta-Boldú et al., (2012)
	Corn cob	1.2	15.8	15.5	97.8	Rahul et al., (2013)
	Scoria-compost	1.5	53.6	52.5	98	Amin et al., (2014)
	Date palm tree bark	2	3-214	3-192.6	>90	Natarajan et al., (2014)

	Pressmud	2.8	4.1	4	99	Saravanan et al., (2015)
	Compost	0.9-1.3	20-500	13-325	65	Chang et al., (2015)
	Biochar	0.5	120	103.2	86	Baltrėnas et al., (2016)
	Charcoal	30	0.2-1.6	0.2-1.5	>95	Singh et al., (2017)
		12	8-11	5.6-8.3	70-75	
	Compost	0.4	0.015-0.022	0.012-0.013	60-80	Luengas et al., (2017)
	Black slag	0.8	68	26.5	39	Gallastegui et al., (2017)
		1.5	28	18.5	66	
		3	18	18	100	
	Compost	2.5	4.2	3.6	87	Rene et al., (2018)
	Scoria-compost	1.5	61	42.7	70	Heidari et al., (2019)
	Polyurethane foam	1	150	139.5	93	Li et al., (2020)
	Inorganic-based bed	4.5	10-30	9-24	80-90	Merouani et al., (2022)
EB	Sawdust-animal manure	0.7-2.3	35	34	97	Prenafeta-Boldú et al., (2012)
	Perlite	1	127	57.2	45	Hinojosa-Reyes et al., (2012)
	Macadamia nutshells	1.5	12-50	11.4-30	60-95	Volckaert et al., (2013)
	Organic waste soil	1.7-3.8	10-30	9-21	70-90	Gallastegui et al., (2013)
	Tree bark	4.7	12.76	12.5	98	Natarajan et al., (2015)
	Black slag	3	4.5-16.1	4-14.4	90	Gallastegui et al., (2017)
	Perlite	0.5-1.5	1.4-232	1.2-192.6	83	Mohammad et al., (2017)
	Inorganic-based bed	4.5	10-30	9-25.5	85-90	Merouani et al., (2022)
X+EB	Date palm tree bark	4.7	X-IL: 13-51 EB-IL: 13-51	X-EC: 10.14-29.6 EB-EC: 11.6-34.7	X-RE: 58-78 EB-RE: 68-89	Natarajan et al., (2017)
X+CH_4	Inorganic-based bed	4.5	CH_4-IL: 20-100 X-IL: 10-32	CH_4-IL: 11-54 X-IL: 8-29	CH_4-RE: 50-60 X-RE: 75-90	Merouani et al., (2022)
EB+CH_4			CH_4-IL: 20-100 EB-IL: 10-30	CH_4-IL: 11-54 EB-IL: 8-28	CH_4-RE: 50-60 EB-RE: 75-90	
BTEX	Corn cob	1.15	63	60.48	96	Rahul et al., (2013)
	Polyurethane	45	25.8	15.74	61	Sun et al., (2020)
BTEX+CH_4	Compost/expanded clay	1680	CH_4-IL: 12 BTEX-IL: 0.005	CH_4-EC: 10.8 BTEX-EC 0.005	CH_4-RE: 90 BTEX-RE: >99	Zdeb and Lebiocka, (2016)

The simultaneous presence of CH_4 and VOCs in LE can affect the individual elimination of each component either negatively (antagonistic effect), positively (synergistic effect) or neutrally (neutral effect) (Yang et al., 2018). The presence of another carbon source in the mixture of CH_4/VOCs could increase the microorganisms growth and further enhance the CH_4 elimination (Vergara-Fernández et al., 2006). For Example, Vergara-Fernandez et al., (2020) reported that n-pentane addition at an IL of 107 $g.m^{-3}.h^{-1}$ increased CH_4 EC from 12 to 21 $g.m^{-3}.h^{-1}$ for a CH_4-IL of 60 $g.m^{-3}.h^{-1}$ and an EBRT of 13 min. Kim et al., (2013) indicated that dimethyl sulfide (DMS) at an IL of 1 $g.m^{-3}.h^{-1}$ had a synergistic effect on CH_4 biodegradation as CH_4-RE was 83% compared to 76% in DMS absence for CH_4-ILs between 30-110 $g.m^{-3}.h^{-1}$ and an EBRT of 18 min. On the other hand, the addition of benzene and toluene at an IL of 0.5 $g.m^{-3}.h^{-1}$ each negated the synergistic effect of DMS on CH_4 and dropped CH_4-RE to 64%.

An important parameter for biofiltration of binary and ternary mixtures is EBRT as it directly affects the transfer of pollutants from gas phase to the liquid phase. This parameter is inversely proportional to gas flow rate and directly proportional to the volume of the biofilter. It is therefore a determining parameter in the design of the biofilter. A high EBRT (low gas flow rate with high biofilter volume) will provide sufficient time for pollutants to be transferred to the biofilm. On the other hand, a low EBRT will induce the opposite effect and part of the pollutants such as hydrophobic compounds will leave the biofilter untreated. The effect of EBRT on individual CH_4, X and EB REs in biofilters has already been studied and EBRTs between 3-40 min were suggested for CH_4-REs above 50% while EBRTs less than 3 min were usually sufficient to obtain VOC-REs above 90% (Iranpour et al., 2005; La et al., 2018a). The EBRT in a mixture containing CH_4 and VOCs needs to provide a proper transfer time for all pollutants into the biofilm and particularly for CH_4 since it is less soluble than VOCs and more abundant in the mixture of LE (Nikiema and Heitz, 2009; Vergara-Fernandez et al., 2020). However, an increase in EBRT can also result in a saturation of the biofilm with a particular pollutant compared to other mixture's components causing an inhibition for the other substrates.

The novelty of this study refers to the simultaneous biofiltration of CH_4, X and EB in a ternary mixture that was studied for the first time to the authors' best knowledge. Since anaerobic reactions in landfills are affected by several parameters such as external weather and the composition of the deposit wastes, the concentration of LE is in permanent fluctuation (Pecorini and Iannelli, 2020). A biofilter treating LE must consider the effect of changes in operating parameters that could affect its performance. Furthermore, the changes in operating parameters such as pollutant concentrations and EBRT might also influence each pollutant's biodegradation differently and most therefore be studied.

The main objective of this study was to achieve a better comprehension of interaction effects between CH_4, X and EB under different concentration changes and absence/presence of either CH_4 or the VOCs. The effect of different ILs of VOCs on CH_4 biodegradation and different CH_4-ILs effect on VOCs elimination were studied under different EBRTs. Carbon dioxide production (PCO_2) and composition of biofilters' leachates were also analyzed.

4.4. Material and methods

4.4.1. Biofilters experimental set-up

Nine (9) lab-scale biofilter units were used for the experiments with each biofilter functioning at different operating conditions for a duration of approximately 242 days depending on the required time to reach a pseudo-steady state. The biofiltration experiments were carried out in

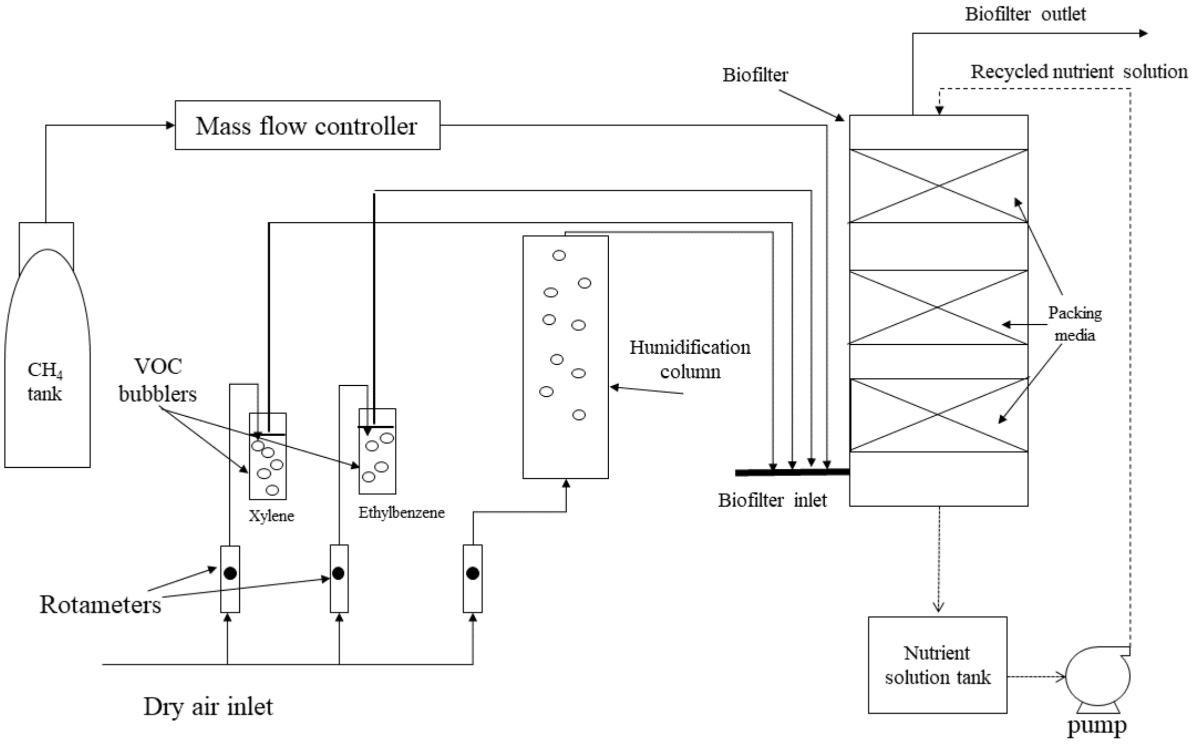

Figure 4.1 : Experimental set-up for biofiltration of CH_4 and VOCs (X and EB)

9 Phases. The biofilter columns (Figure 4.1) were made of plexiglass with 1 m height and 0.15 m diameter (a total volume of 0.018 m^3). The biofilter columns contained 3 sections of 0.3 m each along with measurement ports (4 in total including inlet measurement port). Biofilter packings were inorganic stone materials whose name cannot be mentioned for confidentiality agreements. Upper and middle sections' packings had a lower void fraction than bottom section as a precaution to avoid excess biomass accumulation (Ferdowsi et al., 2019). The properties of both types of packings are presented in Table 4.2 (Nikiema and Heitz, 2010).

Mass flow controllers were used to control the flow rate of CH_4 from a cylinder (Praxair Inc., Canada). Dry air was divided into 3 flows controlled by rotameters (Brooks, USA), one was passed through a humidifier column (0.1 m diameter) providing humid air with a relative humidity of 90%. The two other flows (dry air) were injected through two VOC bubblers: one for EB (>99%, Sigma-Aldrich, USA) and the other for X (>99%, Fisher chemicals, USA). The humid air, VOCs and CH_4 were injected at the bottom of the biofilter column. The biofilters were irrigated by a nutrient solution (NS) every 2 days at a $60*10^{-3}$ $m^3.h^{-1}$ rate for 2 min long. The NS was recycled in 0.02 m^3 tanks; the composition of the NS was reported by Khabiri et al. (2020a). The pH of the NS was neutral around 7.

4.4.2. Analytical tools

Methane and VOCs concentrations were analyzed from different biofilter sampling ports using a total hydrocarbon analyzer (FIA 510, Horiba, Japan). Carbon dioxide emissions were measured using a CO_2 gas analyzer (Ultramat 22P, Siemens, Germany). For leachate analysis, an ion chromatograph (ICS-1000, Dionex, USA) equipped with an AS23-4 column and conductivity/UV detector (225µm) was used to determine the concentration of nitrates (NO_3^-), phosphates (PO_4^{3-}) and sulphates (SO_4^{2-}) in leachate samples.

Table 4. 2: Packing media properties

Section	Top and middle	Bottom
Average diameter (mm)	5.0	7.5
Void fraction (dimensionless)	0.43	0.55
Water holding capacity (dimensionless)	0.07	0.15
Density ($kg.m^{-3}$)	1200	750
Specific surface area ($m^2.m^{-3}$)	1250	470

A total organic carbon analyzer (TOC-VE, Shimadzu, Japan) was used to determine the concentration of organic carbon in leachate samples. Pressure drop was measured using a differential manometer (Type 4, Air Flow Developments, UK) and remained relatively low at around 0.03-0.05 mmHg/m during the study.

4.4.3. Performance parameters

The following parameters were used to assess the performances of the biofilters:

- Inlet load: $IL= C_{in}\ Q/V\ [g.m^{-3}.h^{-1}]$ (5)

- Elimination capacity: $EC= (C_{in} - C_{out})\ Q/V\ [g.m^{-3}.h^{-1}]$ (6)

- Removal efficiency: $RE=100*(C_{in} - C_{out})/C_{in}\ [\%]$ (7)

- CO_2 production rate: $PCO_2 = (C(CO_2)_{out}-C(CO_2)_{in})\ Q/V\ [g.m^{-3}.h^{-1}]$ (8)

C_{in} and C_{out} indicate the inlet and outlet pollutant concentrations, respectively ($g.m^{-3}$) whereas $C(CO_2)_{in}$ and $C(CO_2)_{out}$ are the CO_2 concentrations in the biofilters at the inlet and outlet, respectively ($g.m^{-3}$) while $Q(m^3.h^{-1})$ and $V(m^3)$ are the flow rate and bed volume of the biofilter, respectively.

4.4.4. Experimental methods and operating conditions

The biofiltration was initiated without inoculation to allow the development of microorganisms based on the pollutants present in the feed (Ferdowsi et al., 2019). The packing media being inorganic, the possible sources of microorganisms were inlet air, tap water used for humidification, the NS and possible MOs present on the surface of the packing media.

The experiments were divided in two parts: The first part was assigned to the study of CH_4 and VOCs concentration effects while EBRT was fixed at 4.5 min in biofilters treating a) only CH_4 (P1), b) a binary mixture of X and EB (P2) and c) a ternary mixture of CH_4, X and EB (P3).

In the first Phase (P1), concentration of CH_4 as single pollutant increased from 2000 to 10000 ppmv. In Phase 2 (P2) for a binary mixture of X and EB, the individual concentrations of each VOC increased from 200 to 600 ppmv and in Phase 3 (P3) for CH_4,

X and EB, designed for a comparison with P1 and P2, CH_4 concentration was increased from 2000 to 10000 ppmv while both VOCs (X and EB) individual concentrations were increased from 200 to 600 ppmv.

The second part aimed to study the effect of EBRT on CH_4 elimination (CH_4 concentration in range of 2000 to 10000 ppmv) in the absence and presence of the 2 VOCs (X and EB) having fixed concentrations of 200 ppmv each. Three (3) Phases (P4, P5 and P6) were dedicated to CH_4 alone for the evaluation of EBRT effect on CH_4 removal in the absence of X/EB while EBRT was increased from 2.25 to 4.5 then to 9 min; meanwhile, 3 other Phases (P7, P8 and P9) were assigned to CH_4, X/EB in a mixture wherein CH_4 concentration was increased from 2000 to 10000 ppmv and EBRT was varied from 2.25 to 4.5 and to 9 min.

Table 4. 3: Operating conditions during the experiments

Part	Phase	CH_4 concentration (ppmv)	X and EB concentration (ppmv)	EBRT (min)
1	P1	2000 -» 6000 -» 10000	-	4.5
	P2	-	200/200 -» 400/400 -» 600/600	
	P3	2000 -» 6000 -» 10000	200/200 -» 400/400 -» 600/600	
2	P4	2000 -» 6000 -» 10000	-	2.25
	P5	2000 -» 6000 -» 10000	-	4.5
	P6	2000 -» 6000 -» 10000	-	9
	P7	2000 -» 6000 -» 10000	200/200	2.25
	P8	2000 -» 6000 -» 10000	200/200	4.5
	P9	2000 -» 6000 -» 10000	200/200	9

The VOC's individual concentrations were kept constant at 200 ppmv each. Sample analysis for CH_4 and VOCs and CO_2 were carried out each 3 days and leachate samples were taken from the NS tanks every week. Table 4.3 provides a summary of the different operating conditions during this study.

4.5. Results and discussion

4.5.1. The effect of CH_4 and VOCs concentrations on CH_4 elimination

Figure 4.2 shows CH_4-REs as a function of its concentration (2000, 6000 and 10000 ppmv) in the absence of X/EB and in a ternary mixture with 3 levels of X/EB concentrations (200/200, 400/400 and 600/600 ppmv) at a fixed EBRT of 4.5 min. The REs presented are the average values obtained in the pseudo-steady state conditions for each concentration of pollutant.

In absence of X/EB, CH_4-RE reached the highest value of 57±3% for a CH_4 concentration of 2000 ppmv (corresponding to a CH_4-IL of 38±1 $g.m^{-3}.h^{-1}$). For a CH_4-IL around 40 $g.m^{-3}.h^{-1}$ and a similar EBRT, Girard et al., (2011) obtained a CH_4-RE of 38% in a gravel packed-bed biofilter. On the other hand, Lebrero et al., (2016) obtained a 90% CH_4-RE for an IL of 41 $g.m^{-3}.h^{-1}$ and an EBRT of 20 min in a compost biofilter. The higher CH_4-RE obtained by

Lebrero et al. [18] could be related to the high EBRT and the nature of the packing (the authors inoculated a compost bed with a pure strain of *Graphium* sp.).

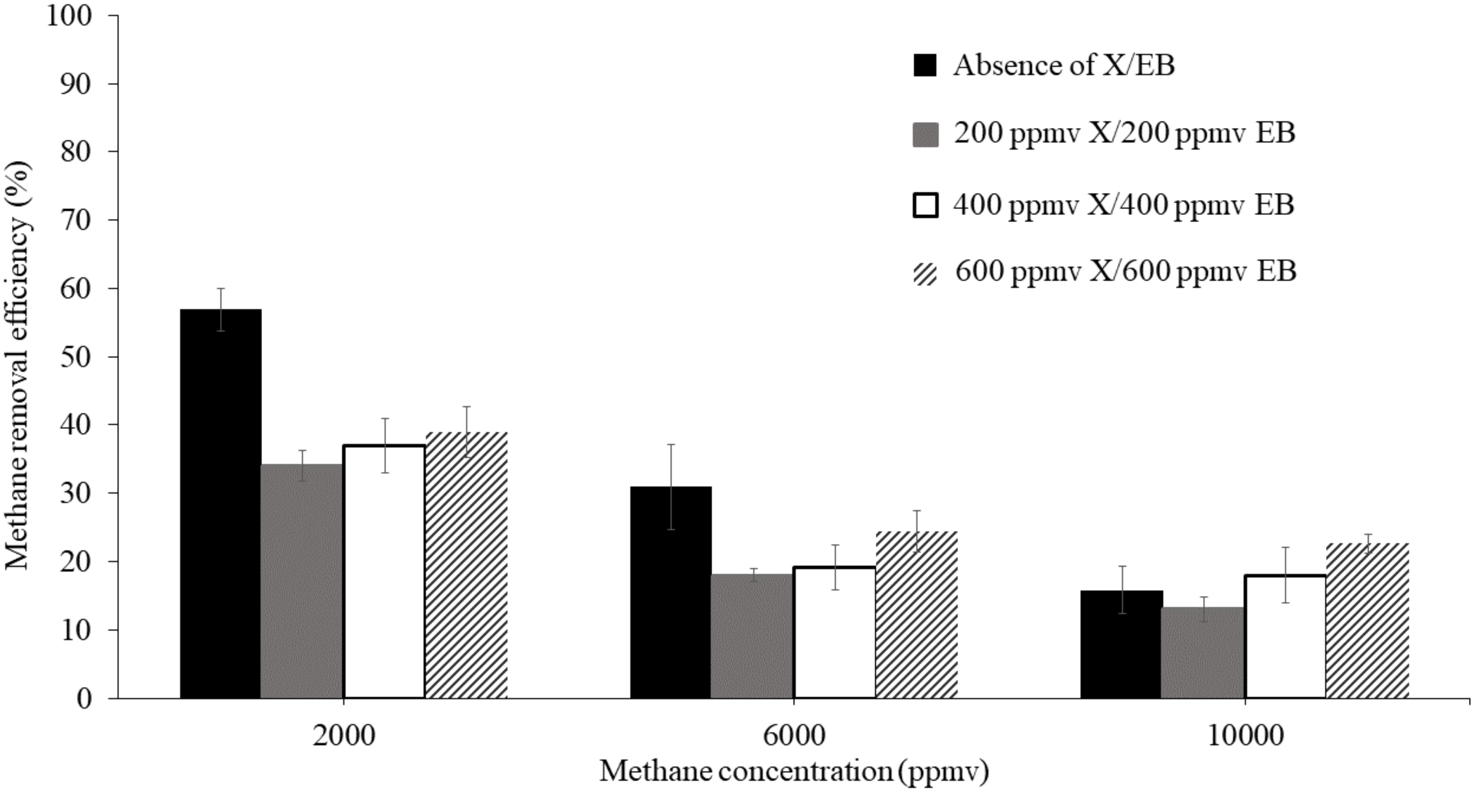

Figure 4.2 : Methane removal efficiency as a function of CH_4 concentration in presence (ternary mixture) and absence of X/EB (single pollutant) at an EBRT of 4.5 min

According to Figure 4.2, increasing CH_4 concentration to 6000 and then to 10000 ppmv (corresponding to ILs of 113±2 and 190±2 $g.m^{-3}.h^{-1}$, respectively) reduced CH_4-RE by 45% and 48%, respectively in VOCs absence. The RE decrease by increasing CH_4 concentration has been commonly reported in the literature and is usually attributed to kinetic limitations due to an increase in CH_4 presence in the biofilm phase (Ferdowsi et al., 2016; La et al., 2018a).

According to Figure 4.2, for CH_4 concentrations of 2000 and 6000 ppmv (corresponding to ILs of 38±1 and 113±2 $g.m^{-3}.h^{-1}$, respectively), CH_4-REs in presence of X/EB were lower than CH_4-REs in X/EB absence. For a CH_4 concentration of 2000 ppmv in the presence of VOCs at individual concentrations in the range of 200-600 ppmv, CH_4-REs between 34-39% were obtained in VOCs presence compared to 57±3% in the VOCs absence. Furthermore, CH_4-REs were in the range of 18-24% in VOCs presence compared to 31±6% in VOCs absence for CH_4

concentration of 6000 ppmv. When CH_4 concentration was increased to 10000 ppmv (corresponding to an IL of 192±1 $g.m^{-3}.h^{-1}$), CH_4-REs were relatively close in case of X/EB absence (16±3%) and presence (13-23%). The overall higher CH_4 conversion in case of X/EB absence can be related to X/EB causing inhibition on microorganisms (MOs) responsible for CH_4 elimination by blocking the substrate-enzyme binding (Lee et al., 2011). Xylene was already proven to have an inhibitive effect on CH_4 biodegradation while EB was found to have a mildly neutral effect (Merouani et al., 2022). A BTEX (benzene-toluene-EB-X) mixture at a concentration lower than 1 $g.m^{-3}$ was proven to have an inhibiting effect on CH_4 elimination by decreasing the CH_4-RE from 100 to 91% even for a high EBRT of 28 h and a low IL of 12 $g.m^{-3}.h^{-1}$ (Zdeb and Lebiocka, 2016). Other aromatic VOCs have also been reported to have an inhibitory effect on CH_4 elimination such as toluene (Ménard et al., 2014) or styrene (Khabiri et al., 2020b).

Although the presence of X/EB generally reduced CH_4 biodegradation compared to their absence, increasing the VOCs concentrations resulted in a slight CH_4-RE increase for a constant CH_4 inlet concentration. As shown in Figure 4.2, increasing the X/EB concentrations from 200/200 ppmv to 600/600 ppmv resulted in CH_4-RE increases from 34±4 to 39±2%, from 18±3 to 24±1% and from 13±1 to 23±2% for constant respective CH_4 inlet concentrations of 2000, 6000 and 10000 ppmv. This increasing trend indicated that despite VOCs presence having a negative impact on CH_4 elimination, the abundance of VOCs in the biofilm when their inlet concentration was increased could have stimulated the growth and development of MOs and lead to higher CH_4-REs (Vergara-Fernandez et al., 2020).

Kim et al., (2013) mentioned that the presence of several substrates (benzene and toluene in the presence and absence of DMS) in a CH_4 biofilter could alter the microbial structure in the biofilm and would result in changes to MOs communities. For example, the presence of DMS favoured the development of *Methylosarcina* while *Methylomonas* was the dominant species in presence of toluene and benzene. This diversity of MOs could have a positive, negative or neutral effect on methanotrophs depending on the nature of substrates present in the biofilm (Liao et al., 2018). In the present study, the simultaneous presence of X and EB with CH_4 had an inhibiting effect on CH_4 biodegradation. On the other hand, a change in pollutants concentrations for a mixture can possibly influence the MOs diversity in biofilm resulting in a synergistic effect in the favour of CH_4 degradation (Albanna et al., 2010).

4.5.2. Methane and the VOCs concentrations combined effects on the VOCs elimination

Figures 4.3 (a) and (b) present X and EB-REs in the absence and presence of CH_4 (in P2 and P3) as a function of their concentrations, respectively. In case of CH_4 absence, the concentrations of X/EB were increased from 200 to 600 ppmv corresponding to an IL increase from 27±1 to 75±2 $g.m^{-3}.h^{-1}$ and 26±5 to 75±1 $g.m^{-3}.h^{-1}$ for X or EB, respectively at a fixed EBRT of 4.5 min. As a result, X and EB-REs decreased from 57±1 to 6±2% and 60±1 to 9±2%, respectively. The X and EB-REs decreasing trend as a function of their concentrations augmentation in a binary mixture was similar to the results reported by Natarajan et al., (2017) who treated a X/EB binary mixture and observed REs decreases from 78 to 58% and from 89 to 68% for X and EB, respectively, after the individual VOC-ILs were increased from 13 to 51 $g.m^{-3}.h^{-1}$. Since EBRT was 4.7 min (close to 4.5 min used in the current study), the biofilter used by Natarajan et al., being inoculated with a mixed microbial culture could be the reason for higher REs compared to the current study in which the biofilter had not been inoculated.

Higher REs were obtained in the individual biofiltration of X or EB. For instance, Li et al., (2020) obtained a X-RE of 93% for an IL of 22.5 $g.m^{-3}.h^{-1}$ and an EBRT of 80 s. Heidari et al., (2019) obtained a X-RE of 70% for an IL of 61 $g.m^{-3}.h^{-1}$ and an EBRT of 90 s. Ethylbenzene-REs above 90% were obtained by both Volckaert et al., (2013) at an IL of 85 $g.m^{-3}.h^{-1}$ and an EBRT of 90 s and Gallastegui et al., (2017) at an IL of 27 $g.m^{-3}.h^{-1}$ and an EBRT of 90 s, respectively. The REs of X and EB in a mixture in the current study were found to be lower than in case of individual biofiltration of the VOCs under similar concentrations and lower EBRTs probably due to interactions between the different substrates. The biofiltration of aromatic VOCs in complex mixtures usually causes inhibition for components biodegradation (Aizpuru et al., 2001; Yang et al., 2018).

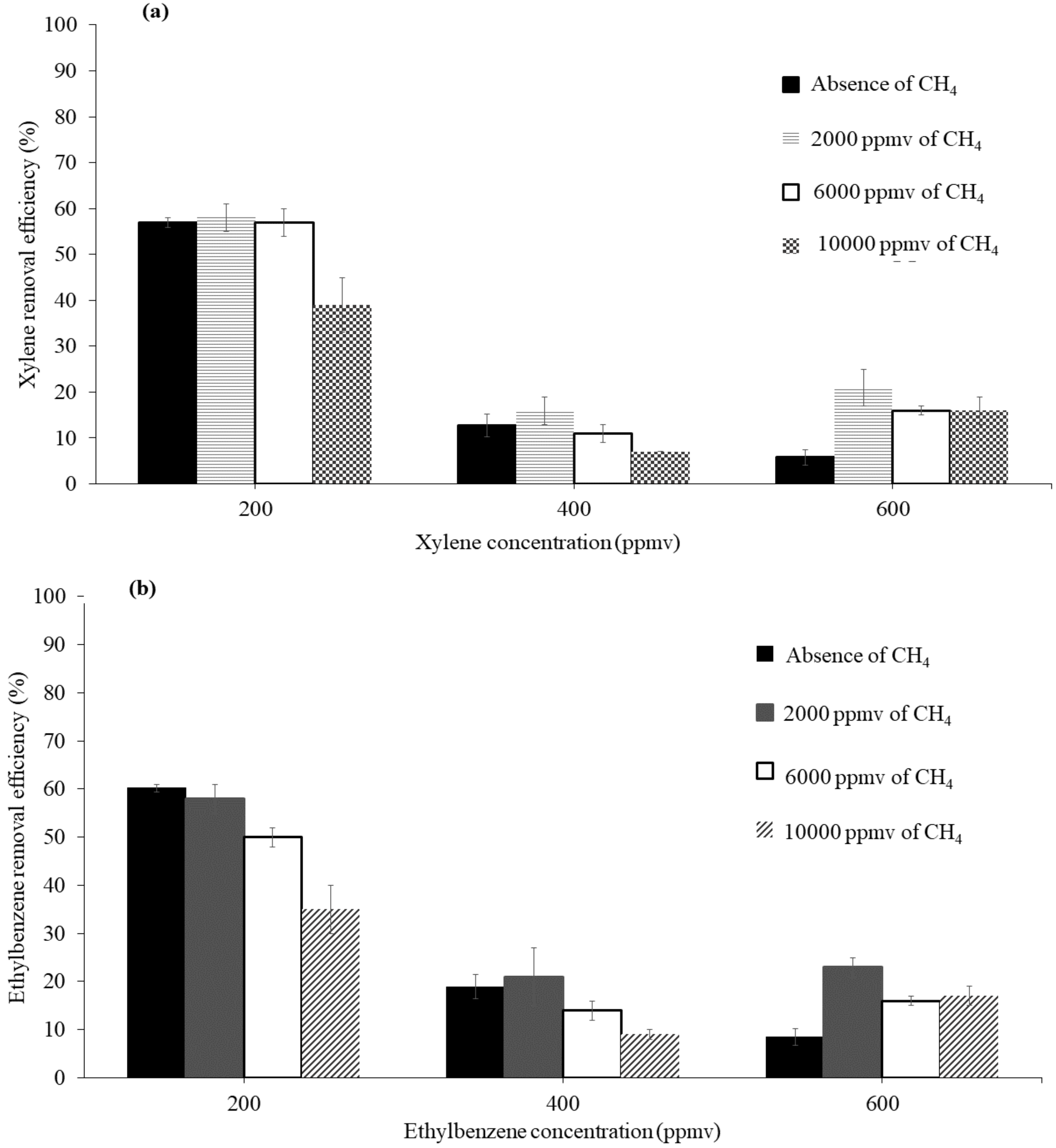

Figure 4.3 : Removal efficiencies of (a) X and (b) EB as a function of their concentrations in the presence (ternary mixture) and absence (binary mixture) of CH_4 at an EBRT of 4.5 min

In biofiltration of BTEX mixtures, X was usually the compound with the lowest REs due to inhibition by the rest of the pollutants. Previous studies confirmed that X is more sensitive to EB presence than EB to X (Akmirza et al., 2017; Rene et al., 2018; Strauss et al., 2004; Yang et al., 2018). This could explain the reason behind X-REs being generally around 10% lower compared to EB-REs in the current study.

According to Figure 4.3 (a), in CH_4 presence, for X concentrations of 200 ppmv, X-RE remained constant at 58±3% for CH_4 concentrations varying from 2000 to 6000 ppmv, then decreased from 58±3 to 39±3% with CH_4 concentration increasing from 6000 to 10000 ppmv. For a X concentration of 400 ppmv, X-RE decreased from 16±3 to 7±0% when CH_4 concentration was increased from 2000 to 10000 ppmv. For X concentration of 600 ppmv, X-REs were slightly higher (X-RE in the range of 21-16%) compared to a X concentration of 400 ppmv, and no significant decrease was observed as a function of CH_4 concentration increase. The same EB-RE decreasing trend was observed for all EB concentrations (Figure 4.3 (b)) when CH_4 concentration was increased from 2000 to 10000 ppmv with slightly higher EB-REs compared to X-REs. Ethylbenzene-RE decreased from 58±3 to 35±5% and from 21±6 to 9±1% as a function of CH_4 concentration increase from 2000 to 10000 ppmv for EB concentrations of 200 and 400 ppmv, respectively. Similarly, to the trend of X-RE under high X concentration of 600 ppmv (Figure 4.3 (a)), for an EB concentration of 600 ppmv, EB-REs did not significantly change and were in the range of 17-24% for CH_4 concentrations increasing from 2000 to 10000 ppmv. In a study conducted on the biofiltration of binary mixtures (CH_4-X and CH_4-EB) under an EBRT of 4.5 min with the same inorganic packing materials as the present study, increasing CH_4 concentrations from 2000 to 10000 ppmv had a lower inhibitory effect on X and EB biodegradation at VOCs concentrations of 500 ppmv as VOCs-REs only decreased from 90 to 75% (Merouani et al., 2022). In the current study, more complex interactions between the 3 pollutants in the ternary mixture could explain the lower X and EB-REs by more than 30% compared to the binary mixture (Merouani et al., 2022). The observed decrease in X and EB-REs induced by CH_4 concentration increase could be attributed to the kinetic limitations related to substrate overload in the biofilm being higher than the threshold that MOs could withstand and resulting in a decrease bacterial activity (Cabrol and Malhautier, 2011; Vergara-Fernandez et al., 2020).

It is worth mentioning that in case of high X/EB concentrations (Figure 4.3 at concentrations of 600 ppmv) X and EB-REs in CH_4 presence were around 50% higher than in CH_4 absence. A possible explanation could be that abundance of CH_4 led to a higher development of methanotrophs and other MOs and possibly triggered a more diverse microbial community able to biodegrade X and EB at a higher extent. Methanotrophs were reported to be able to biodegrade VOCs like methanol, trichloroethylene and aromatic compounds like benzene and toluene (Hanson and Hanson, 1996; Lee et al., 2010).

4.5.3. Effect of EBRT on the pollutants' removal efficiencies

4.5.3.1. Absence of VOCs

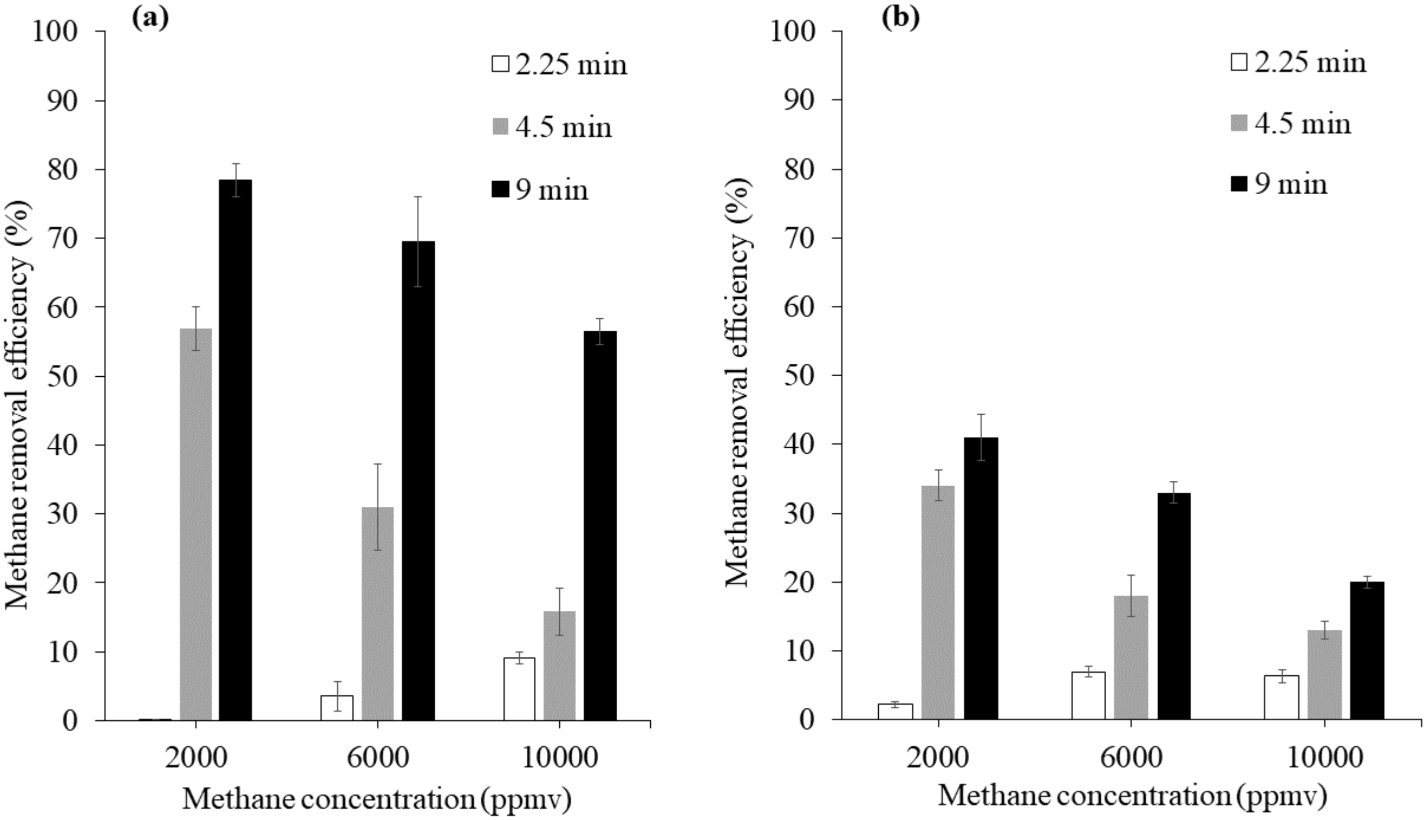

Figure 4.4 : Methane removal efficiency as a function of CH_4 concentration and EBRT (a) in X/EB absence and (b) in X/EB presence (200/200 ppmv)

The effect of EBRT on CH_4-RE in absence of VOCs (P4, P5 and P6) and presence of VOCs at individual concentrations of 200 ppmv for X and EB (P7, P8 and P9) are presented in Figures 4.4 (a) and (b), respectively. According to Figure 4.4 (a), CH_4-REs at an EBRT of 9 min were

78±2, 69±7 and 56±2% for CH_4 concentrations of 2000, 6000 and 10000 ppmv, respectively, corresponding to ILs of 10±1, 30±1 and 48±0 $g.m^{-3}.h^{-1}$. Furthermore, a maximum EC of 35±4 $g.m^{-3}.h^{-1}$ at a critical IL of 113±2 $g.m^{-3}.h^{-1}$ was obtained which could be explained with the high EBRT and the absence of other pollutants that could have inhibited CH_4 biodegradation.

Methane-REs at an EBRT of 4.5 min were lower than at an EBRT of 9 min by 27, 55 and 71% for CH_4 concentrations of 2000, 6000 and 10000 ppmv, respectively, corresponding to ILs of 19±0, 58±2 and 97±2 $g.m^{-3}.h^{-1}$, respectively. In absence of VOCs, CH_4-REs were the lowest at an EBRT of 2.25 min compared to 4.5 min and 9 min. For an EBRT of 2.25 min, increasing CH_4 concentration from 2000 to 10000 ppmv caused a CH_4-RE increase from 0 to 9±1%.

Methane-RE increase as the result of increasing CH_4 concentration under a short EBRT of 2.25 min could be related to an increased diffusion of CH_4 to biofilm due to an elevated concentration gradient between the gaseous and liquid phases. In contrary, under higher EBRTs of 4.5 and 9 min, the biofilm phase was already saturated with CH_4 such that increasing CH_4 concentration from 2000 to 10000 ppmv would further inhibit the MOs probably with no significant improvement on the gas-liquid CH_4 concentration gradient (La et al., 2018a).

The effect of EBRT on CH_4-REs agreed previous studies on a CH_4 biodegradation. For instance, Nikiema et al., 2009 reported a CH_4-RE increase from 35 to 95% when EBRT was increased from 3.2 to 9 min for a CH_4 concentration of 7500 ppmv. The reason behind CH_4-RE increase with increasing EBRT was related to a longer contact time between the pollutant and the biofilm, enhancing the mass transfer of CH_4 to the liquid phase (La et al., 2018a).

4.5.3.2. Presence of VOCs

In case of X/EB presence at individual concentrations of 200 ppmv (Figure 4.4 (b)), CH_4-REs for EBRTs of 4.5 min and 9 min were up to 50% lower than in absence of X/EB under the same EBRTs (Figure 4.4 (a)). However, the REs decreasing trend as a function of CH_4 concentration rise as well as EBRT reduction followed the same tendency as in X/EB absence for EBRTs of 4.5 and 9 min (moderate and high EBRTs, respectively). For example, at an EBRT of 9 min, CH_4-REs decreased from 41±3 to 33±2 and 20±1% when CH_4 concentrations increased from 2000 to 6000 and 10000 ppmv, respectively. For an EBRT of 4.5 min, CH_4-REs were around 40% lower than for an EBRT of 9 min. According to Figure 4.4 (b), for an EBRT of 2.25 min, the tendency of CH_4-RE as a function of CH_4 inlet concentration was increasing from 2000 to 6000 ppmv and slightly reversed for a CH_4 concentration variation from 6000 to 10000 ppmv, opposite to what occurred in the absence of X/EB (Figure 4.4 (a)) where CH_4-RE increased from 0 to 9±1%.

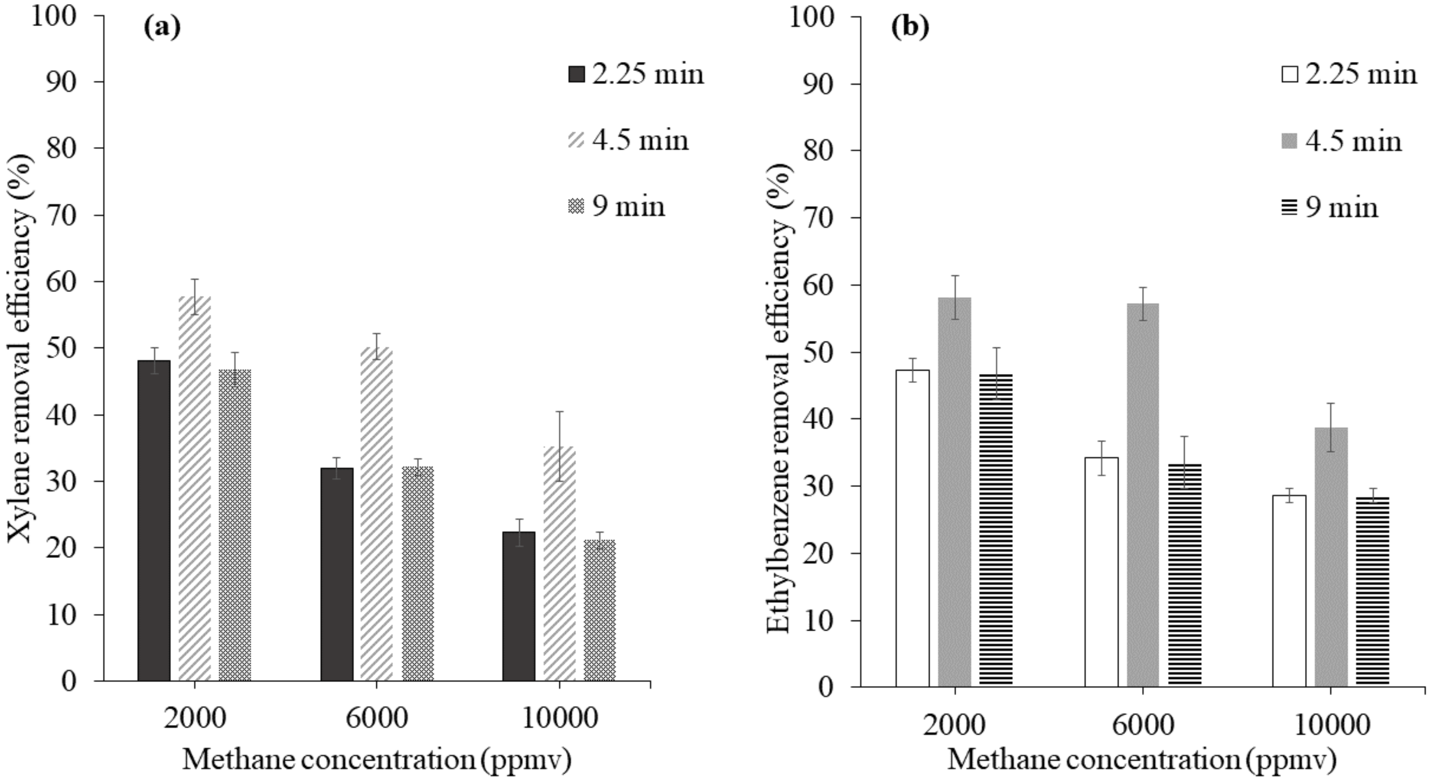

Figure 4.5 : Methane removal efficiency as a function of CH_4 concentration and EBRT (a) in X/EB absence and (b) in X/EB presence (200/200 ppmv)

Figures 4.5 (a) and (b) present X and EB-REs, respectively, as a function of CH_4 concentration while both VOCs concentrations were fixed at 200 ppmv at different EBRTs (2.25 min, 4.5 min and 9 min). For an EBRT of 2.25 min, X-REs were 48±2, 32±1 and 22±2% for CH_4 concentrations of 2000, 6000 and 10000 ppmv, respectively (Figure 4.5 (a)). Ethylbenzene-REs were nearly the same as X-REs with 47±2, 34±3 and 29±1% for CH_4 concentrations of 2000, 6000 and 10000 ppmv, respectively (Figure 4.5 (b)). An increase in CH_4 concentration in the range of 2000 to 10000 ppmv resulted in a decrease in VOC-REs regardless of EBRT. For example, the highest decrease in VOCs-REs as much as 30% was observed for a CH_4 concentration variation from 6000 to 10000 ppmv at an EBRT of 4.5 min. The extended availability of CH_4 in the biofilm phase could have inhibited VOCs biodegradation either by

CH_4 inhibitory effect on VOC-eliminating MOs or by competition between different MOs for nutrients (Albanna et al., 2010; Khabiri et al., 2020b).

For an EBRT of 4.5 min, both X and EB-REs were around 30% higher compared to the REs obtained for EBRTs of 2.25 and 9 min. Increasing EBRT from 4.5 min to 9 min caused a decrease in X and EB-REs with a respective reduction percentage of 20 and 19% for a CH_4 concentration of 2000 ppmv, 40 and 36% for a CH_4 concentration of 6000 ppmv and 25 and 40% for a CH_4 concentration of 10000 ppmv.

Although X and EB-REs were relatively in the same range of 20-58% for CH_4 concentrations between 2000 and 10000 ppmv and an EBRT ranges of 2.5 – 9 min (ternary mixture), the REs were lower than those previously reported in the literature for their individual elimination (Álvarez-Hornos et al., 2008; Cho et al., 2008; Gorka Gallastegui et al., 2017). Cho et al., (2008) investigated the elimination of X (inlet concentration of 155 ppmv) and EB (inlet concentration of 175 ppmv) separately in an organic packed biofilter and obtained REs of 69 and 68%, for X and EB respectively, for an EBRT of 0.8 min. The authors indicated that EBRTs lower than 1 min were sufficient to obtain REs higher than 90%. The relatively lower REs in the present study despite higher EBRTs could be related to the biofiltration of a ternary mixture inducing interaction effects between the VOCs (X and EB) and CH_4, the nature of packing (inorganic) and absence of initial inoculation.

It is worth mentioning that an EBRT of 9 min and a CH_4 concentration of 2000 ppmv (Figure 4.4 (b)) also coincided with the highest CH_4-REs in case of VOC-presence (200/200 ppmv) which indicates an abundance of CH_4 in the biofilm and the dominance of CH_4 degraders. Therefore, the decrease in VOC-RE in the present study when EBRT was increased from 4.5 to 9 min could be attributed to a saturated biofilm phase by CH_4 and the VOCs under a long EBRT of 9 min (Gómez-Cuervo et al., 2017).

The most suitable operating conditions for the elimination of X/EB (200/200 ppmv) in a ternary mixture with CH_4 was found to be an EBRT of 4.5 min at low CH_4 inlet concentration of 2000 ppmv.

4.5.4. The pollutants removal efficiency share by different biofilter sections

4.5.4.1. Methane removal efficiency

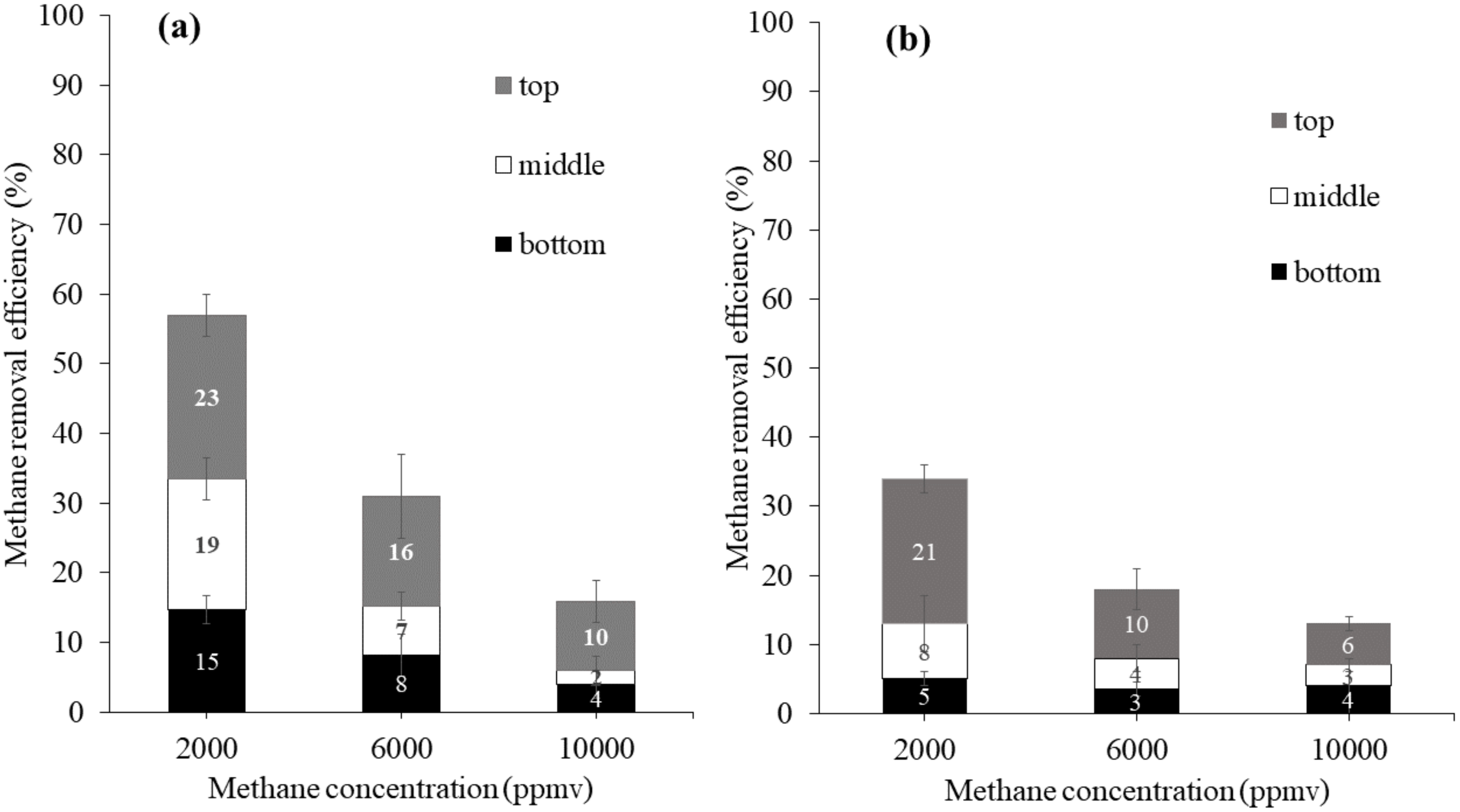

Figure 4.6 : Methane removal efficiency for the 3 sections of the biofilter as a function of CH_4 concentration (a) in X/EB absence and (b) X/EB presence (200/200 ppmv) at an EBRT of 4.5 min

Figures 4.6 (a) and (b) present CH_4-REs as a function of CH_4 inlet concentration for the 3 sections of the biofilter: bottom, middle and top in case of VOCs absence and presence, respectively for a fixed EBRT of 4.5 min. The highest CH_4-REs were located on the top section in ranges of 10-23% and 6-21% in VOCs absence and presence, respectively, contributing to more than 40% of the total CH_4 biodegradation in the bioreactor. The middle section was less effective on CH_4 elimination with CH_4-REs of 2-19% and 3-8% in VOCs absence and presence, respectively, which represented around 13-33% of the total CH_4 biodegradation in the biofilter. The bottom section had a lower contribution to CH_4-REs than the middle and top sections with CH_4-REs in the range of 4-15% and 3-5% in VOCs absence and presence, respectively, not exceeding 30% of total CH_4 biodegradation in the biofilter. The difference in pollutants REs between the middle-top sections and the bottom section could be due to the difference in specific surface area between the packings used for the middle-top sections (1250 $m^2.m^{-3}$) and bottom section (470 $m^2.m^{-3}$) (Courtois et al., 2015). An increase in CH_4 concentrations from 2000 to 10000 ppmv resulted in a decrease in CH_4-REs for all sections of the biofilter in both absence and presence of VOCs.

Several studies indicated that CH_4-REs are usually higher in bottom sections of up-flow biofilters and explained the decreasing trend across the height of the biofilters by the limitations of oxygen (O_2) while ascending along the biofilter (Fjelsted et al., 2020; Park et al., 2009; Pecorini et al., 2020b). For example, Pecorini et al., (2020b) obtained 50% of total CH_4-RE in the first 0.4 m of a 1 m height biofilter. The increasing CH_4-REs from bottom to top sections in the present study is an uncommon trend in CH_4 biofiltration. The same increasing CH_4-RE trend from bottom to upper sections was observed in absence and presence of VOCs which indicates that VOCs presence had no considerable impact on CH_4 biodegradation tendency in the

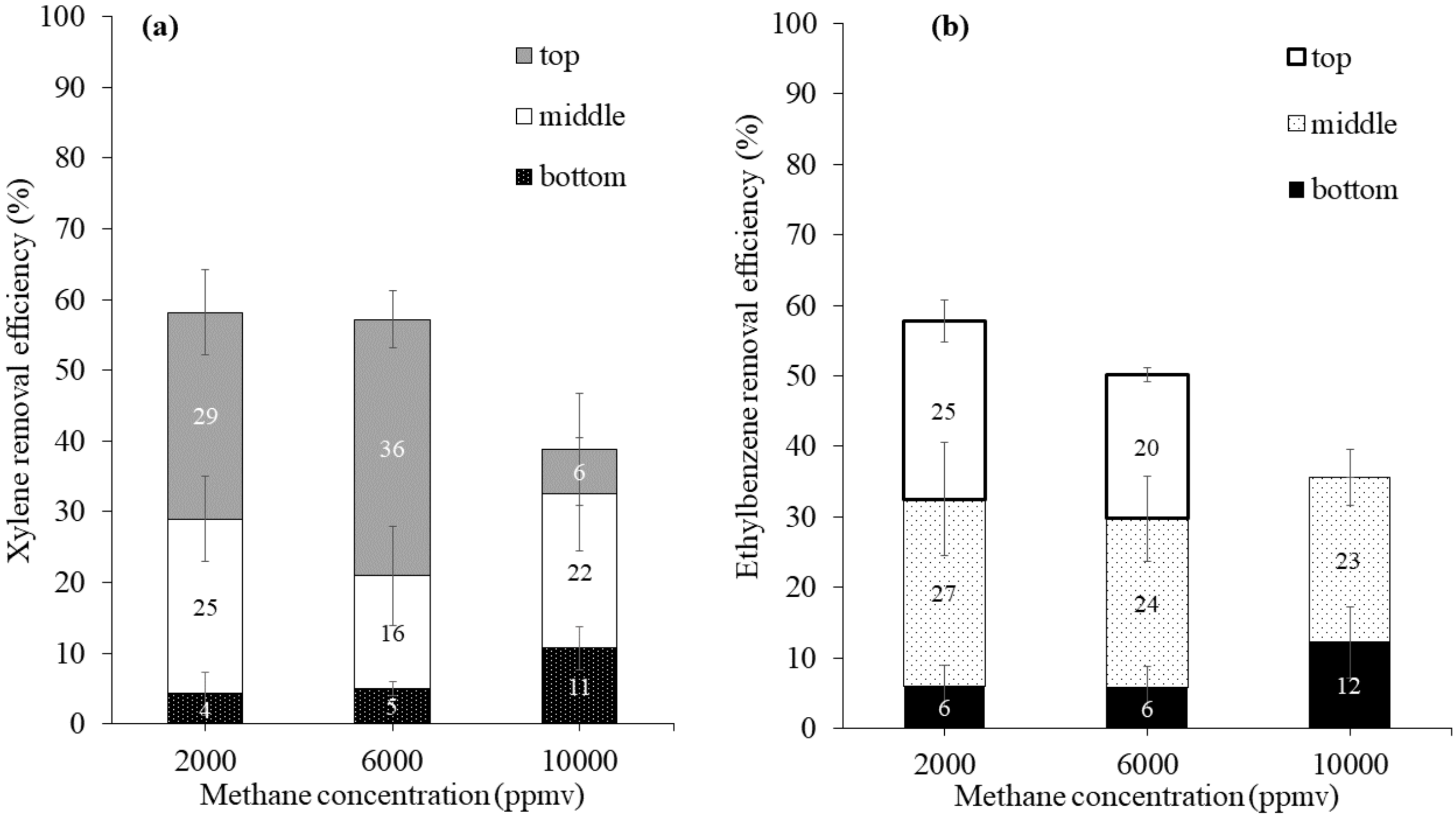

Figure 4.7 : Removal efficiencies of (a) X and (b) EB for the 3 sections of the biofilter as a function of CH_4 concentration at X/EB concentrations of 200/200 ppmv and an EBRT of 4.5 min

different sections of the biofilter. According to our knowledge, no such CH_4 elimination tendency was observed in previous studies of CH_4 biodegradation in up-flow biofilters.

4.5.4.2. VOCs removal efficiency

Xylene and EB-REs for each section of the biofilter under different CH_4 concentrations are presented in Figures 4.7 (a) and (b) respectively. For X (Figure 4.7 (a)), the upper section had the highest X-REs of 36±4% for CH_4 concentrations of 6000 ppmv. For CH_4 concentrations of 2000 and 10000 ppmv, X-RE were 29±6 and 6±8%, respectively. The middle section was less affected by increasing CH_4 concentration from 2000 to 10000 ppmv compared to top and bottom sections and remained in the range of 16-25% corresponding to 40% of the total X biodegradation. Methane concentration increase had an opposite effect on X biodegradation at the bottom part as X-REs increased from 4±3 to 11±3% by increasing CH_4 concentration from 2000 to 10000 ppmv.

According to Figure 4.7 (b), EB-REs on the top sections followed the same trend as X-REs and decreased from 25±3 to 0% when CH_4 concentrations were increased from 2000 to 10000 ppmv. Ethylbenzene-REs in the middle section were in the range of 23-27%, which corresponded to 50% of the total EB biodegradation in the biofilter. Similarly to X, 65% of total EB biodegradation happened in the middle section of the biofilter at a CH_4 concentration of 10000 ppmv. Ethylbenzene-RE increased at the bottom section from 6±7 to 12±5% with CH_4 concentration in the range of 2000 to 10000 ppmv.

The RE of X and EB in the 3 sections of the bioreactor was influenced differently by the change in CH_4 concentrations. The top sections were affected negatively and both X and EB-REs decreased by increasing CH_4 concentration to 10000 ppmv except for X at a CH_4 concentration of 6000 ppmv. An opposite behaviour was observed at the bottom section as VOCs-REs mildly increased by elevating CH_4 concentration to 10000 ppmv. Unlike the top and bottom sections being dependant on CH_4 concentrations, X and EB biodegradation in the middle section was nearly independent from CH_4 concentrations.

4.5.5. Comparison between CH_4 and VOCs removal efficiencies

Increasing CH_4 concentrations from 2000 to 10000 ppmv resulted in a higher biodegradation of CH_4 on top sections compared to middle and bottom section whereas VOC-REs on the top sections generally decreased as a result of increasing CH_4 concentrations. The biodegradation of VOCs was mostly localized in the middle section. An opposite RE trend was observed at the bottom sections as CH_4-REs decreased due to higher CH_4 concentrations increase while VOCs-REs slightly increased. The opposite RE tendencies of VOCs compared to CH_4 between bottom and top sections following CH_4 concentration increase could be explained by the CH_4 biodegradation activity on top sections. Increasing CH_4 concentration probably inhibited the VOCs biodegradation on the top section while a lower CH_4 biodegradation in the middle section might have been the reason behind high VOC biodegradation in the middle section.

The low CH_4 and VOC-REs observed in bottom sections of the biofilters might be linked to the high total IL of pollutants at the inlet of the biofilter as well as their toxicity which might have caused a decrease in MO development in that section in addition to the higher void fraction of the packing and lower nutrients availability since NS was irrigated from top sections and nutrients would probably been consumed by MOs in top and middle sections. Since X/EB are more biodegradable and soluble than CH_4, a higher proportion of the VOCs was eliminated in the middle section resulting in the flourishment of X and EB degraders (Khabiri et al., 2021). Methane degraders probably flourished on the top section where there was less competition with X and EB degraders (Malhautier et al., 2005).

The stratification pattern of degradation activities has been reported in the biofiltration of pollutant mixtures as compounds with a higher biodegradability were usually eliminated within the first sections of up-flow biofilters while the recalcitrant compounds would be removed in the upper sections (Aizpuru et al., 2001). For example, Malhautier et al., (2021) found that ethanol was biodegraded in the first sections of the biofilter (first 50 cm of bed height) while a group of alkanes was eliminated at a height of 150 cm. A similar pattern is expected to occur during the biofiltration of CH_4 in the presence of other VOCs due to the difference in

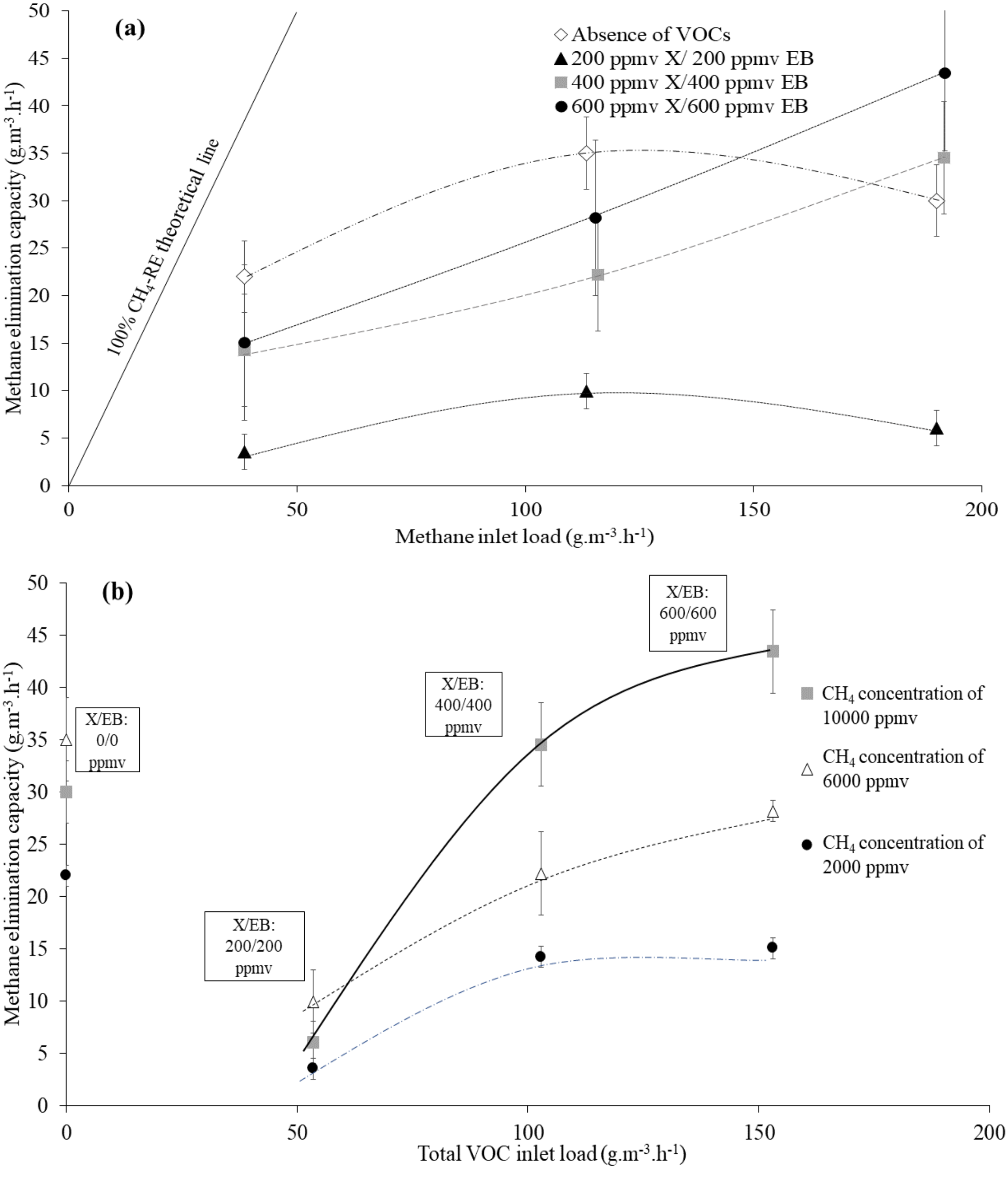

Figure 4.8 : Methane elimination capacity as a function of (a) CH_4 inlet load and (b) total VOC inlet load at an EBRT of 4.5 min

biodegradability of mixture components.

4.5.6. Methane EC versus CH_4-IL under different concentrations of VOCs

Figure 4.8 (a) presents CH_4-EC as a function of CH_4-IL in VOCs absence and presence for an EBRT of 4.5 min (the "optimal" EBRT for the removal of the ternary mixture) and VOCs concentrations varying between 200 and 600 ppmv. In absence of VOCs, CH_4-EC followed a kinetically limited regime trend and reached EC_{max} of 35±4 $g.m^{-3}.h^{-1}$ for a critical IL of 113±2 $g.m^{-3}.h^{-1}$ and then decreased to 30±3 $g.m^{-3}.h^{-1}$ at an IL of 190±2 $g.m^{-3}.h^{-1}$ which was in agreement with previous studies on CH_4 biofiltration. Several authors reported kinetic limitations for ILs higher than 80-100 $g.m^{-3}.h^{-1}$. For example, Limbri et al., (2014) obtained an CH_4-EC_{max} of 27 $g.m^{-3}.h^{-1}$ for a critical IL of 139 $g.m^{-3}.h^{-1}$ at an EBRT of 2.4 min while Gómez-Cuervo et al., (2016) obtained an EC_{max} of 21 $g.m^{-3}.h^{-1}$ for a critical IL of 85 $g.m^{-3}.h^{-1}$ and an EBRT of 4.4 min**.** The EC_{max} (35±4 $g.m^{-3}.h^{-1}$) obtained in the current study in absence of VOCs is higher compared to results in the literature. For example, Hernández et al., (2015) obtained an EC_{max} of 11 $g.m^{-3}.h^{-1}$ for a critical IL of 18 $g.m^{-3}.h^{-1}$ at an EBRT of 4.4 min compared to an EC_{max} of 35±4 $g.m^{-3}.h^{-1}$ for a critical IL of 113±2 $g.m^{-3}.h^{-1}$ in the current study for a relatively similar EBRT of 4.7 min. This could be considered as an indicator of significant development of indigenous CH_4 degrading MOs in the biofilm and their ability to surpass the biodegradation performances of pure methanotroph strains in the organic packed-bed used by Hernández et al., (2015). The inorganic packing media used in this study has already been reported to perform higher than an organic packing composed of compost (Nikiema et al., 2005). More adequate structural properties in the surface of the inorganic packing used in this study could be at origin of this difference in CH_4-ECs.

In case of VOCs presence (200 ppmv), Figure 4.8 (a) shows a similar kinetic limitation as in absence of VOCs and an EC_{max} of 10±3 $g.m^{-3}.h^{-1}$ was obtained at a critical IL of 115±2 $g.m^{-3}.h^{-1}$. For CH_4-ILs increasing from 39±1 to 192±0 $g.m^{-3}.h^{-1}$, CH_4-ECs increased from 14±1 to 35±4 $g.m^{-3}.h^{-1}$ and from 15±1 to 43±3 $g.m^{-3}.h^{-1}$ for VOCs concentrations of 400 and 600 ppmv, respectively. For VOCs concentrations in the range of 400-600 ppmv, CH_4-ECs were 60-90% higher compared to VOCs concentration around 200 ppmv; CH_4 elimination became limited by mass transfer as no CH_4-EC_{max} could be obtained in that IL range.

Methane-EC as a function of total VOC-IL (the sum of both X and EB-ILs) is presented in Figure 4.8 (b). An increase in total VOC-IL from 52±5 to 154±3 $g.m^{-3}.h^{-1}$ resulted in a linear increase in CH_4-ECs from 10±3 to 28±1 $g.m^{-3}.h^{-1}$ and 6±2 to 43±4 $g.m^{-3}.h^{-1}$ for CH_4 concentrations of 6000 and 10000 ppmv, respectively. At a CH_4 concentration of 2000 ppmv, CH_4-EC increased from 4±1 to 14±1 $g.m^{-3}.h^{-1}$ when total VOC-IL was increased from 52±7 to 103±1 $g.m^{-3}.h^{-1}$. However, CH_4-EC remained relatively constant at values of 14-15 $g.m^{-3}.h^{-1}$ at total VOC-IL range of 103-154 $g.m^{-3}.h^{-1}$. In absence of VOCs, CH_4-EC also increased from 22±1 to 35±4 $g.m^{-3}.h^{-1}$.

The presence of X/EB at concentrations of 200/200 ppmv causing inhibition of CH_4 biodegradation might be linked to a competition between 2 groups of MOs (CH_4 degraders and VOC degraders) which decreased the ability of CH_4 degraders to metabolize CH_4. Nevertheless, increasing X/EB concentration to the range of 400-600 ppmv reversed the inhibition effect which could be due to a co-metabolism mechanism that favoured CH_4 biodegradation.

4.5.7. Relationship between leachate composition, CO_2 production and the total inlet load

Carbon dioxide production rate is an indicator of the nature of biodegradation activities occurring in a biofilter. Under similar ECs, a high PCO_2 indicates that the carbon source (substrate) was consumed in the oxidation bioreactions meanwhile a low PCO_2 is often related to the use of the substrate for the production of biomass and other by-products such as extracellular polymeric substances (EPS) (La et al., 2018a). Table 4.4 presents the variations of total IL (CH_4-IL+VOCs-IL), total EC, nutrient (PO_4^-, SO_4^{2-} and NO_3^-) concentrations in the leachate, PCO_2 and TOC as a function of time and pollutants concentrations at an EBRT of 4.5 min. Figure 4.9 (a) presents the leachate composition including essential nutrients PO_4^-, SO_4^{2-} and NO_3^- as a function of total IL at a fixed EBRT of 4.5 min. Methane and VOCs concentrations were in the range of 2000-10000 ppmv and 200-600 ppmv, respectively. Figure 4.9 (b) presents PCO_2 and TOC in the leachate as a function of total IL. Nitrates concentration was 2000 ppm in the initial NS and was completely consumed after total IL was increased from 92 to 294 $g.m^{-3}.h^{-1}$ (day 161). Sulfates gradually decreased from 100 ppm in the initial NS to 17 ppm at a total IL of 342 $g.m^{-3}.h^{-1}$ (day 242). A low consumption of PO_4^- was observed as the concentration decreased from 980 to 870 ppm (day 242, IL = 342 $g.m^{-3}.h^{-1}$). The highest PCO_2 (59±3 $g.m^{-3}.h^{-1}$) coincided with the lowest total IL of 92 $g.m^{-3}.h^{-1}$ (day 32) when the nutrients were more likely to be available. Increasing total IL (from day 32 to 242) caused a gradual and progressive decrease in PCO_2 reaching 12 $g.m^{-3}.h^{-1}$ for a total IL of 345 $g.m^{-3}.h^{-1}$ (day 242). On the other hand, TOC increased from 70 to 1050 ppm when total IL was increased to 345 $g.m^{-3}.h^{-1}$.

According to Figures 4.9 (a) and (b), an increase in TOC and decrease in nutrients could be related to a factor of time as the study was conducted for a long period (242 days). MOs would naturally consume nutrients and release carbon compounds such as EPS in the leachate.

A high NO_3^- consumption (higher than 99%) was in agreement with the literature as it was proven that methanotrophic bacteria require a N source for growth (Karthikeyan et al., 2016). Khabiri et al., (2020a) reported that NO_3^- (initial concentration of 2200 ppm) was consumed up to 80% in a period of 200 days with CH_4 concentration increasing from 1000 to 9500 ppmv and an EBRT of 6 min in a CH_4 biofilter that was irrigated each 24 h with 2 L of a recycled NS at a rate of 1.1 $L.min^{-1}$. Girard et al., (2011) evaluated that a biofilter treating CH_4 at an IL of 14 $g.m^{-3}.h^{-1}$ and an EBRT of 4.2 min yielded a CH_4-RE of 18% in complete absence of an inorganic nitrogen source for a period of 8 weeks. The authors suggested that methanotrophs could fix atmospheric nitrogen. This could be a possible explanation of the removal of pollutants (CH_4, X and EB REs of 23, 16 and 17%, respectively) at a high total IL (342 $g.m^{-3}.h^{-1}$) in the present study when NO_3^- was completely consumed.

Phosphates decrease (a relatively linear tendency) was low and indicates that general microbial community was slightly dependent on PO_4^-. Jugnia et al., (2012) reported that P addition was not necessary for CH_4 bioelimination. Sulfate consumption was in agreement with other works. A decrease by 83% of SO_4^{2-} in the present study was close to the reduction of 77% observed by

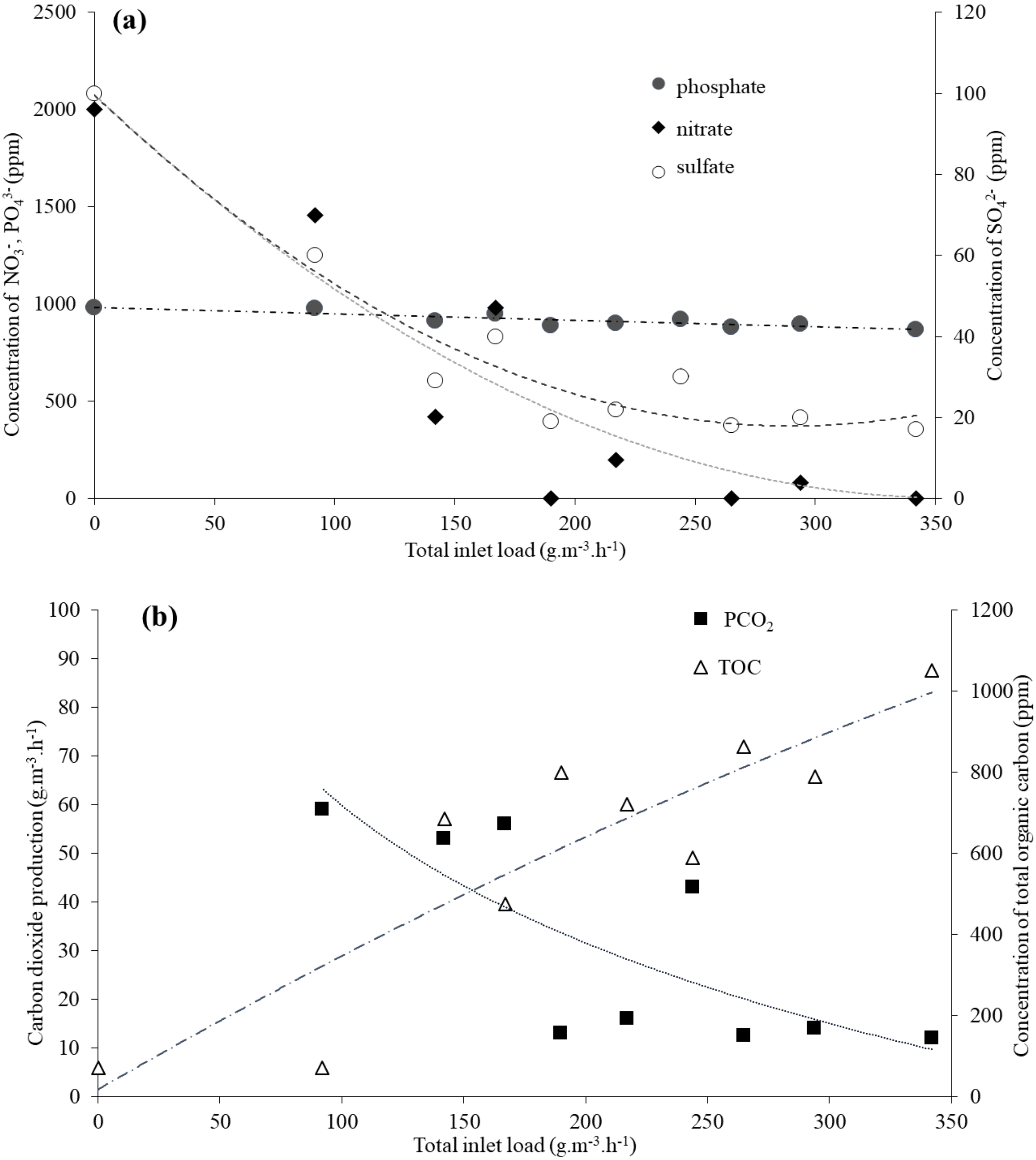

Figure 4.9 : (a) Concentration of ions (PO_4^{3-}, SO_4^{2-} and NO_3^-) present in the leachate and (b) total organic carbon (TOC) and carbon dioxide production (PCO_2) as a function of total (CH_4, X and EB) inlet load at an EBRT of 4.5 min

Khabiri et al., (2020a) in a biofilter with a similar packing and CH_4 concentrations in the range of 1000-9500 ppmv (EBRT = 6 min) during a period of 210 days.

Table 4. 4: Variation of total EC, concentration of ions (PO_4^{3-}, SO_4^{2-} and NO_3^-) present in the leachate, TOC and PCO2 for different CH4 and VOCs (X or EB) concentrations and total IL

Day	CH_4 concentration (ppmv)	Individual VOCs (X or EB) concentration (ppmv)	Total IL ($g.m^{-3}.h^{-1}$)	Total EC ($g.m^{-3}.h^{-1}$)	PO_4^{3-} (ppm)	SO_4^{2-} (ppm)	NO_3^- (ppm)	TOC (ppm)	PCO_2 ($g.m^{-3}.h^{-1}$)
0	-	-	-	-	980	100	2000	0	-
32	2000	200	92	34	975	60	1458	71	59
59	6000	200	167	41	950	40	980	474	56
85	10000	200	244	26	922	30	630	590	43
110	2000	400	142	33	914	29	420	684	53
140	6000	400	217	35	900	22	200	720	16
161	10000	400	294	43	895	20	80	788	14
186	2000	600	190	49	889	19	0	798	13
212	6000	600	265	53	879	18	0	863	13
242	10000	600	342	69	870	17	0	1050	12

4.6. Conclusion

Methane was treated by biofiltration as a single pollutant and in a ternary mixture with xylene (X) and ethylbenzene (EB) in up-flow biofilters. The 2 VOCs were also treated as a binary mixture in CH_4 absence. Pollutant concentrations were varied from 2000 to 10000 ppmv for

CH_4 and from 200 to 600 ppmv for both VOCs. Empty bed residence time varied from 2.25 to 9 min.

The performance of the biofilters were strongly influenced by pollutant concentrations in the ternary mixture. The addition of the X and EB at individual concentrations of 200 ppmv for all CH_4 concentrations reduced CH_4-RE by around 40% due to inhibition caused by the simultaneous presence of both VOCs. However, increasing VOCs individual concentration to 400 and 600 ppmv slightly increased the biodegradation of CH_4.

Empty bed residence time was an important operating factor on elimination of CH_4 and VOCs alone or in a mixture. For CH_4, the highest EBRT of 9 min resulted in the highest performance in absence and presence (CH_4-RE of 78±2% and 41±3%, respectively) of the VOCs. But for VOCs in CH_4 presence, X and EB-REs at an EBRT of 4.5 min were 30% and 20% higher than at EBRTs of 2.25 and 9 min, respectively.

In case of a short EBRT of 2.25 min, an increase in CH_4 concentrations from 2000 to 10000 ppmv improved the CH_4 biodegradation performance from 0 to 9% and from 2 to 6% in VOC absence and presence, respectively. In general, an EBRT of 4.5 min was found to be optimal for the ternary mixture.

The biodegradation of pollutants was localized in different sections across the bioreactor. An increasing CH_4-RE profile was observed along the height of the biofilter and the highest portion of CH_4 biodegradation was always located on the top section meanwhile both X and EB-REs were the highest in the middle section and were uninfluenced by CH_4 concentrations.

The decrease of nutrient concentrations elements in NS especially NO_3^- strongly influenced the REs of the pollutants which resulted in a TOC increase in leachate and a PCO_2 decrease.

Acknowledgments:

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CHAPITRE 5. Modélisation par réseau de neurones artificiels de la biofiltration du méthane en présence de composés organiques volatils

Avant-propos: La version finale de l'article " Modélisation par réseau de neurones artificiels de la biofiltration du méthane en présence de composés organiques volatiles " a été traduite en anglais et soumise dans le journal «Clean Technologies and Environmental Policy » en août 2023.

TITRE: Modélisation par réseau de neurones artificiels de la biofiltration du méthane en présence de composés organiques volatiles

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Contribution du document: Cet article est pertinent sur le 3ième objectif de cette étude basée sur la modélisation de la biofiltration du méthane seul ou en mélange avec des COVs par réseau de neurones artificiels. L'étude compare des résultats obtenus à l'échelle laboratoire à ceux issus de la modélisation à partir d'une base de données constituée de travaux antérieurs provenant dans la littérature.

5.1. Résumé:

Cette étude a examiné la modélisation par réseaux de neurones artificiels (RNA) de la biofiltration simultanée du méthane (CH_4) en présence de deux composés organiques volatils (COVs) : le xylène (X) et l'éthylbenzène (EB), en utilisant un biofiltre à garnissage inorganique. Les résultats ont montré que la conversion du CH_4 était située entre 50 et 60% pour des concentrations de 1000 à 10000 ppmv alors que la conversion des COVs était entre 70 à 90% pour des concentrations variant entre 200 et 500 ppmv. Des RNAs ont été utilisés pour prédire et simuler les performances du biofiltre pour la biodégradation du CH_4 et des COVs, en se basant sur des bases de données générées à partir de travaux antérieurs de biofiltration disponibles dans la littérature. Le RNA1 (architecture de : 3(couches d'entrée)-18(couches cachées)-1(couches de sortie)) a prédit avec précision la conversion du CH_4 à l'état pseudo-stationnaire, tandis que le RNA2 (architecture de 4(couches d'entrée)-18(couches cachées)-2(couches de sortie)) a prédit la conversion simultanée du CH_4 et des COVs avec une précision légèrement inférieure à RNA1. Le RNA3 (architecture de : 4(couches d'entrée)-30(couches cachées)-1(couches de sortie)) a permis de prédire avec précision la phase d'acclimatation et la phase finale du biofiltre. Cependant, il n'a pas pu prédire avec précision les phases transitoires et a présenté des déviations par rapport aux résultats expérimentaux lors des changements de concentration de CH_4. Cette étude a permis de poser les bases d'un outil d'aide à la décision et à la prédiction pour anticiper les performances de biofiltres lors du biotraitement de gaz résiduaires contenant du CH_4 et des COVs, et permettra d'éviter les coûts et les délais liés à l'expérimentation.

Mots clés : Biotechnologies, gaz à effet de serre, sites d'enfouissement sanitaire, xylène, éthylbenzène

5.2. Introduction

Les accords de Paris de 2016 insistent sur la nécessité de limiter l'augmentation de la température globale afin d'éviter des répercussions drastiques du changement climatique sur les populations (Bodansky, 2016). Par conséquent, le Canada et plusieurs pays de l'Union Européenne ce sont engagés à réduire les émissions de gaz à effet de serre (GES) de 30% d'ici 2030 (Nisbet et al., 2019). Le méthane (CH_4) est considéré comme étant entre 21 et 25 fois plus important que le dioxyde de carbone (CO_2) en termes d'impacts sur le réchauffement climatique, ce qui le classe comme le deuxième GES le plus impactant sur le réchauffement climatique (Ganesan et al., 2019). Parmi les secteurs émetteurs de CH_4, les sites d'enfouissement sanitaire (SES) représentent 60% du total de CH_4 anthropogénique émis dans le monde (Gautam et Agrawal, 2021). Afin d'éliminer le CH_4 dans les effluents gazeux de SES, plusieurs procédés existent tels que les torches ou les brûleurs catalytiques. Cependant, ces techniques ne sont pas efficaces et/ou rentables pour des faibles concentrations de CH_4 en dessous de 3-5 % v/v (Gómez-Cuervo et al., 2016). Les procédés conventionnels ne peuvent donc pas être utilisés pour les anciens SES ou les SES de faibles tailles. Les biotechnologies qui utilisent les microorganismes comme biocatalyseurs pour convertir le CH_4 en CO_2, eau (H_2O), biomasse, etc. sont une solution plus adéquate pour le traitement des effluents gazeux de SES (Barbusinski et al., 2017b). Parmi les différentes biotechnologies utilisées, la biofiltration est la méthode la plus prometteuse vu ses coûts modérés en termes d'investissement et de mise en œuvre, ainsi que la simplicité de la technologie et sa maintenance relativement facile. Néanmoins, la biofiltration est un bioprocédé triphasique complexe en termes de mécanismes biologiques, chimiques et physiques agissant simultanément comme la diffusion des composés gazeux vers le biofilm, les cinétiques des bioréactions, les interactions entre les différents substrats, l'inhibition de la biodégradation et la toxicité, l'absorption, les changements de température, etc. (Delhoménie et Heitz, 2005). L'utilisation de biofiltres pour la biodégradation du CH_4 a permis d'obtenir des conversions (RE) élevées du CH_4 pouvant dépasser les 90%. Par exemple, Lebrero et al., (2016) a obtenu une RE de CH_4 de 90% sous un temps de séjour en fût vide (EBRT) de 40 min et une charge à l'entrée (CH_4-IL) de 20 $g.m^{-3}.h^{-1}$. Ferdowsi et al., (2016) a obtenu une CH_4-RE de 87% pour un EBRT de 6 min et une CH_4-IL de 7 $g.m^{-3}.h^{-1}$.

Le CH_4 n'est pas le seul composé nocif dans les émissions de SES. Plusieurs composés organiques volatils (COVs) tels que le xylène (X) et l'éthylbenzène (EB) sont aussi présents à des concentrations variant entre 40 et 1000 $mg.m^{-3}$ (Gong et al., 2019b). La présence de ces COVs renforce l'importance de traiter les effluents de SES, étant donné qu'ils peuvent provoquer des affections cardiorespiratoires en plus de générer des désagréments olfactifs ainsi que des inconvénients écologiques et environnementaux (Borhani et Noorpoor, 2017). La présence de ces composés peut constituer un frein en termes de performance et de faisabilité de la biofiltration du CH_4 issus de SES au niveau du site. La biofiltration de plusieurs composés de différents types et structures chimiques présents dans un mélange peut être difficile en raison de l'augmentation de la complexité des mécanismes de régulations génétique et enzymatique lors de la co-dégradation. Différents travaux ont montré que l'X et l'EB ont un effet inhibiteur sur la biodégradation du CH_4 lors de la biofiltration de mélanges (Merouani et al., 2022, 2023).

Plusieurs auteurs se sont intéressés à la modélisation du procédé de biofiltration pour deux raisons majeures. D'une part, elle permet de prédire rapidement le résultat de cette opération sans avoir recours à l'expérimentation souvent longue et parfois onéreuse et ouvre la voie à l'optimisation du bioprocédé. Le premier modèle fût développé par Ottengraf et Van der Oever (1986) et portait sur une cinétique de premier ordre tenant compte de l'équilibre de transfert de matière à travers l'interface gaz-biofilm. D'autres modèles comme celui de Michaelis-Menten ou Haldane sont également utilisés pour l'étude des micro et macro-cinétiques lors de la biofiltration et considèrent certains paramètres comme la limitation en oxygène, l'inhibition entre différents substrats, l'épaisseur du biofilm, le développement de la biomasse, etc. (Gallastegui et al., 2011a; Ménard et al., 2014). Plusieurs cinétiques reliées à divers composés sont raportées dans la littérature : biofiltration du CH_4 et du toluène (Ménard et al., 2012a), xylène ((Heidari et al., 2019), CH_4 (Vergara-Fernandez et al., 2020a), éthyle-acétate et toluène (Álvarez-Hornos et al., 2009), xylène (Gallastegui et al., 2011b), méthanol (Avalos Ramirez et al., 2010), CH_4 et styrène (Khabiri et al., 2020a). Cependant, malgré les avancées réalisées dans le domaine de la modélisation de la biofiltration, les modèles fondamentaux ne conduisent pas toujours aux résultats désirés. Ceci est dû en grande partie à la complexité des mécanismes physico-chimiques et biologiques régissant le phénomène de la biofiltration. Les interactions entre les différentes variables telles que la concentration des substrats, la concentration en oxygène, l'épaisseur du biofilm et le développement de la biomasse sont extrêmement complexes et difficiles à modéliser de manière précise. Face à ces limitations, une approche alternative qui gagne en popularité est l'utilisation de l'intelligence artificielle et de techniques de modélisation qui considèrent le bioprocédé comme une boîte noire. Ces méthodes exploitent la capacité d’algorithmes d'apprentissage automatique à extraire des modèles complexes à partir de données d'entrée-sortie. En utilisant des techniques telles que les réseaux de neurones artificiels (RNAs), il est possible de créer des modèles prédictifs capables de prendre en compte les interactions complexes et non linéaires entre les variables opératoires de la biofiltration.

Les RNAs sont des modèles inspirés du fonctionnement du cerveau humain et sont basés sur le principe de neurones artificiels interconnectés. Le fondement des RNAs en tant qu'approximateurs universels repose sur le théorème d'approximation universelle, formulé par George Cybenko en 1989 et confirmé par la suite par d'autres chercheurs (Haykin, 2008). Ce théorème établit que les réseaux neuronaux à une couche cachée et contenant un nombre suffisamment grand de neurones peuvent approximer n'importe quelle fonction continue sur un espace compact à une précision arbitraire (Haykin, 2008).

La structure d'un RNA comprend généralement une couche d'entrée, une ou plusieurs couches cachées et une couche de sortie. La couche d'entrée reçoit les données brutes et les transmet aux neurones de la première couche cachée. Chaque neurone reçoit des signaux pondérés provenant des neurones de la couche précédente, multipliés par des poids synaptiques. Les poids déterminent l'importance de chaque connexion et sont ajustés pendant l'apprentissage afin d’optimiser les performances du RNA (Ferentinos, 2005). L'apprentissage d'un RNA est généralement réalisé par un processus itératif appelé rétropropagation de l'erreur. Lors de la phase d'apprentissage, le réseau est exposé à des exemples d'entraînement avec des entrées connues et des sorties attendues. En comparant les sorties prédites avec les sorties attendues, une fonction de perte est calculée pour mesurer l'écart entre les deux. Les gradients de cette fonction de perte sont ensuite propagés en arrière à travers le réseau, et les poids synaptiques sont ajustés pour minimiser l'erreur de prédiction. Lorsque le processus d'apprentissage est terminé, le RNA est capable de faire des prédictions sur des exemples qu'il n'a pas rencontrés auparavant (Goodfellow et al., 2016).

L'utilisation des RNAs dans le domaine de la biofiltration est encore récente et peu d'études ont été menées sur cette méthodologie. Deshmukh et al., (2012) ont utilisé un RNA pour modéliser et optimiser les performances d'un biofiltre traitant le toluène avec comme paramètres d'entrée: la concentration à l'entrée, le temps de séjour en fût vide, l'humidité du lit de garnissage, la température et le pH. La conversion était l'unique paramètre de sortie. Les performances expérimentales du biofiltre ont été utilisées pour former la base de données et construire le RNA (67 données ont été utilisées, 60% pour l'apprentissage et 40% pour le test). La valeur du coefficient de corrélation (R^2) obtenue était de 0.9755. Dans une étude plus récente, (Baskaran et al., 2020) ont utilisé un RNA à 3 couches (entrée-couche cachée-sortie) pour un biofiltre ayant un garnissage de bambou et de compost et traitant le trichloréthylène. Les paramètres d'entrée étaient la concentration du composé, le débit volumique et le temps d'opération; le paramètre de sortie était la conversion. La base de données utilisée était les résultats expérimentaux pour une expérience de 165 jours (70% pour l'apprentissage, 15% pour la validation et 15% pour le test); une valeur de R^2 de 0,9969 a été obtenue.

La nouveauté de la présente étude est l'utilisation d'une base de données composée de plusieurs travaux antérieurs pour créer un RNA généralisé pouvant prédire les performances de biofiltration du CH_4 seul (en régime pseudo-stationnaire ou dynamique) ou en mélange avec des COVs (X et EB). La biofiltration simultanée d'un mélange ternaire (CH_4, X et EB) a été étudié à l'échelle laboratoire dans un biofiltre à garnissage inorganique. Le RNA créé a été utilisé pour prédire les résultats d'expériences et les comparer à ceux obtenus expérimentalement.

5.3. Matériel et méthodes

5.3.1. Dispositif expérimental de biofiltres

L'expérience de biofiltration s'est déroulée sur une durée de 386 jours. Le biofiltre était constitué d'une colonne en plexiglass composé de 3 sections distinctes. Chaque section avait un diamètre de 0.15 m et une longueur de 0.3 m. La hauteur totale du biofiltre était de 1 m et son volume total de 0.018 m^3. Le biofiltre était rempli d'un garnissage inorganique dont la nature exacte ne peut être dévoilée pour des raisons de confidentialité. Le biofiltre étant un bioprocédé aérobie, de l'air comprimé était injecté en bas de la colonne. Le débit volumique de l'air a été fixé à 0.24 m^3 h^{-1} grâce à des rotamètres volumiques ce qui correspond à un EBRT de 4.5 min (Brooks, USA). Le courant d'air était divisé en 3 courants avant d'être injecté dans le biofiltre; 2 courants étaient injectés dans des bulleurs de COVs (EB (>99%, Sigma-Aldrich, USA) et X (>99%, Fisher chemicals, USA) et le 3ème courant passait dans une colonne d'humidification pour obtenir une humidité relative de l'air de 90% v/v pour fournir l'humidité nécessaire à la formation du biofilm autour du garnissage. Le débit de CH_4 provenant d'un cylindre (Praxair Inc., Canada) était régulé par des contrôleurs de débit massique. Le schéma expérimental est similaire à celui reporté par Merouani et al., (2023).

Le biofiltre a été inoculé par le lixiviat d'un biofiltre en opération traitant du CH_4. Le lixiviat a été recirculé 3 fois pour assurer une distribution homogène des microorganismes à travers le biofiltre. Ce dernier a été irrigué par une solution nutritive (la composition est reportée par Khabiri et al., (2020b)) chaque 2 jours durant toute l'expérience sous un débit volumique de 60.10^{-3} $m^3.h^{-1}$.

5.3.2. Outils d'analyse

Des échantillons de gaz ont été prélevés à l'entrée et à la sortie du biofiltre afin d'analyser la concentration des polluants (CH_4, EB et X) et du CO_2. Un analyseur d'hydrocarbures totaux à ionisation de flamme (FIA 510, Horiba, Japon) a été utilisé pour mesurer les concentrations de CH_4, X et EB tandis qu'un analyseur (Ultramat 22P, Siemens, Allemagne) a permis de mesurer les concentrations de CO_2.

5.3.3. Conditions opératoires

Les expériences ont été menées sur 10 phases consécutives. Les concentrations de CH_4 et de COV variaient respectivement entre 1000 et 10000 ppmv et entre 200 à 500 ppmv. Durant les 4 premières phases, le CH_4 a été injecté seul à une concentration de 1000 ppmv, ensuite, la concentration de CH_4 a été graduellement augmentée de 2000 à 6000 puis à 10000 ppmv. Par la suite, le X et l'EB ont été injectés à une concentration individuelle fixe de 500 ppmv; la concentration de CH_4 variait entre 2000-10000 ppmv. Les concentrations de X et EB ont été ensuite diminuées à 200 ppmv tandis que la concentration de CH_4 a été, encore une fois, variée de 2000 à 6000 et à 10000 ppmv.

5.3.4. Le réseau de neurones artificiels (RNA)

Pour cette étude, un RNA non-bouclé, également connu sous le nom de « feedforward » a été choisi. Ce type de réseau est particulièrement adapté à des problèmes où la relation entre les données en entrée et en sortie est généralement directe et sans dépendance récurrente tels que le cas d'un bioprocédé. Cela signifie que les informations se propagent dans une seule direction, de la couche d'entrée à la couche de sortie (Goodfellow et al., 2016). Le nombre de couches cachées peut varier selon la complexité des relations entre les variables d'entrée et les variables prédites. Cependant, la littérature a révélé qu'un RNA constitué d'une seule couche cachée a la capacité d'approximer la plupart des fonctions mathématiques continues (Akakuru et al., 2023).

Les variables d'entrée dans la couche d'entrée sont les résultats expérimentaux; les données sont ensuite transférées vers la ou les couches cachées et traitées à l'aide d'une fonction de transfert ("f") qui peut prendre la forme d'une hyperbole tangente, sigmoïde ou linéaire pour estimer la variable de sortie (Deshmukh et al., 2012). Chaque paire de neurones est connectée par des poids de connexion (w_{ij}) du neurone i au neurone j. Pour estimer la valeur de sortie du réseau (u_i), chacun des neurones d'entrée traite les données en multipliant la variable d'entrée (a_i) par son poids de connexion (w_{ij}) via la fonction de transfert. Un paramètre (b_j) sélectionné au hasard est ajouté à l'équation pour générer des données transmises à la ou aux couches cachées. Le neurone utilise alors l'équation suivante Eq. (1) pour estimer le signal de sortie :

$$u_i = f\left(\sum_{i=1}^{n}\left(w_{ij}\, a_i\right) + b_j\right) \qquad (1)$$

La base de données utilisée pour créer le réseau est divisé en trois groupes, la partie apprentissage (70%), la partie validation (15%) et la partie test (15%). Un algorithme itératif utilise la partie apprentissage pour créer le modèle et déterminer les valeurs de w_{ij} et b_j pour tous les neurones; ensuite la partie validation est utilisée pour confirmer la convergence du modèle établi pendant le processus d'apprentissage. La partie test permet de vérifier l'exactitude du réseau formé en termes de prédiction après avoir terminé l'apprentissage et la validation du réseau (Amdoun et al., 2019).

Le logiciel MATLAB R2022 (MathWorks, USA) a été utilisée pour créer un réseau à trois couches (entrée-cachée-sortie) avec la fonction tangente hyperbolique comme fonction d'activation. Les dérivées des fonctions de transfert sigmoïdes sont des fonctions non linéaires qui sont couramment utilisées pour le développement des RNAs. Les fonctions de transfert sigmoïdes sont relativement simples, ce qui facilite le calcul des gradients nécessaires pour la rétropropagation de l'erreur et l'optimisation du réseau (Goodfellow et al., 2016).

L'algorithme Levenberg-Marquardt a été utilisé pour déterminer les valeurs de w_{ij} et b_j. L'algorithme de Levenberg-Marquardt est une méthode itérative qui combine des caractéristiques de la méthode de Gauss-Newton et de la méthode du gradient conjugué. Les poids et les biais du réseau sont ajustés progressivement pour trouver un minimum local de l'erreur de prédiction. L'un des avantages de l'algorithme de Levenberg-Marquardt est sa capacité à converger rapidement vers une solution. De plus, il peut éviter certains problèmes rencontrés par d'autres algorithmes, tels que la divergence (Moré, 1978). Le nombre optimal de neurones dans la couche cachée a été sélectionné par tâtonnements en fonction de la valeur des R^2 obtenue lors des phases d'apprentissage, de validation et de test.

5.3.5. Constitution de la base de données

Pour développer les RNAs visant à prédire les résultats expérimentaux de la biofiltration du CH_4, du X et de l'EB, une base de données expérimentales regroupant plusieurs travaux de recherche issus de la littérature a été constituée. L'utilisation de travaux antérieurs pour créer une vaste base de données présente de nombreux avantages. En premier lieu, la fiabilité des résultats dépend souvent de la taille de la base de données utilisée lors des expériences. En intégrant des travaux provenant de diverses sources, il devient possible d'augmenter la taille de la base de données, ce qui renforce la robustesse des résultats obtenus. Une plus grande diversité de données permet également de mieux appréhender la variabilité et la complexité des problèmes auxquels le RNA est confronté (Larbi et al., 2019). Par ailleurs, l'utilisation de travaux provenant de plusieurs auteurs confère au RNAs développé un caractère plus général et représentatif de la réalité. Cette approche évite l'introduction de biais inhérents à une seule source de données ou à une seule méthodologie, et renforce ainsi la crédibilité et la validité des résultats obtenus.

Vu que les travaux constituant les bases de données ont été effectués dans des conditions différentes, les paramètres opératoires communs entre les différentes études ont été choisis comme paramètres d'entrée tandis que le paramètre de performance du biofiltre (RE) a été sélectionné comme paramètre de sortie. Trois (3) ensembles de données différents ont été utilisés pour créer 3 RNA différents :

RNA1: Un ensemble de données contenant 84 points issus de travaux de biofiltration du CH_4 comme polluant unique (Tableau 5.1) a été utilisé pour créer un RNA à 3 entrées (concentration en CH_4 [ppmv], EBRT [min] et type de garnissage) et 1 sortie (CH_4-RE [%] à l'état pseudo-stationnaire). Les travaux de Khabiri et al., (2020a), Ménard et al., (2014) et ceux de la présente étude ont été utilisés pour tester les capacités prédictives du RNA.

Table 5.1: Base de données pour la création du RNA1

Auteur	Type de garnissage	EBRT (min)	CH_4 (ppmv)	RE (%)
Rose et al., (2012)	organique	4.2	6900-7085	36-30
Avalos Ramirez et al., (2012)	inorganique	4.2	7170-7600	34-42
Girard et al., (2012)	inorganique	4.2	4086-5090	39-43
Kim et al., (2013)	inorganique	20	15000-39500	55-92
Kim et al., (2014)	inorganique	20	54000	61
Limbri et al., (2014)	organique	1.6-19.5	8570	17-29
Hernández et al., (2015)	inorganique	4.4	1900	62
Ganendra et al., (2015)	inorganique	0.8	1000	30
Syed et al., (2016)	inorganique	58	76600	57
Brandt et al., (2016)	inorganique	7.4-42.8	4000-28000	5-55
Ferdowsi et al., (2016)	inorganique	6	1000-13000	52-87
Lebrero et al., (2016)	organique	20-40	20000	93-100
Gómez-Cuervo et al., (2016)	organique	6.5	2000	30
	inorganique	4	2200	21
Farrokhzadeh et al., (2017)	organique	39-115	65000	77-92
La et al., (2018)	organique-inorganique	82.8	75700	100
Fjelsted et al., (2020)	organique	24-186	17800-23430	55-73
Khabiri et al., (2020)	inorganique	6	1000-9500	48-67
Vergara-Fernandez et al., (2020)	inorganique	5.9-23.5	66700	13.7-19.5
Jawad et al., (2021)	organique	100	46-488	6-61
Gómez-Borraz et al., (2022)	organique	23	13440	77

RNA2: Un ensemble de données contenant 70 points issus de travaux de biofiltration lors du mélange du CH_4 avec d'autres polluants (Tableau 5.2) a été utilisé pour créer un RNA à 5 entrées (concentration en CH_4 [ppmv], EBRT [min], type de garnissage, concentration en COV [ppmv] et type COV) et 2 sorties (CH_4-RE [%] et COV-RE [%] en régime pseudo-stationnaire). Les

travaux de Merouani et al., (2023) et ceux de la présente étude ont été utilisés pour tester la précision du RNA.

Table 5.2: Base de données pour la création du RNA2

Auteur	COV	Type de garnissage	EBRT (min)	CH_4 (ppmv)	COV (ppmv)	CH_4-RE (%)	COV-RE (%)
Ménard et al., (2012)	Toluène	Inorganique	4.2	2000-9000	0-1008	2.2-48	0-100
	Chlorobenzène		4.2	2000-9000	0-104	6-40	0-100
Kim et al., (2013)	Benzène, toluène	Organique+ inorganique	18	22500-35500	0-190	64-83	0-100
Ferdowsi et al., (2017)	Méthanol	Inorganique	6	1980	0-2812	31-55	0-100
Ferdowsi et al., (2019)	Méthanol	Inorganique	1.3-6	0-4500	0-380	0-50	0-100
	Éthanol		1.3-6	0-4500	0-265	0-28	0-100
Khabiri et al., (2020)	Styrène	Inorganique	6	1000-9000	0-700	43-80	0-100
Merouani et al., (2022)	Éthylbenzène	Inorganique	4.5	0-10000	200-500	0-64	75-90
	Xylène		4.5	0-10000	200-500	0-59	74-90

RNA3: Un ensemble de données contenant 364 points issus de travaux de biofiltration dynamique du CH_4 comme polluant unique (Tableau 5.3) a été utilisé pour créer un ARN à 4 entrées (concentration en CH_4 [ppmv], EBRT [min], type de garnissage et durée [jours]) et 1 sortie (CH_4-RE [%] en état dynamique). Les résultats de la biofiltration du CH_4 en function du temps de la présente étude ont été utilisés pour tester la prédiction de la conversion de CH_4 en fonction du temps.

Table 5.3: Base de données pour la création du RNA3

Auteur	Temps (jours)	Type de garnissage	EBRT (min)	CH_4 (ppmv)	RE (%)
Rose et al., (2012)	5-102	organique	4.2	7000	7-93
Girard et al., (2012)	3-110	inorganique	4.2	5000	5-64
Kim et al., (2014)	1-63	inorganique	20	54000	0-100
Hernández et al., (2015)	0-93	inorganique	4.4	1900	21-60
Ganendra et al., (2015)	0-97	inorganique	0.8	1000	5-65
Syed et al., (2016)	0-90	inorganique	58	76600	0-58
Ferdowsi et al., (2016)	0-38	inorganique	6	2000	14-78
Gómez-Cuervo et al., (2016)	1-70	organique	6.5	2000	28-37
Khabiri et al., (2020)	0-100	inorganique	4.5	1000-9500	48-67

5.4. Résultats et discussion

5.4.1. Résultats expérimentaux de l'étude

Les résultats expérimentaux de cette étude sont présentés sur la Figure 5.1. En sélectionnant des matériaux inorganiques, une solution nutritive appropriée et en utilisant un type d'inoculum spécifique (lixiviat d'un biofiltre traitant du CH_4), un biofilm microbien s'est rapidement développé au sein du biofiltre. La RE du CH_4 à une concentration de 1000 ppmv a atteint 17% au premier jour et a augmenté jusqu'à 58% après 30 jours. Par la suite, la concentration de CH_4 a été augmentée à 2000 ppmv et la CH_4-RE a varié entre 60 et 73%. L'augmentation de la concentration de CH_4 de 2000 à 6000 ppmv a causé une diminution de la CH_4-RE de 73% à

56%. Lors de l'augmentation de la concentration de CH_4 jusqu'à 10000 ppmv, la CH_4-RE a chuté jusqu'à 37% avant de se stabiliser à une valeur de 58%.

L'ajout de 2 COVs (xylène à 500 ppmv et éthylbenzène à 500 ppmv) au CH_4 (concentration de 2000 ppmv) a causé la diminution de la CH_4-RE de 58 à 35%. Cependant, la CH_4-RE a graduellement augmenté jusqu'à 57% indiquant l'adaptation de la communauté microbienne à la présence des 2 COVs. L'augmentation de la concentration de CH_4 à 6000 et 10000 ppmv a entraîné la diminution de CH_4-RE (à 52 et 38%, respectivement). L'effet de l'augmentation de la concentration de CH_4 a aussi diminué la COVs-RE. La RE des COVs (xylène et éthylbenzène) a décru de 92 à 22% et de 88 à 12% quand la concentration de CH_4 a augmenté de 2000 à 6000 ppmv et de 6000 à 10000 ppmv, respectivement.

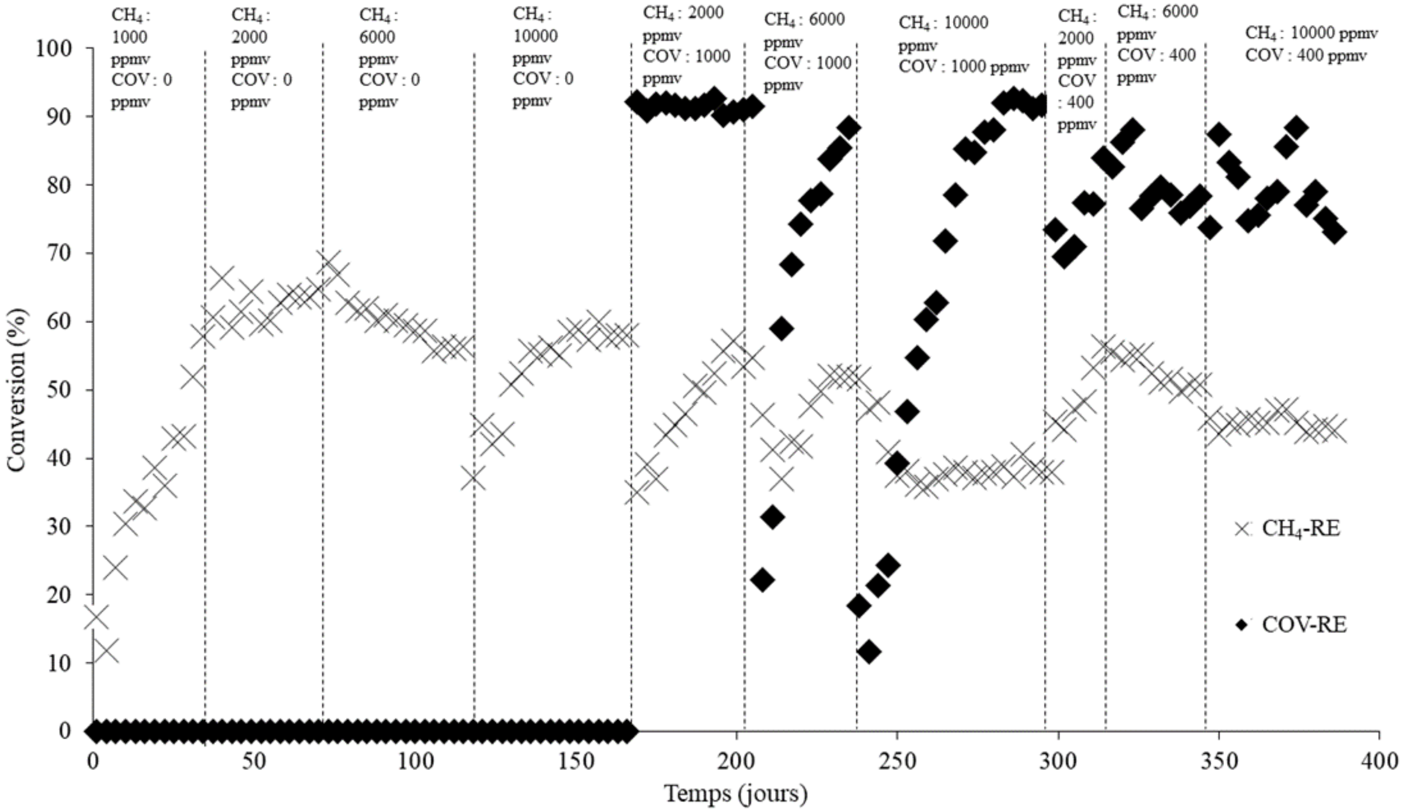


Figure 5.1: Résultats expérimentaux de l'étude de biofiltration du mélange ternaire (CH_4, X et EB)

Une diminution de la concentration des COVs de 500 à 200 ppmv a légèrement réduit l'effet inhibiteur des COVs sur le CH_4 et la CH_4-RE a augmenté dans l'intervalle de 45-53% pour des concentrations de CH_4 entre 2000 et 10000 ppmv. À une concentration de COVs de 400 ppmv, les COVs-RE étaient situés dans l'intervalle de 70-88% comparé à 90-92% pour une concentration de COVs de 1000 ppmv. Les microorganismes responsables de l'élimination des COVs semblent présenter une résistance supérieure à ceux responsables de la biodégradation du CH_4 face aux fluctuations de concentration de CH_4.

5.4.2. Développement et résultats des réseaux de neurones artificiels

La Figure 5.2 illustre la concordance entre les résultats obtenus par simulation avec le RNA1 et les résultats expérimentaux. Une approche itérative basée sur des essais et erreurs a été utilisée pour optimiser les paramètres de formation du RNA1. Le Tableau 5.4 présente les valeurs optimales des différents paramètres (nombre de couches cachées, nombre de neurones, fonction d'activation, etc.) utilisés dans le développement du modèle. Un nombre de 18 neurones dans la couche cachée s'est avéré adéquat pour obtenir des coefficients de corrélation (R^2) pour l'apprentissage, la validation et le test de 0.9063, 0.7609 et 0.9829, respectivement. L'architecture du RNA1 était donc de 3(input)-18(couche cachée)-1(output). La Figure 5.3 présente les résultats du test de la capacité prédictive de RNA1 des travaux de cette étude. Les résultats montrent que le RNA1 a pu prédire la majorité des REs de CH_4 (78%) avec précision. Cependant un léger écart peut être observé entre les points expérimentaux et ceux obtenus par simulation. Cette divergence des résultats peut être attribuée à des facteurs qui n'ont pas été pris en compte lors de la modélisation du RNA1, tels que l'inhibition de CH_4-RE par les concentrations de CH_4 élevées, l'accumulation de biomasse, etc.

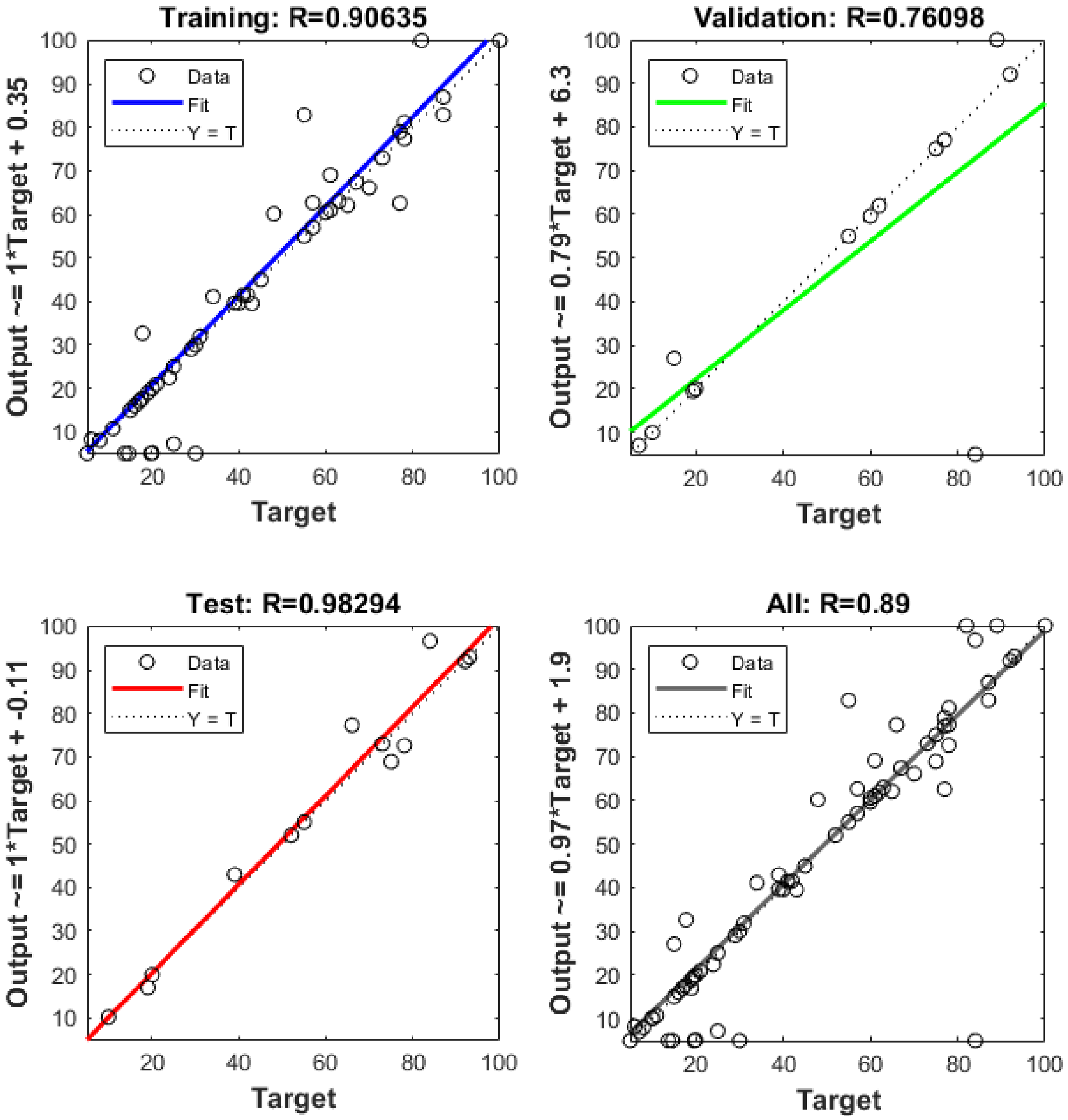


Figure 5.2: Corrélation entre les valeurs de RE observées et prédites pendant l'entrainement (Training) du réseau RNA1, la validation du RNA1 (Validation), le test du RNA1 (Test), les données combinées (All) et les valeurs de R (coefficient de corrélation : R^2) correspondantes (Data : données, Fit : bissectrice, Output : résultats de modélisation, Target : résultats expérimentaux)

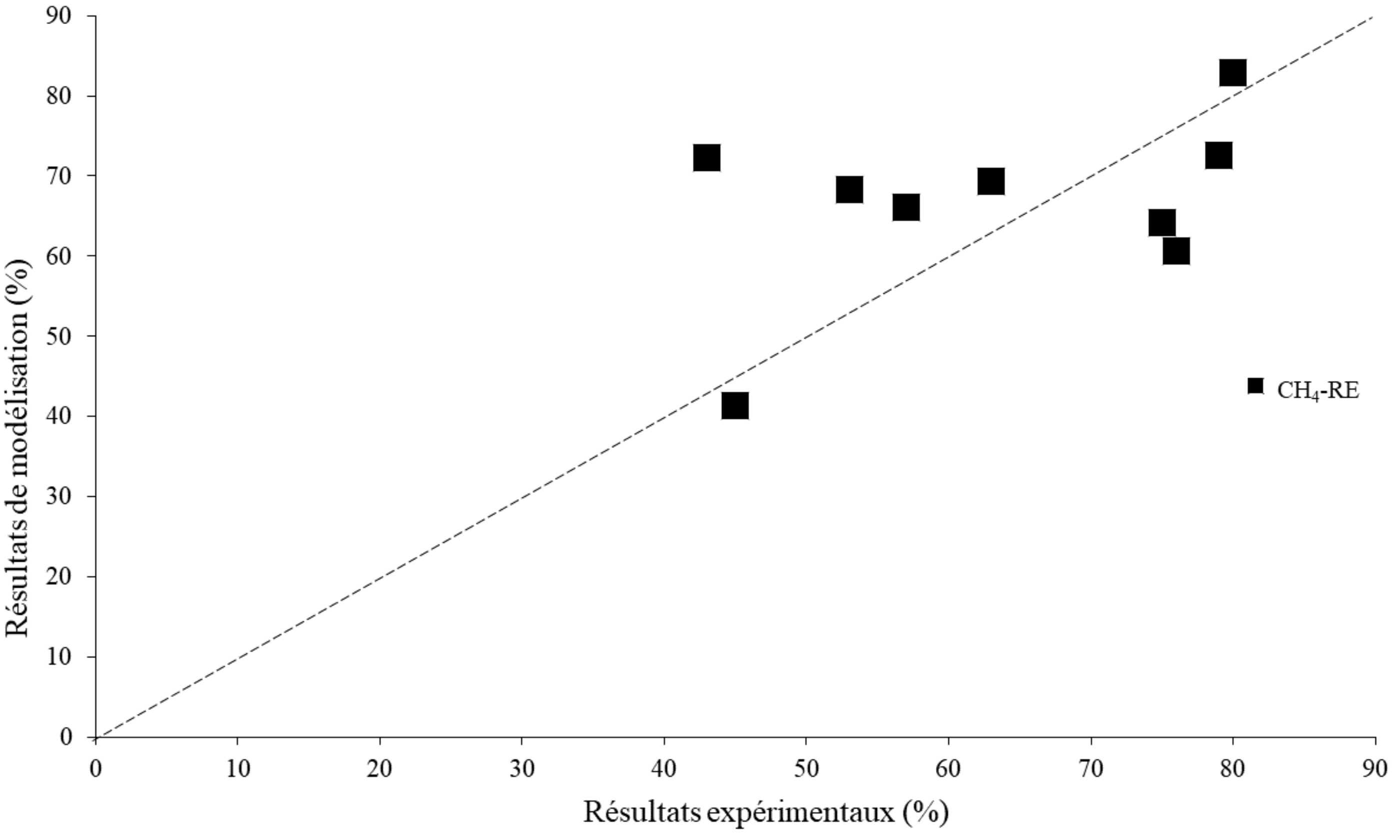
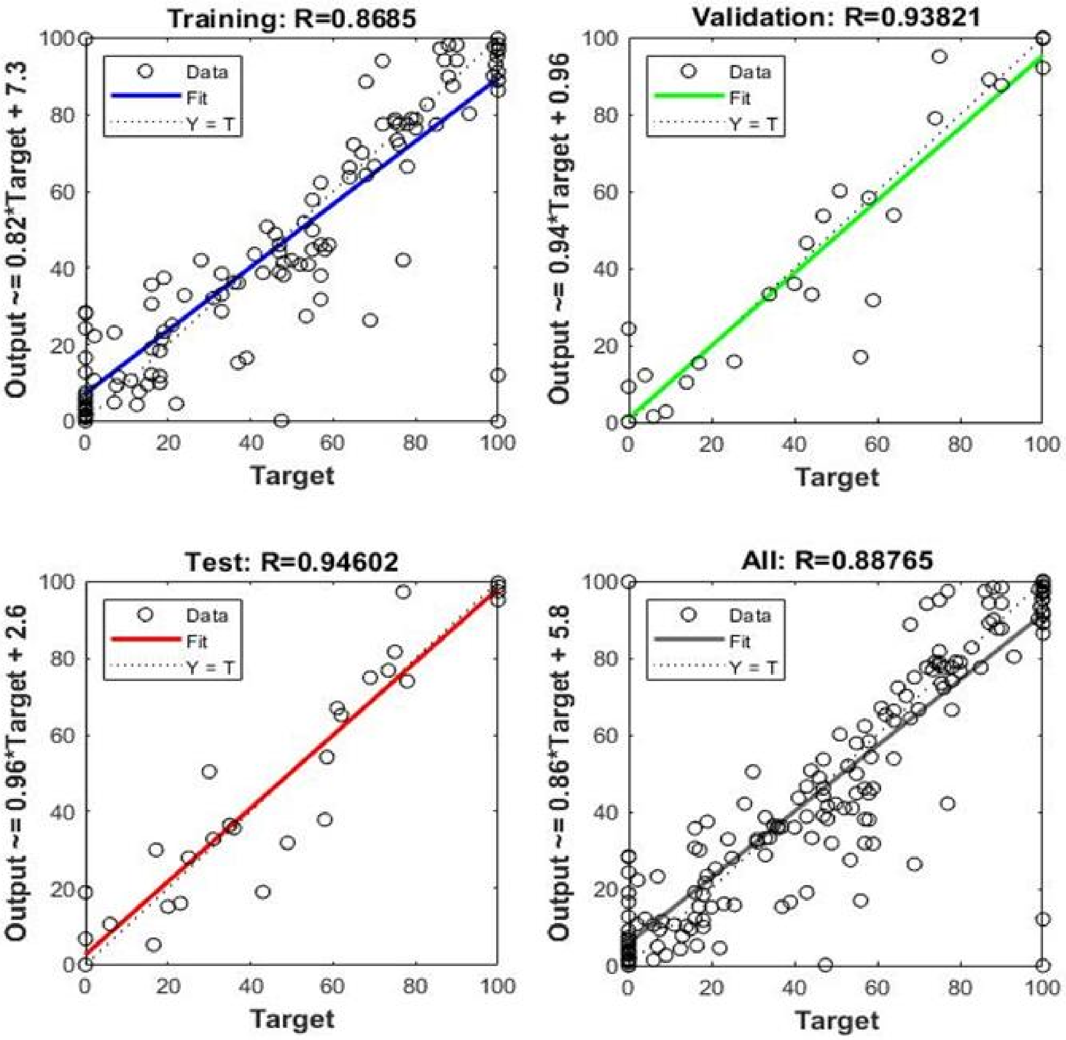


Figure 5. 3: Comparaison des CH_4-RE prédites par le RNA1 (Output) avec celles obtenues expérimentalement (Target)

Table 5.4:Paramètres optimaux pour la création du RNA1

Paramètres	
Type de réseau de neurones artificiel	Perceptron multicouches
Algorithme	Levenberg-Marquardt
Nombre de couches cachées	1
Nombre de neurones dans la couche cachée	18
Fonction d’activation	Tangente sigmoïde
Nombre d’itérations	10000

La Figure 5.4 présente les résultats simulés par le RNA2 comparés aux résultats expérimentaux. Le Tableau 5.5 donne les valeurs optimales des différents paramètres utilisés dans le développement du modèle. Un nombre de 18 neurones dans la couche cachée a permis d'obtenir des R^2 de 0.8241, 0.7673 et 0.8837 respectivement pour l'apprentissage, la validation et le test. L'architecture de RNA2 était donc de 4, 18 et 2 neurones dans les couches d'entrée, cachée et sortie, respectivement. Les valeurs de R^2 pour RNA2 étaient 10% inférieures à celles obtenues pour RNA1. Ceci peut être dû au fait que les 2 COVs ont été considérés comme un unique composé ayant les mêmes propriétés et effets sur la biodégradation du CH_4; seule la concentration en COV [ppmv] a été utilisée comme input. Cependant, l'effet des différents COVs présents dans les études constituant la base de données du RNA2 (Tableau 5.2) n'est pas le même sur la biofiltration du CH_4. Par exemple, Merouani et al., (2022) ont montré que le X (500 ppmv) peut avoir un effet inhibiteur sur la conversion du CH_4 (2000-1000 ppmv) tandis que l'EB (500 ppmv) a un effet neutre. L'ajout d'un paramètre d'entrée supplémentaire et une taille de base de données inférieure (70 points) par rapport à celle du RNA1 (84 points) peuvent également avoir eu un effet négatif sur la précision du RNA2. Il a été prouvé par Larbi et al., (2019) que la taille de la base de données influence la précision du réseau et que l'augmentation du nombre de données augmente la précision du réseau. Les Figures 5.5 (a) et (b) montrent les résultats du test de la capacité prédictive du RNA2 pour la conversion du CH_4 et des 2 COVs respectivement. Les résultats montrent que le RNA2 a pu prédire avec précision 60% des CH_4-REs contre 66% des COV-REs. Un léger écart peut être observé pour les CH_4-RE par rapport aux COV-RE. Une explication possible est que les CH_4-RE dans la base de données étaient situées dans une large plage comprise entre 6% et 80%, tandis que les valeurs de COV-RE étaient comprises entre 75% et 100% (en excluant les points de 0% lorsque la concentration des polluants était de 0 ppmv). La comparaison entre les résultats simulés par RNA3 et ceux de la base de données sont présentés sur la Figure 5.6.



Training: R=0.8685

Validation: R=0.93821

Test: R=0.94602

All: R=0.88765

Figure 5.4 : Corrélation entre les valeurs de RE observées et prédites pendant l'entrainement (Training) du réseau RNA2, la validation du RNA2 (Validation), le test du RNA2 (Test), les données combinées (All) et les valeurs de R (coefficient de corrélation : R^2) correspondantes (Data : données, Fit : bissectrice, Output : résultats de modélisation, Target : résultats expérimentaux)

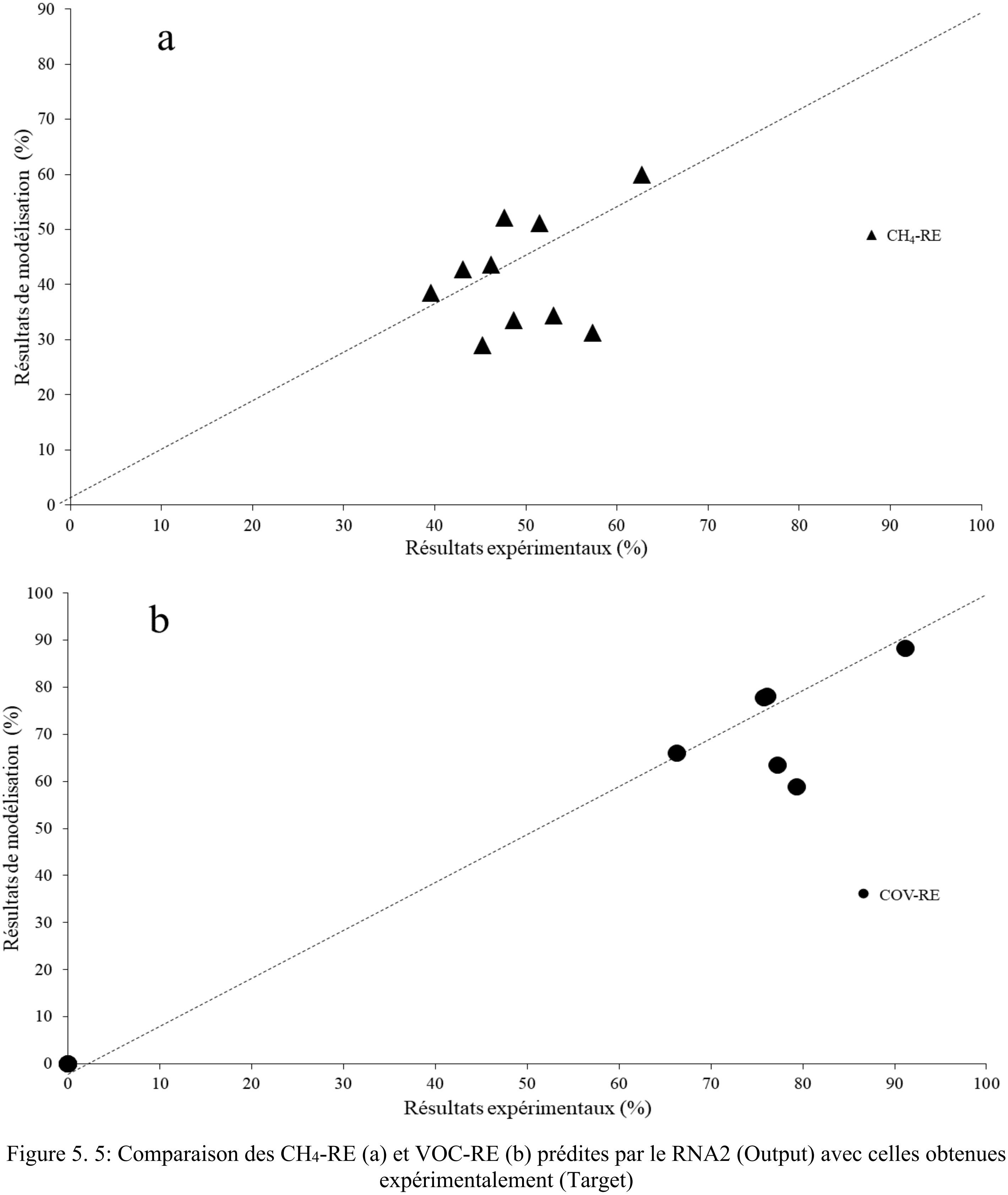


Figure 5. 5: Comparaison des CH_4-RE (a) et VOC-RE (b) prédites par le RNA2 (Output) avec celles obtenues expérimentalement (Target)

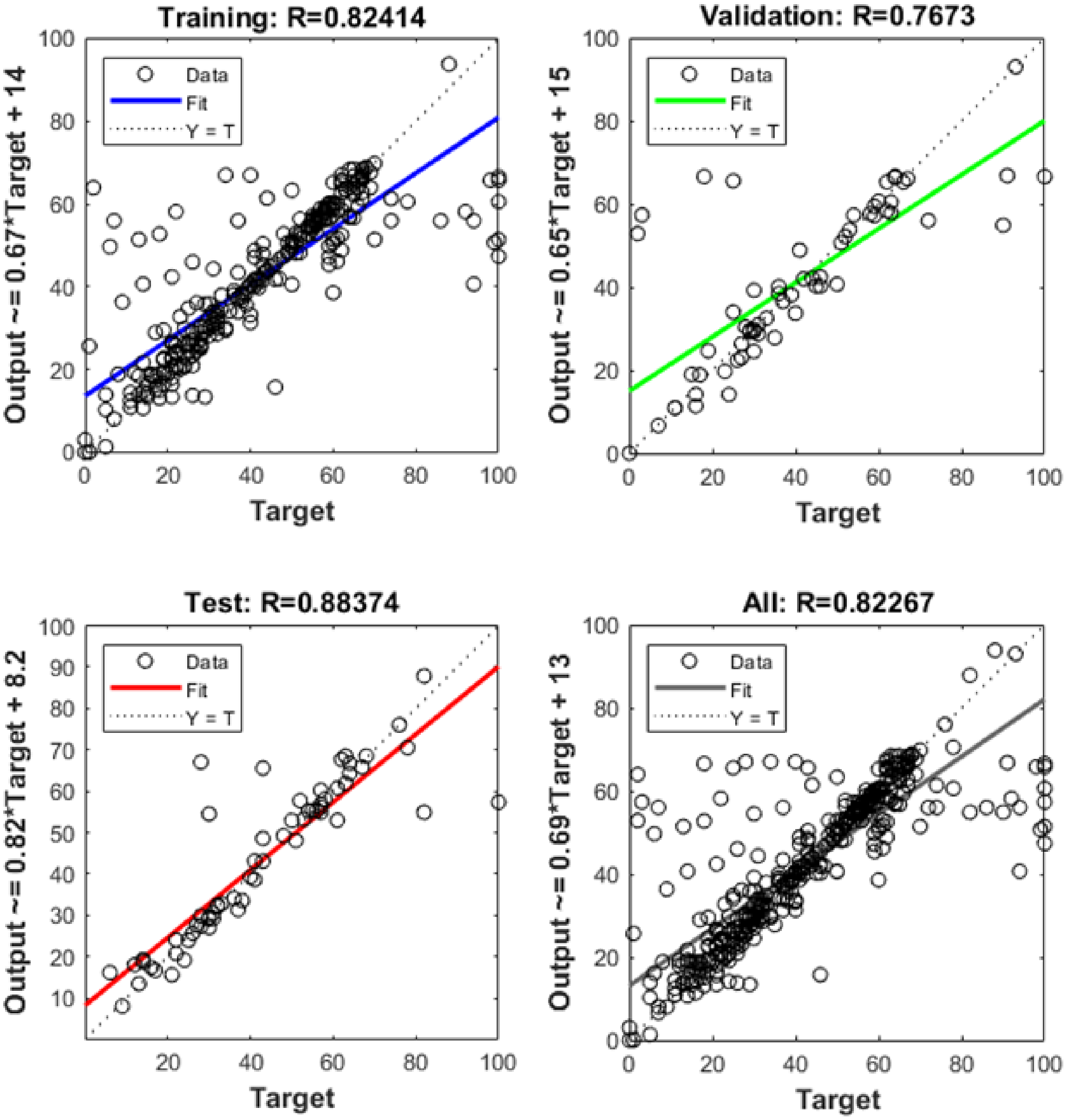


Figure 5. 6: Corrélation entre les valeurs de RE observées et prédites pendant l'entrainement (Training) du réseau RNA3, la validation du RNA3 (Validation), le test du RNA3 (Test), les données combinées (All) et les valeurs de R (coefficient de corrélation : R^2) correspondantes (Data : données, Fit : bissectrice, Output : résultats de modélisation, Target : résultats expérimentaux)

Table 5.5:Paramètres optimaux pour la création du RNA2

Paramètres	
Type de réseau de neurones artificiel	Perceptron multicouches
Algorithme	Levenberg-Marquardt
Nombre de couches cachées	1
Nombre de neurones dans la couche cachée	18
Fonction d'activation	Tangente sigmoïde
Nombre d'itérations	10000

Table 5.6:Paramètres optimaux pour la création du RNA3

Paramètres	
Type de réseau de neurones artificiel	Perceptron multicouches
Algorithme	Levenberg-Marquardt
Nombre de couches cachées	1
Nombre de neurones dans la couche cachée	30
Fonction d'activation	Tangente sigmoïde
Nombre d'itérations	10000

Un nombre de neurones optimales de 30 dans la couche cachée a permis d'obtenir des R^2 respectifs de 0.8241, 0.7673 et 0.8837 pour l'apprentissage, la validation et le test. Le Tableau 6 présente les valeurs et paramètres utilisés pour la formation de RNA3. Les valeurs de R^2 pour l'apprentissage, la validation et le test pour RNA3 étaient inférieures à celles des RNA1 et RNA2. Ceci peut être dû à une base de données considérablement supérieure en nombre de points pour le RNA3 en plus de la grande dispersion des points en termes de REs observées dans la biofiltration de CH_4 en fonction du temps (RNA3) comparés à celle observée pour un régime pseudo-stationnaire (RNA1 et RNA2). Une comparaison de la cinétique de biofiltration du CH_4 obtenue expérimentalement avec celle simulées par RNA3 est présentée sur la Figure 5.7. Le réseau RNA3 a pu prédire avec précision la phase d'acclimatation à une concentration de CH_4 de 1000 ppmv ainsi que la phase finale à une concentration de CH_4 de 10000 ppmv. Cependant, un écart plus important a été noté en phase transitoire entre 1000 et 2000 ppmv, alors que la CH_4-RE variait entre 60 et 70%. Le RNA3 a prédit une diminution de CH_4-RE jusqu'à 44%. De plus, le RNA3 a prédit une augmentation de CH_4-RE de 44% à 69% entre les jours 52 et 73 suivie par une diminution de la CH_4-RE jusqu'à 42% au jour 94 alors que les résultats expérimentaux montrent que la CH_4-RE est restée relativement stable entre 60 et 73%. Cette différence entre les résultats expérimentaux et simulés durant les périodes de changements de concentration du CH_4 indique que le RNA3 s'est basé sur les résultats de la base de données pour prédire des diminutions de CH_4-RE après une augmentation de concentration du CH_4 ou après une durée dépassant les 20 jours alors que le biofiltre de la présente étude a réussi à maintenir des performances relativement stables durant les différents changements de concentrations de CH_4.

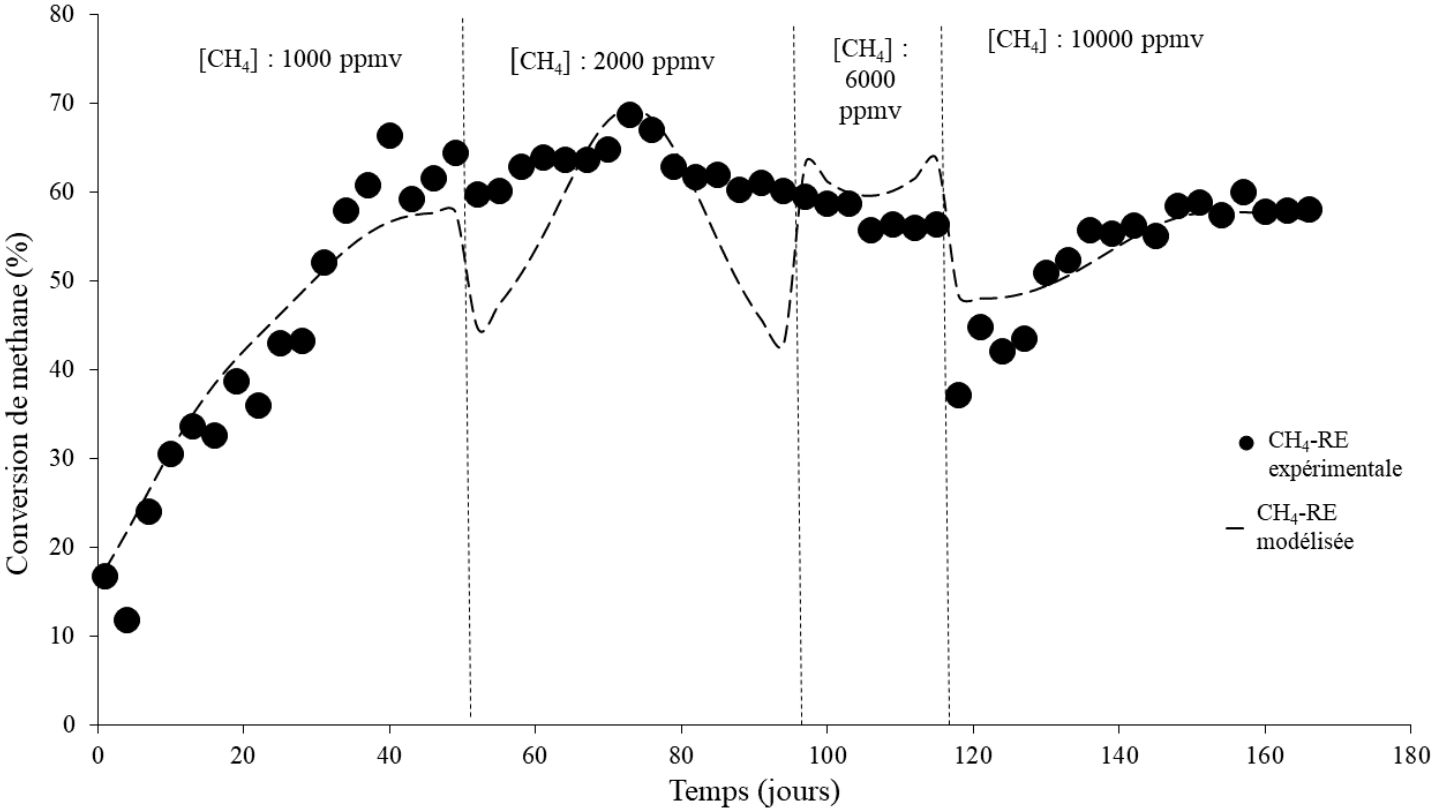


Figure 5.7: Comparaison des CH_4-RE prédites par le RNA3 (Output) avec celles obtenues expérimentalement (Target) en fonction du temps

Plusieurs auteurs ont utilisé des données obtenues expérimentalement pour gérer des RNAs et modéliser la biofiltration de divers composés. Par exemple, René et al., (2008) ont modélisé la cinétique de biofiltration du sulfure d'hydrogène (H_2S) par un RNA avec une architecture sous forme 4(input)-4(couche cachée)-2(output) avec le débit volumique, la charge à l'entrée, la perte de charge et la concentration en H_2S comme paramètres d'entrée et la RE et la capacité d'élimination comme paramètres de sortie. Les auteurs ont utilisé une base de données de faible taille (51 points) et ont obtenu des résultats simulés présentant un faible écart comparé à celui obtenu expérimentalement (R^2 variant entre 0.91 et 0.99). Dans l'étude de Dewidar et al., (2022), les auteurs ont utilisé un RNA pour la modélisation de la biofiltration d'un mélange binaire de 2 COVs (toluène-styrène) en utilisant comme paramètres d'entrée : les concentrations du toluène et du styrène, le temps de séjour en fût vide et le ratio molaire toluène/styrène; les conversions du toluène et du styrène comme paramètres de sortie (output). L'architecture du RNA sous forme de 4(input)-9(couche cachée)-2(output) avec une base de donnée constituée de 160 points expérimentaux a permis d'obtenir un modèle présentant une grande précision de prédiction (R^2 de 0.993).

Malgré de meilleures précisions (R^2 entre 0.91-0.99) que celles obtenue dans cette étude (R^2 entre 0.82-0.89), les travaux de modélisations par RNA traitant une série de résultats portant sur la biofiltration d'un seul composé obtenus expérimentalement pour la prédiction des performances de biofiltres ne peuvent être généralisés ou considérés comme fiables pour la modélisation des bioréacteurs même si ces derniers ont été utilisés sous les mêmes conditions opératoires. La présente approche se veut être très générale par la considération de résultats de biofiltration de différents auteurs et dans des domaines de conditions opératoires très larges. Cette approche devrait permettre de prédire les performances de biofiltres et l'évolution de leurs comportements dans le temps avec un précision acceptable et ceci même si les conditions opératoires sont différentes de celles utilisées lors de la génération de la base de données.

5.5. Conclusion

La biofiltration simultanée du CH_4 en présence de 2 COVs (xylène et éthylbenzène) a été étudiée dans un biofiltre à garnissage inorganique sous un EBRT de 4.5 min. Les résultats expérimentaux ont montré que la RE du CH_4 était située dans l'intervalle de 50-60% pour des concentrations de CH_4 variant entre 1000 et 10000 ppmv. L'augmentation de la concentration de CH_4 de 2000 à 10000 ppmv a entraîné une diminution de la RE des COVs de 90 à 70%. Des RNAs construits à partir de bases de données issues de travaux de recherches antérieurs sur la biofiltration du CH_4 et de différents COVs ont été utilisés pour prédire et simuler les performances du biofiltre de la présente étude.

Le RNA1 ayant une architecture de 3(input)-18(couches cachées) -1(output) a permis de prédire avec précision les résultats de RE du CH_4 seul à l'état pseudo-stationnaire (R^2 : 0.89). Le RNA2, utilisé pour la prédiction de la RE du CH_4 en présence COVs (X et EB) lors de la biofiltration simultanée a donné des résultats avec une précision légèrement inférieure (R^2 : 0.88) au RNA1 pour une architecture similaire (4-18-1). Les résultats montrent que le RNA3, avec un nombre optimal de 30 neurones dans la couche cachée, est capable de prédire avec précision la phase d'acclimatation et la dernière phase du biofiltre lors de la bioélimination du CH_4. Cependant, le réseau n'a pas réussi à prédire avec précision les phases transitoires pour des concentrations de CH_4 comprises entre 1000 et 6000 ppmv. Le RNA3 a également présenté des différences significatives par rapport aux résultats expérimentaux lors des périodes de changement de concentration de CH_4 (R^2 : 0.82). Ces résultats soulignent l'importance de l'utilisation d'une base de données étendue pour améliorer les performances des RNAs lors de la simulation de phénomènes complexes tels que la biofiltration de CH_4 seul ou en présence de COVs en fonction du temps.

Le principal objectif de la présente étude était de développer un outil d'aide à la décision permettant de prédire la concentration en polluants (CH_4 et X/EB) à la sortie du biofiltre et le comportement de ce dernier lors de son vieillissement. Cette étude a fourni des résultats intéressants sur l'utilisation des RNAs pour prédire les performances de la biofiltration du CH_4 en régimes dynamique et pseudo-stationnaire ainsi qu'en présence de COVs. L'architecture du RNA proposée dans cette étude pourrait avoir une application industrielle prometteuse pour améliorer les performances des biofiltres dans le traitement des gaz résiduaires contenant du CH_4 et des COVs ainsi que pour anticiper les performances de biofiltration après de longues durées d'utilisation. Cette approche permettrait de s'affranchir d'une expérimentation chronophage et coûteuse.

Logiciel :

MATLAB R2022 (MathWorks, USA) Numéro de licence: 41112427

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Chapitre 6: Conclusion

Reducing anthropogenic CH_4 emissions from industrial gaseous effluents is increasingly urgent due to global warming. By 2030, several CH_4-emitting sectors must reduce their emissions by up to 30%. To achieve this goal, various CH_4 valorization (i.e. heat generation in burners) and elimination techniques (i.e. thermal/catalytic oxidation, flares, etc.). However, due to capital and operational costs, some sectors, like old and small landfills with low CH_4 concentrations (below 3% v/v), avoid traditional abatement techniques. Biofiltration offers a more affordable and reliable solution for CH_4 mitigation compared to the conventional processes. Studies conducted over the past two decades have provided optimal parameters for CH_4 biofiltration.

Landfills offer certain advantages that have the potential to enhance LFG biofiltration, including nutrient-rich soil and landfill leachate. These factors can provide valuable resources for the MOs involved in the biofiltration process. Nutrient-rich soil serves as a source of essential nutrients for the microorganisms, supporting their growth and activity within the BF. Furthermore, landfill leachate can be used as an inoculum, a nutrient solution, and a mean to maintain the appropriate humidity level in the BF. However, LFG biofiltration encounters various challenges that need to be addressed such as the impact of weather conditions on the operation of the BF. Fluctuations in rainfall, temperature and humidity can influence the performances of the BFs. Another significant challenge is the simultaneous biofiltration of CH_4 and VOCs present in LFG. While CH_4 is the primary target for removal, the presence of VOCs can complicate the biofiltration process. The interactions and synergistic effects between CH_4 and VOCs during biofiltration require further investigations to optimize the treatment efficiency and understand the underlying mechanisms. Addressing these challenges is crucial for effective CH_4 emissions reduction and environmental protection. Further research and development efforts should focus on optimizing BF design and advancing the understanding of the biofiltration process for the simultaneous removal of CH_4, VOCs and VICs in LFG.

The primary aim of this study was to investigate the simultaneous biofiltration of CH_4 along with two specific VOCs in binary mixtures: CH_4/X and CH_4/EB. Two identical BFs, equipped with inorganic packing materials, were used in the experiments, applying variable concentrations of CH_4 and VOCs. The BFs exhibited comparable behaviors, likely attributed to the structural similarities shared by the 2 target VOCs. Both BFs successfully acclimated to the individual VOCs, achieving VOC-REs exceeding 90% for VOC-ILs up to 32 $g.m^{-3}.h^{-1}$. Furthermore, the inclusion of CH_4 was well accommodated in both BFs, owing to the presence of an initial CH_4-degrading inoculum derived from the original leachate (obtained from another BF treating CH_4) used for inoculation. However, differences in certain substrate characteristics, such as biodegradability, inhibitory effects, and microbial toxicity contributed to divergent behaviors observed in the two BFs. In the case of removing binary VOC/CH_4 mixtures, the concentration of EB (500 ppmv) partially mitigated the inhibitory effect of CH_4 concentration (6000-10000 ppmv) on EB biodegradation, unlike X. This suggests a potential simultaneous contribution of certain microorganisms involved in EB degradation to CH_4 removal. Under a CH_4 concentration of 2000 ppmv, both BFs achieved approximately 60% CH_4-REs with a VOC concentration of 200 ppmv. The observed increase in PCO_2 when EB or X were present with CH_4 further confirmed microbial development and activity in both BFs during operation.

The second objective of this study was to evaluate the interaction effects between CH_4, X and EB in a ternary mixture under different concentrations and EBRTs ranges and in absence/presence of either CH_4 or the VOCs. The concentrations of the pollutants varied within the range of 2000 to 10000 ppmv for CH_4 and 200 to 600 ppmv for both VOCs. The EBRT ranged from 2.25 to 9 minutes. The performance of BFs was affected by pollutant concentrations in the ternary mixture. Adding X and EB individually at 200 ppmv led to a 40% decrease in CH_4-REs for all CH_4 concentrations due to inhibition from both VOCs. However, increasing X and EB concentrations to 400 and 600 ppmv slightly improved CH_4 biodegradation. Empty bed residence time played a crucial role in CH_4 biodegradation. The highest CH_4-RE in the absence (78%) and presence (41%) of VOCs was achieved at an EBRT of 9 min, while at an EBRT of 4.5 min, X and EB removal efficiencies (X-RE and EB-RE) were 30% and 20% higher compared to VOC-REs at other EBRTs. The biodegradation of pollutants occurred in different sections of the BF, with CH_4-RE increasing along its height and was the highest at the top section. Xylene-RE and EB-RE were highest in the middle section, unaffected by CH_4 concentrations. The authors linked the difference in pollutant biodegradation across the BF to high ILs of pollutants at the bottom section, pollutant toxicity, difference in void fraction of the packings and lower nutrient availability due to irrigation from top section. The increase in total pollutant IL resulted in the decrease of nutrient concentrations, especially NO_3^-. As a result, the nutrient-starved conditions negatively affected pollutant biodegradation and resulted in increased levels of TOC in the leachate, indicating biomass production.

The third objective of this study was the ANN modeling of the simultaneous biofiltration of CH_4 (pseudo-steady state and dynamic), X and EB. Experimental results showed that CH_4-REs of 50-60% could be obtained for concentrations between 1000 and 10000 ppmv. Increasing CH_4 concentration (from 2000 to 10000 ppmv) reduced X and EB-REs from 90% to 70%. The ANNs were constructed using previous research databases to predict BF performance. The ANN1 (architecture: 3 (input)-18 (hidden layer)-1 (output)) accurately predicted pseudo-steady-state CH_4 conversion. The ANN2 (4-18-1) slightly underperformed ANN1 for simultaneous CH_4 and VOC conversion prediction. The ANN3 (optimal 30 neurons in hidden layer) accurately predicted the acclimation and final BF phases. However, transient phases between 1000 and 2000 ppmv of CH_4 were challenging to predict, showing deviations from experimental results. These findings highlight the need for comprehensive databases to enhance ANN performance in simulating complex CH_4 biofiltration kinetics. The proposed ANN architecture in this study holds promising industrial applications to enhance BF performance in treating waste gases containing CH_4 and VOCs like X and EB, as well as anticipating biofiltration performance after long durations of operation.

This study presented promising results regarding the simultaneous biofiltration of CH_4 in the presence of two common aromatics compounds found in LFG: X and EB. This study emphasized the significance and impact of various operating factors such as pollutant concentrations and EBRT. Additionally, it demonstrated the variations in biofiltration performance based on the complexity of the gaseous mixture. The results conclusively demonstrated that the inorganic packing material employed in this research effectively eliminated binary and ternary mixtures of CH_4, X, and EB. Moreover, the study highlighted the influence of some nutrients, particularly the N source, on biofiltration performance for pollutant biodegradation. This study offers valuable insights into the application of ANNs for predicting the performance of CH_4 biofiltration under dynamic and pseudo-steady-state conditions, as well as in the presence of VOCs. This approach has the potential to save time and money by circumventing the need for extensive and costly experimentation.

6.1 Conclusion en français

Réduire les émissions anthropogéniques de CH_4 provenant des effluents gazeux industriels est de plus en plus urgent en raison du réchauffement climatique. D'ici 2030, plusieurs secteurs émetteurs de CH_4 doivent réduire leurs émissions jusqu'à 30 %. Pour atteindre cet objectif, diverses techniques de valorisation du CH_4 (comme la génération de chaleur dans des chaudières) et d'élimination (comme l'oxydation thermique/catalytique, les torchères, etc.) sont utilisées. Cependant, en raison des coûts en capital et en exploitation, certains secteurs, tels que les anciens et petit SES émettant de faibles concentrations de CH_4 (inférieures à 3 % v/v), évitent les techniques d'abattement traditionnelles. La biofiltration offre une solution plus abordable et fiable pour la réduction du CH_4 par rapport aux procédés conventionnels. Des études menées au cours des deux dernières décennies ont fourni des paramètres optimaux pour la biofiltration du CH_4.

Les SES offrent certains avantages qui ont le potentiel d'améliorer la biofiltration du gaz issu de SES, notamment un sol et un lixiviat riches en nutriments. Ces derniers peuvent fournir des ressources précieuses aux micro-organismes impliqués dans le processus de biofiltration. Le sol riche en nutriments sert de source de nutriments essentiels pour les micro-organismes, favorisant leurs croissances et leurs activités dans le biofiltre. De plus, le lixiviat de SES peut être utilisé comme inoculum, solution nutritive et un moyen de maintenir le niveau d'humidité approprié dans le BF. Cependant, la biofiltration du LFG rencontre divers défis qui doivent être résolus, tels que l'impact des conditions météorologiques sur le fonctionnement du biofiltre. Les fluctuations des précipitations dans les BFs ouvert et de la température peuvent influencer les performances des BFs. Un autre défi important est la biofiltration simultanée du CH_4 et des COVs présents dans le gaz issu de SES. Bien que le CH_4 soit la cible principale pour l'élimination, la présence de COVs peut compliquer le processus de biofiltration du GES. Les interactions et les effets synergiques entre le CH_4 et les COVs pendant la biofiltration nécessitent des recherches supplémentaires pour optimiser l'efficacité du traitement du gaz issu de SES. Aborder ces défis est essentiel pour une réduction efficace des émissions de CH_4 et pour la protection de l'environnement. Des efforts supplémentaires de recherche et de développement devraient se concentrer sur l'optimisation de la conception des BFs et sur l'avancement de la compréhension du processus de biofiltration pour l'élimination simultanée du CH_4, des COV et des CIV dans le LFG.

Le premier objectif de cette étude était d'étudier la biofiltration simultanée du CH_4 en présence de deux COVs spécifiques dans des mélanges binaires : CH_4/X et CH_4/EB. Deux BFs identiques, garni d’un matériau inorganique, ont été utilisés dans les expériences, en appliquant des concentrations variables de CH_4 et de COVs. Les BFs ont montré des comportements comparables, probablement attribuables aux similarités structurelles partagées par les 2 COV ciblés. Les deux BFs se sont acclimatés avec succès aux COVs; des REs de COVs dépassant les 90 % pour des COV-ILs allant jusqu'à 32 $g.m^{-3}.h^{-1}$ ont été atteintes. De plus, les deux BFs se sont adaptés à l’ajout du CH_4, grâce à la présence d'un inoculum dégradant le CH_4 dérivé d’un lixiviat original obtenu à partir d'un autre BF traitant le CH_4 et utilisé pour l'inoculation. Cependant, des différences dans certaines caractéristiques des substrats, telles que la biodégradabilité, les effets inhibiteurs et la toxicité microbienne, ont contribué aux comportements divergents observés dans les deux BFs. Dans le cas de l'élimination de mélanges binaires COV/CH_4, la concentration d'EB (500 ppmv) a partiellement atténué l'effet inhibiteur de la concentration de CH_4 (6000-10000 ppmv) sur la biodégradation de l'EB, contrairement à celle de X. Ceci suggère une contribution simultanée potentielle de certains microorganismes impliqués dans la dégradation de l'EB à l'élimination du CH_4. Sous une concentration de CH_4 de 2000 ppmv, les deux BFs ont atteint environ 60 % de RE du CH_4 avec une concentration de COV de 200 ppmv. L'augmentation observée de la production de CO_2 (PCO_2) lorsque l'EB ou le X étaient présents avec le CH_4 a confirmé le développement et l'activité microbienne dans les deux BFs pendant le fonctionnement.

Le deuxième objectif de cette étude était d'évaluer les effets d'interaction entre le CH_4, le X et l'EB dans un mélange ternaire à différentes concentrations et EBRTs, en l'absence/présence de CH_4 ou des COVs. Les concentrations des polluants ont varié dans la plage de 2000 à 10000 ppmv pour le CH_4 et de 200 à 600 ppmv pour les deux COVs. L'EBRT variait de 2.25 à 9 minutes. Les performances des BFs ont été affectées par les concentrations de polluants dans le mélange ternaire. L'ajout individuel de X et d'EB à 200 ppmv a entraîné une diminution de 40 % des RE s de CH_4 pour toutes les concentrations de CH_4 utilisées en raison de l'inhibition des deux COVs. Cependant, l'augmentation des concentrations de X et d'EB à 400 et 600 ppmv a légèrement amélioré la biodégradation du CH_4. L’EBRT a joué un rôle crucial dans la biodégradation du CH_4. La plus haute RE de CH_4 en absence (78 %) et en présence (41 %) de COVs a été atteinte à un EBRT de 9 minutes, tandis que pour un EBRT de 4.5 minutes, les REs du X et de l'EB (X-RE et EB-RE) étaient de 30 % et 20 % plus élevés par rapport aux RE s des COVs sous d'autres EBRTs. La biodégradation des polluants s'est produite dans différentes sections du BF, avec une augmentation de la RE du CH_4 le long de la hauteur du BF et la plus élevée a été atteinte dans la section supérieure. Les RE s du X et de l'EB étaient les plus élevés dans la section centrale et n’ont pas été affectés par les concentrations de CH_4. Les auteurs ont lié la différence de biodégradation des polluants à travers le BF à des charges à l’entrée (Ils) élevées des polluants dans la section inférieure, à la toxicité des polluants et à une disponibilité plus faible des nutriments en raison de l'irrigation du garnissage par une solution nutritive depuis la section supérieure. L'augmentation totale des IL des polluants a entraîné la diminution des concentrations de nutriments, en particulier du NO_3^-. En conséquence, les conditions appauvries en nutriments ont eu un impact négatif sur la biodégradation des polluants et ont entraîné une augmentation des niveaux de carbone organique total dans le lixiviat, indiquant une production de biomasse.

Le troisième objectif de cette étude était la modélisation de la biofiltration simultanée du CH_4 (état pseudo-stationnaire et dynamique), du X et de l'EB par RNA. Les résultats expérimentaux ont montré que des RE de CH_4 variant entre 50 et 60 % pouvaient être obtenues pour des concentrations comprises entre 1000 et 10000 ppmv. L'augmentation de la concentration de CH_4 (de 2000 à 10000 ppmv) a réduit les RE du X et de l'EB de 90 % à 70 %. Les RNAs ont été développés en utilisant des bases de données issues de recherche antérieures pour prédire les performances des BFs. Le RNA1 (architecture : 3 (entrée) - 18 (couches cachées) - 1 (sortie)) a prédit avec précision la RE pseudo-stationnaire du CH_4. L'RNA2 (4-18-1) a présenté une performance légèrement moindre que celle du RNA1 lors de la prédiction de la RE du CH_4. Le RNA3 (30 neurones optimaux dans la couche cachée) a prédit avec précision les phases d'acclimatation et finales du BF. Cependant, les phases transitoires entre 1000 et 6000 ppmv de CH_4 ont été difficiles à prédire, montrant des écarts par rapport aux résultats expérimentaux. Ces résultats soulignent la nécessité de larges bases de données pour améliorer les performances des RNAs lors de la simulation de la biofiltration du CH_4. L'architecture du RNA proposée dans cette étude offre des applications industrielles prometteuses pour améliorer les performances des BFs dans le traitement des gaz de SES contenant du CH_4 et des COVs tels que le X et l'EB, ainsi que pour anticiper les performances de biofiltration après de longues durées de fonctionnement.

Cette étude a présenté des résultats prometteurs concernant la biofiltration simultanée du CH_4 en présence de deux composés aromatiques trouvés dans le LFG : le X et l'EB. Cette étude a souligné l'importance et l'impact de divers paramètres opérationnels tels que les concentrations de polluants et l'EBRT. De plus, elle a démontré les variations des performances de biofiltration en fonction de la complexité du mélange gazeux. Les résultats ont clairement démontré que le matériau de garnissage inorganique utilisé dans cette recherche est adéquat pour la biodégradation de mélanges binaire et ternaire de CH_4, de X et de l'EB. De plus, l'étude a mis en évidence l'influence de certains nutriments, en particulier la source d'azote, sur les performances de biofiltration lors de la biodégradation des polluants. Cette étude offre des informations précieuses sur l'application des RNAs pour prédire la performance de la biofiltration du CH_4 dans des conditions dynamiques et pseudo-stationnaires, ainsi qu'en présence de COVs. Cette approche de modélisation a le potentiel d'économiser du temps et des ressources en contournant la nécessité d'expérimentations approfondies et coûteuses.

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