UNIVERSITÉ DE SHERBROOKE
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TRAITEMENT DU MÉTHANE ET DU LISIER ISSUS DE L'INDUSTRIE PORCINE PAR BIOFILTRATION

TREATMENT OF METHANE AND SWINE SLURRY FROM THE PIGGERY INDUSTRY BY BIOFILTRATION

Thèse de doctorat

Spécialité : génie chimique

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RÉSUMÉ

L'industrie porcine est très importante au Canada, mais les conditions d'entreposage et l'épandage excessif du lisier de porc contribuent respectivement aux émissions de méthane, un puissant gaz à effet de serre, et à la pollution de l'eau. Il existe de nombreuses techniques pour atténuer ces problématiques, mais le procédé de biofiltration s'impose comme étant capable de traiter le méthane et le lisier. Les objectifs principaux de cette thèse sont d'étudier la biofiltration du méthane à des concentrations représentatives de l'industrie porcine et d'effectuer le traitement simultané du méthane et du lisier de porc dans un même biofiltre.

Des essais expérimentaux à l'échelle laboratoire ont permis de mieux comprendre la biofiltration du méthane issu de l'industrie porcine. En utilisant un lit filtrant inorganique, il a été possible d'atteindre une capacité d'élimination maximale de 14,5 ± 0.6 $g \cdot m^{-3} \cdot h^{-1}$ pour une charge à l'entrée de 38 ± 1 $g \cdot m^{-3} \cdot h^{-1}$. L'efficacité d'enlèvement était relativement stable en fonction de la concentration de méthane et le biofiltre présentait une cinétique de premier ordre. En diminuant la concentration de nitrate dans la solution nutritive, une concentration de 0,1 $gN \cdot L^{-1}$ s'est avérée suffisante pour assurer l'opération adéquate du biofiltre. De plus, en éliminant tout apport d'azote inorganique, la présence de microorganismes capables de fixer l'azote atmosphérique a été établie. Des bilans de masse sur le carbone et l'azote ont illustré que le carbone accumulé dans le biofiltre était utilisé pour la production de matières de stockage plutôt que pour la synthèse cellulaire.

La viabilité de traiter simultanément le méthane et le lisier a été démontrée en utilisant un design innovateur de biofiltre pour éviter l'inhibition de la biodégradation du méthane par le lisier. Quoique généralement moins performant que la biofiltration du méthane seul, ce système a permis d'obtenir une capacité d'élimination de méthane de 18.8 ± 1.0 $g \cdot m^{-3} \cdot h^{-1}$ pour une charge de 46.7 ± 0.9 $g \cdot m^{-3} \cdot h^{-1}$. Des souches pures de champignons ont été utilisées afin d'améliorer la performance, mais aucun effet significatif n'a été observé. Pour le traitement du lisier de porc, des taux d'enlèvement moyens de 67 ± 10 % pour le carbone organique total et de 70 ± 7 % pour l'ammonium ont été obtenus. L'influence de l'alimentation en lisier a été analysée et le mode d'alimentation idéal fut de 6 doses de 50 ml par jour.

Des essais à l'échelle pilote effectués directement sur une ferme porcine ont permis de valider les résultats obtenus au laboratoire pour le traitement du méthane dans l'air de ventilation d'un bâtiment d'élevage. Après une phase de démarrage de 30 jours, des efficacités d'épuration jusqu'à 83% ont été observées pour une charge de méthane à l'entrée de 1.6 ± 0.8 $g \cdot m^{-3} \cdot h^{-1}$. Du lisier de porc traité a été testé pour remplacer la solution nutritive synthétique, mais dû à la présence de composés inhibiteurs dans le lisier traité, les résultats obtenus n'étaient pas satisfaisants. Pour le traitement simultané, l'efficacité d'épuration du méthane a seulement diminué de 58 ± 5% à 53 ± 8% lorsque le lisier a été alimenté au biofiltre. En intégrant les résultats de cette étude aux techniques agricoles modernes, l'industrie porcine pourrait réduire ses émissions de gaz à effet de serre et traiter une partie des nutriments du lisier de porc.

Mots-clés : Biofiltration, méthane, lisier de porc, traitement simultané, gaz à effet de serre, industrie porcine

ABSTRACT

The piggery industry is very important in Canada, but localized production of large quantities of swine slurry causes severe environmental problems such as aquatic pollution and emissions of methane, a potent greenhouse gas. There are many technologies that can reduce the impact of these issues, but biofiltration is the only viable process that can treat both pollutants. The main objectives of this thesis are to study the biofiltration of methane at concentrations representative of the piggery industry and to achieve the simultaneous treatment of methane and swine slurry with a single biofilter.

Laboratory-scale experiments were used to better understand the biofiltration of methane from the piggery industry. Using an inorganic filter bed, it was possible to reach a maximum elimination capacity of 14.5 ± 0.6 $g \cdot m^{-3} \cdot h^{-1}$ for an inlet load of 38 ± 1 $g \cdot m^{-3} \cdot h^{-1}$. The removal efficiency was relatively stable with the methane concentration and the biofilter satisfied first order kinetics. By decreasing the nitrate concentration in the nutrient solution, a concentration of 0.1 $gN \cdot L^{-1}$ proved to be sufficient for proper biofilter operation. Furthermore, once all inorganic sources of nitrogen were removed, the presence of microorganisms capable of fixing atmospheric nitrogen was established. Carbon and nitrogen mass balances suggested that the carbon accumulated within the biofilter was probably used for the production of storage compounds rather than for cell synthesis.

The viability of simultaneously treating methane and swine slurry was demonstrated by using an innovative biofilter design to overcome the inhibition of methane biodegradation by swine slurry. Although generally less efficient than the biofiltration of methane alone, an elimination capacity for methane of 18.8 ± 1.0 $g \cdot m^{-3} \cdot h^{-1}$ was obtained with this system at an inlet load of 46.7 ± 0.9 $g \cdot m^{-3} \cdot h^{-1}$. Pure fungal strains were used in an attempt to improve performance, but no significant increase in the methane removal efficiency was observed. For swine slurry treatment, average removal efficiencies of 67 ± 10 % for total organic carbon and 70 ± 7 % for ammonium were achieved. The influence of the slurry supply was analyzed and the ideal supply method found in this study was 6 doses of 50 ml per day.

Pilot-scale tests carried out directly on a pig farm were used to validate the results obtained in the laboratory for the treatment of methane from swine house ventilation air. After a start-up period of 30 days, removal efficiencies up to 83% were observed for a methane inlet load of 1.6 ± 0.8 $g \cdot m^{-3} \cdot h^{-1}$. Treated swine slurry was tested as a replacement for the synthetic nutrient solution, but due to inhibitory compounds in the treated slurry, the results were not satisfactory. For the simultaneous treatment, the methane removal efficiency only dropped from 58 ± 5% to 53 ± 8% when slurry was supplied to the biofilter. By integrating the results obtained in this study with modern farming techniques, the piggery industry could reduce its greenhouse gas emissions and treat part of the nutrients in swine slurry.

Keywords: Biofiltration, Methane, Swine Slurry, Simultaneous Treatment, Greenhouse Gases, Piggery Industry

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PRÉSENTATION GÉNÉRALE

Au Québec, l'industrie porcine occupe une place importante dans le secteur agroalimentaire produisant des retombées économiques de 1,5 milliards de dollars en 2008 et fournissant 23 750 emplois directs et indirects (FPPQ, 2011). En 2010, 7,8 millions de porcs ont été produits au Québec, ce qui représente près de 30% de la production canadienne (CPC, 2011). Toutefois, le lisier de porc, le rejet principal de cette industrie, a un impact considérable sur l'environnement, tant au niveau du réchauffement climatique qu'au niveau de la pollution aquatique.

La gestion du lisier de porc est une source importante de gaz à effet de serre (GES). Une fois émis à l'atmosphère, ces gaz contribuent à retenir la chaleur près de la surface de la terre (MDDEP, 2011a). Les principaux GES de l'industrie porcine sont le méthane (CH_4) et l'oxyde nitreux (N_2O). Le CH_4 provient de la dégradation anaérobie de la matière organique du lisier et a lieu surtout lors du stockage. Le N_2O est un sous-produit de la transformation de l'azote contenu dans le lisier par nitrification et dénitrification, ce qui se produit lorsque le lisier est épandu sur les sols agricoles. Puisqu'il n'est pas possible de traiter les sources diffuses de GES comme le N_2O, cette étude s'est concentrée sur le CH_4 qui provient de sources ponctuelles. Au Canada, en 2008, la gestion du lisier porcin a libéré 1,3 million de tonnes d'équivalent en dioxyde de carbone (CO_2) de CH_4 (Jaques, 2010). Sur une ferme porcine, les deux sources principales de CH_4 sont la fosse de stockage et l'air de ventilation des bâtisses d'élevage.

En plus d'émettre des GES, la gestion du lisier de porc peut également engendrer de la pollution de l'eau. Le lisier contient des nutriments essentiels aux plantes et il est généralement valorisé comme fertilisant. Par contre, une sur-fertilisation au-delà des besoins des cultures peut causer l'enrichissement des eaux souterraines et des eaux de surface en éléments nutritifs et accélérer l'eutrophisation (Carpenter et al., 1998; Smith et al., 2007). Certains facteurs externes jouent également un rôle dans la pollution aquatique associée au lisier de porc. Par exemple, de fortes précipitations suite à l'épandage peuvent augmenter la quantité de lisier qui est apporté au système hydrique par les eaux de ruissellement (MDDEP, 2011b).

Le premier chapitre de cette thèse constitue une revue de littérature des problèmes environnementaux de l'industrie porcine et des solutions disponibles pour limiter leur impact. La problématique entourant les émissions de GES et la pollution aquatique est expliquée en détail. Par la suite, les technologies disponibles pour valoriser le lisier, réduire les émissions de GES et traiter les effluents sont présentées. Parmi les procédés de traitement, la biofiltration peut être appliquée autant au traitement du CH_4 qu'à l'élimination des nutriments dans le lisier de porc. Le potentiel et les limites du système de biofiltration pour le traitement simultané de ces deux types de pollution sont également discutés.

Les objectifs principaux de cette recherche sont d'étudier la biofiltration du CH_4 issu de l'industrie porcine et de traiter simultanément le CH_4 et le lisier de porc dans un même biofiltre. Dans le chapitre 2, la biofiltration du CH_4 à des concentrations représentatives de l'industrie porcine est présentée. Un lit filtrant composé d'un matériel inorganique a été utilisé dans les biofiltres, ce qui n'avait jamais été réalisé pour traiter le CH_4 à des concentrations provenant de l'industrie porcine. L'influence de la concentration de CH_4 dans l'air et de la concentration d'azote dans la solution nutritive est analysée. Une étude cinétique a été effectuée afin d'établir l'ordre global de réaction et de calculer la constante cinétique. Des bilans de masse sur le carbone et l'azote ont été utilisés pour déterminer les quantités accumulées dans le système de biofiltration.

L'étude expérimentale du traitement simultané du CH_4 et du lisier de porc par biofiltration est abordée au chapitre 3. Ce type de procédé n'a jamais été testé, mais pourrait être très bénéfique pour l'industrie porcine en permettant de traiter deux polluants à l'aide d'une seule unité. Un design innovateur de biofiltre a été développé pour éviter l'inhibition de la biodégradation du CH_4 par le lisier. Des souches pures de champignons ont été inoculées dans le biofiltre pour tenter d'améliorer l'enlèvement du CH_4. Ces microorganismes sont parfois utilisés en biofiltration pour augmenter l'efficacité d'épuration des composés hydrophobes. L'effet de la concentration de CH_4 sur la conversion du CH_4 et le traitement du lisier est étudié. L'influence de l'alimentation du lisier est évaluée en termes de la fréquence d'arrosage et du volume total alimenté par jour. Pour suivre l'épuration du lisier, deux paramètres sont utilisés : le carbone organique total et l'azote sous forme d'ammonium.

Des essais à l'échelle pilote ont été effectués directement sur une ferme porcine pour traiter le CH_4 provenant de l'air de ventilation d'une porcherie. Les principaux résultats de ces

essais sont présentés au chapitre 4. La biofiltration du CH_4 seul et le traitement simultané sont considérés. Pour la biofiltration du CH_4, l'effet du débit d'air et de l'ajout de CH_4 pur est analysé en fonction de la performance du biofiltre. Pour le traitement simultané du CH_4 et du lisier, l'influence d'injecter du lisier à l'étage du bas sur l'enlèvement du CH_4 est détaillée. Un des désavantages d'utiliser un lit filtrant inorganique pour la biofiltration du CH_4 est la nécessité de fournir une solution nutritive. Pour atténuer cet inconvénient, du lisier traité a été utilisé comme remplacement à la solution nutritive synthétique lors des essais pilotes. Les résultats de ces tests sont également décrits dans le chapitre 4.

CHAPITRE 1. Introduction

Avant-propos

L'article « *A Review of the Environmental Pollution Originating from the Piggery Industry and of the Available Mitigation Technologies: Towards the Simultaneous Biofiltration of Swine Slurry and Methane* » a été publié dans le Canadian Journal of Civil Engineering en 2009 : Vol. 36, pages 1946–1957.

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Résumé

Au Canada, l'industrie porcine occupe une place de choix dans le secteur agroalimentaire, mais le lisier de porc, sous-produit de cette industrie, est particulièrement nocif pour l'environnement. Les conditions d'entreposage et l'épandage excessif contribuent respectivement aux émissions de gaz à effet de serre et à la pollution aquatique. Cet article présente une revue de ces problèmes environnementaux et des technologies disponibles pour limiter leur impact. La pollution de l'eau causée par le lisier de porc est associée aux nutriments qu'il contient, l'azote et le phosphore notamment, tandis que les principaux gaz à effet de serre sont le méthane et l'oxyde nitreux. Les technologies existantes peuvent valoriser le lisier par la fertilisation agricole, réduire l'émission des gaz à effet de serre ou traiter les effluents par la séparation solide/liquide, des torchères ou des procédés biologiques. Une attention particulière a été portée à la biofiltration pour son potentiel à traiter simultanément ces deux types de pollution.

Abstract

In Canada, the piggery industry is an essential part of the agricultural sector, but the main waste product of this industry, swine slurry, is particularly harmful to the environment. The anaerobic storage conditions and the excessive use of slurry for agricultural fertilization contribute respectively to the emission of greenhouse gases and to aquatic pollution. This paper provides a review of these environmental concerns and of the existing mitigation technologies. Water pollution from swine slurry is associated with the nutrients it contains, such as nitrogen and phosphorous, while the main greenhouse gases produced by the piggery industry are methane and nitrous oxide. Available technologies can valorize the slurry through agricultural fertilization, reduce greenhouse gas emissions, by limiting nutrient availability for example, or treat the effluents using solid/liquid separation, flaring or biological processes. Specific attention is paid to biofiltration due to its potential to simultaneously treat these two types of pollution.

1.1. Introduction

Pork is the type of meat most consumed in the world with over 115 million tonnes produced in 2007, which represented approximately 40% of worldwide meat production (FAOSTAT, 2011). China is by far the largest producer with nearly 53% of the market (i.e. 61 million tonnes of meat produced in 2007) (FAOSTAT, 2011). The United States come in second with a little under 10 million tonnes which generated US$34.5 billion in 2007 (National Pork Producers Council, 2008). In Canada, the piggery industry is an essential part of the agricultural sector. In 2007 alone, this industry provided more than 64 000 direct and indirect jobs (Agriculture and Agri-Food Canada, 2007) with exports worth over CAN$3 billion (CPC, 2011). There were over 31 million hogs produced in Canada in 2007, equivalent to 1.9 million tonnes of pork meat (FAOSTAT, 2011).

However, the main waste product of this industry, swine slurry, causes severe environmental problems. Excessive use of slurry for agricultural fertilization can lead to eutrophication in lakes and rivers and greenhouse gases (GHG) can be produced at various stages of slurry management. The objective of this paper is to review these environmental concerns and to examine the available mitigation technologies for each type of pollution. The

process of biofiltration will be explored in detail due to its potential to treat both types of pollution within the same unit.

1.2. Swine Slurry

Swine slurry is a mixture of pig feces and urine with wastewater and sometimes precipitation (BAPE, 2003). On average, each pig produced generates 1 m^3 of slurry during its lifetime (Dubé, 1997). Traditionally in Canada, pig farms were relatively small operations with an average of 91 pigs per farm in 1976, but with the modernisation of the industry, the number of pigs per farm increased dramatically to 1162 in 2006 (CPC, 2011). Increasing the size of a pig farm improves productivity (Samarakone and Gonyou, 2008), but it also implies that there is a major increase in slurry and GHG to manage within a localized area.

1.2.1. Swine Slurry Composition

Swine slurry contains mainly suspended solids, organic matter, nitrogen, phosphorous and potassium. However, the specific concentrations of these components depend on several factors such as the housing system, the type of feed and slurry management (pre-treatment, storage time and dilution) (BAPE, 2003). Therefore, concentrations found in the literature are usually provided as a range of values. Table 1-1 gives the general composition of swine slurry (Dubé, 1997; Dubé et al., 2005).

Table 1-1: General Composition of Swine Slurry

Parameter	Range
pH	6.3 - 6.5
Suspended solids ($mg \cdot L^{-1}$)	20 500 - 46 500
Organic matter as BOD_5 ($mg\ O_2 \cdot L^{-1}$)	13 400 - 40 000
Total Kjeldahl Nitrogen ($mg\ N \cdot L^{-1}$)	3 000 - 5 200
Ammonium nitrogen ($mg\ N \cdot L^{-1}$)	1 820 - 3 330
Phosphorous ($mg \cdot L^{-1}$)	660 - 920
Potassium ($mg \cdot L^{-1}$)	1 810 - 2 690
Fecal coliforms (MPN / 100ml)	1.4×10^7 - 7.8×10^7

Note: BOD_5 = 5 day biological oxygen demand;
MPN = most probable number

The values presented here for suspended solids, BOD_5, total Kjeldahl nitrogen and phosphorous are 60 to 100 times higher than for domestic sewage (Buelna et al., 2008). The quantity of microorganisms in swine slurry is comparable to values reported for domestic wastewater at concentrations between 10^6 and 10^8 most probable number (MPN) of fecal coliforms per 100 ml (Metcalf and Eddy, 2003). The potassium concentration in slurry is also very high when compared to the world average river concentration at 2.3 $mg \cdot L^{-1}$ (Crittenden et al., 2005).

1.2.2. Environmental Concerns

Since swine slurry contains nutrients essential to plants, such as nitrogen and phosphorous, it can be used as fertilizer for agriculture or to improve soil properties (Choudhary et al., 1996; BAPE, 2003). In fact, most of the manure in eastern Canada is currently applied to land as fertilizer (Gregorich et al., 2005). However, fertilization of arable land above crop requirements causes the excess nutrients to seep into both ground and surface waters (Meers et al., 2006). These nutrients can have a devastating effect on water quality by favouring the growth of algae, which reduces the amount of dissolved oxygen in the water and accelerates eutrophication (Gangbazo et al., 2006). External factors, such as high precipitation following slurry spreading or application to frozen land, can increase the severity of the aquatic pollution caused by swine slurry (MDDEP, 2011b; Choudhary et al., 1996).

1.2.3. Odours

Animal wastes in general are an important source of olfactory nuisances with over 160 different malodorous compounds (Wu et al., 1999). In the piggery industry, odours are mainly associated with the pig houses (50%) but also with the transportation and spreading of manure (25%) and the slurry storage pits (25%) (Sheridan et al., 2002). The main odorous compounds associated with swine slurry are ammonia (NH_3), hydrogen sulphide (H_2S) and volatile fatty acids. This type of pollution can cause a wide range of symptoms for the general population, from simple displeasure, nausea or allergies, to more serious problems such as breathing difficulties, insomnia and depression (Météoglobe Canada Inc., 1993). However, odours don't cause significant environmental harm and will not be discussed further in this paper.

1.2.4. Valorization Methods

To deal with these problems, it is possible to either valorize the nutrients contained in swine slurry or to treat this waste product.

Use as a fertilizer

As previously discussed, swine slurry can be used as an agricultural fertilizer. In fact, studies have shown that it provides yields similar to or higher than inorganic fertilizers for both crops and pastures. It can be used for a wide variety of crops, but grasses and cereals are well suited to swine slurry due to their high nitrogen requirements and extensive root systems (Choudhary et al., 1996). However, sufficient land for slurry application is not always available and treatment methods must be considered.

1.2.5. Treatment Methods

Solid-liquid separation

Solid-liquid separation is one of the simplest treatment methods for swine slurry and consists of removing the solid particles from the liquid phase (BAPE, 2003). Table 1-2 presents the main systems available and the solids removal efficiency they provide. These systems utilize a variety of physical and chemical properties resulting in a wide range of separation efficiencies, from 8 to 99%. Other than removing solids, solid-liquid separation also eliminates the compounds trapped in the solid phase: some of the organic matter (56% as BOD_5), a large fraction of the phosphorous (83%) and most of the organic nitrogen (88%) (BAPE, 2003; Dubé et al., 2005). However, this type of process offers only a partial treatment of swine slurry; the solid and liquid fractions obtained must still be valorized or treated.

Table 1-2: Main Systems Available for the Solid-Liquid Separation of Swine Slurry

Type of System	Solids Removal Efficiency	Reference
Natural settling	94%	Buelna et al. (1998)
Separation by slatted floors	> 90%	Aubry (2008)
Sieve separation	8%	Larouche et al. (2005)
Straw filtration (acts like cake-mode filtration)	69%	Melse and Verdoes (2005)
Screw press	n.a.	FPPQ (2001); Melse and Verdoes (2005)
Centrifugation	n.a.	Melse and Verdoes (2005)
Dehydration	n.a.	AMAF (1997)
Evaporation	99%	Melse and Verdoes (2005)
Chemical separation by the addition of coagulants and flocculants	n.a.	FPPQ (2001)
Flotation with addition of coagulants and flocculants	98%	Dubé et al. (2005)

Note: n.a. = non-available

Biological processes in general

Biological systems, whether anaerobic or aerobic, can be used to treat raw swine slurry or the separated solid or liquid fractions (Laridi et al., 2005).

Anaerobic biological processes

Anaerobic processes exploit the ability of certain microorganisms, in the absence of oxygen, to produce biogas which is essentially a mixture of methane (CH_4) and carbon dioxide (CO_2) (Møller et al., 2004). This process has traditionally been used on a small scale by Asian farmers and has since grown extensively, to 5.4 million household anaerobic digesters in China in 1994 (Junfeng, 1997). Other than generating biogas, this process also produces a good quality liquid fertilizer with a carbon to nitrogen (C/N) mass ratio around 13 as compared to around 30 with raw swine slurry (Costa et al., 2007). Theoretically, methane production can reach 530 litres per kg of volatile solids for swine slurry which is slightly higher than the productivity of cattle manure (468 litres per kg of volatile solids) (Møller et al., 2004). Increasing the temperature from 25 to 35°C will improve CH_4 yields by up to 17% (Chae et al., 2008), but the presence of ammonium (NH_4^+) or sulphides can inhibit the process and limit biogas production (Hansen et al., 1999). Simulation tools are available to estimate

biogas production from manures (Batzias et al., 2005). The CH_4 in the biogas can subsequently be used to generate either heat or energy.

Aerobic biological processes

Aerobic biological processes can be relatively simple as in short-term aeration, which can remove up to 90% of the organic matter as BOD_5 and significantly reduce odours (up to 96% as evaluated with volatile fatty acids) during subsequent slurry storage for up to 190 days (Zhang and Zhu, 2006). On the other hand, biological processes designed for wastewater treatment, such as aerated lagoons or activated sludge reactors, can also be utilized for the treatment of swine slurry (BAPE, 2003; Meers et al., 2006). Aerobic biological processes remove organic matter and NH_4^+, but inorganic compounds such as phosphorous, potassium and heavy metals remain unchanged (Daumier et al., 2003) and are generally accumulated within the excess biomass.

Bioreactors using biomass fixed on a porous support have also been used to treat the liquid fraction of slurry. Westerman et al. (2000) were able to remove 88% of the organic matter as BOD_5 and 94% of the NH_4^+ with two 1.5 m^3 upflow aerated biological filters connected in series treating 8 $m^3 \cdot d^{-1}$ of flushed swine slurry. Lanoue (1998) also studied this type of system, but part of the effluent was recirculated to an anoxic reactor at the beginning of the process. On top of removing 72% of the chemical oxygen demand (COD) and 94% of the NH_4^+, this system was able to achieve a denitrification (transformation of nitrate (NO_3^-) to nitrogen gas (N_2)) rate of 92%. A commercial system has also been developed based on this process. The Ekokan® Biofiltration Treatment System was able to remove between 90 and 98% of the NH_4^+ and to reduce the BOD_5 by 40 to 70% from swine slurry pre-treated to remove solids (Westerman and Arogo, 2004).

Aerobic biological reactors are usually operated at ambient temperatures with mesophilic microorganisms to avoid heating, but reactors using a thermophilic biomass at temperatures between 50 and 75°C offer interesting advantages. The main benefit of thermophilic digestion is the improved sanitary quality of the treated slurry, which minimises the risk of spreading pathogenic microorganisms (Hansen et al., 1999). Thermophilic bioreactors are also simple to operate, robust and can be self-heating if operated properly. The nitrogen in slurry is retained as NH_4^+, which can be used as a mineral fertilizer, since no

nitrification (biological transformation of NH_4^+ to NO_3^-) takes place above 40°C (Juteau, 2006).

Two biological treatment systems require specific consideration for their applicability to swine slurry treatment: biofiltration and composting. The biofiltration of swine slurry will be explained in detail in the following section.

Composting

Composting is a treatment method that uses biological reactions to transform organic matter into a stable product rich in humic compounds (BAPE, 2003). Composting of swine slurry is a management tool that improves the properties of the manure to produce a marketable organic fertilizer (Fukumoto et al,. 2006). By the high temperatures reached during this process (40 - 60°C), the quantity of pathogenic microorganisms is reduced by above 92%, which improves the sanitary quality of the end product (Ros et al., 2005). Since swine slurry is composed mainly of water and has high concentrations of nitrogen, it is necessary to add bulking agents that have a high carbon content, such as sawdust, to improve porosity and to increase the C/N mass ratio. A C/N ratio of 25 to 30 is recommended for optimal composting, but lower ratios of 15 to 20 can be used to reduce the quantity of bulking agent required, but this increases maturing time by around 30% (Huang et al., 2004; Zhu, 2007). To maintain proper levels of oxygen, both heap mixing and forced ventilation can be used (FPPQ, 2001). A major drawback of composting is the loss of nitrogen which reduces the quality of the fertilizer produced. On average, 10% of the initial nitrogen is lost as NH_3 and 3% as nitrous oxide (N_2O) (Hassouna et al., 2008). The production of N_2O, a powerful GHG, can be reduced by improving the performance of nitrifying bacteria. Fukumoto et al. (2006) achieved this by adding nitrite (NO_2^-) oxidizing bacteria to provide complete nitrification to NO_3^- and reduced N_2O emission rates by up to 80%.

Advanced Treatment Methods

Several other systems have been developed either to achieve an advanced treatment or to eliminate specific compounds contained in swine slurry. For an enhanced removal of solids, the SELCO-Ecopurin® process uses a polyacrylamide polymer to flocculate more than 90% of the particles (Martinez-Almela and Barrera, 2005). As an intermediate step after a

biological treatment, physico-chemical precipitation can be used to eliminate up to 95% of excess phosphate (Meers et al., 2006). To remove refractory organic compounds (such as proteins, antibiotic compounds and organic acids) after the treatment of slurry in a bioreactor, Laridi et al. (2005) used electrochemical precipitation with both aluminium and iron electrodes. These authors were able to remove up to 68 and 87% of the refractory COD and BOD respectively. Studies have also been carried out on the application of membrane filtration to treat swine slurry, by means of microfiltration (Melse and Verdoes, 2005), ultrafiltration (Fugère et al., 2005) or even reverse osmosis membranes (FPPQ, 2001).

1.2.6. Biofiltration of Swine Slurry

The process of biofiltration is well summarized by Cohen (2001): "In biofiltration the microbial biomass is static – immobilized to the bedding material, while the treated fluid is mobile – it flows through the filter". Biofilters have been used for almost 100 years for wastewater treatment (Metcalf and Eddy, 2003), but they have been applied only recently for the treatment of highly concentrated effluents such as swine slurry. Preliminary tests were carried out in Malaysia using a simple biofilter with passive aeration that removed a maximum of 56% of the organic matter as BOD_5 and 55% of the NH_4^+ (Sommer et al., 2005). Boiran et al. (1996), Senez et al. (1997) and Szögi et al. (2004) were able to remove up to 98% of the ammonium from lagoon piggery waste using biofilters packed with inorganic materials. In Quebec (Canada) several researchers have been involved in this field for over 10 years and have developed an expertise on the biofiltration of swine slurry. These studies have resulted in the development of a patented technology, the BIOSOR^{MD} biofilter (Buelna, 2000) which uses an organic filter bed made up of wood chips, bark and peat moss (BIOSOR Technologies inc., 2008). This technology, as far as we know, is the only commercially available biofilter for the treatment of swine slurry in Canada.

The particular configuration of the BIOSOR^{MD} biofilter offers interesting capabilities with regards to pollutant elimination. After a start-up phase that can last 50 days, the bioreactor eliminates up to 99% of the organic matter as BOD_5 and nitrifies more than 95% of the NH_4^+ (Dubé, 1997; Aubry et al., 2006). During the start-up period, NH_4^+ removal is observed, but it is due to the air stripping of ammonia since no NO_3^- or NO_2^- is produced; this process ceases once nitrification takes place (Garzón-Zúñiga et al., 2005). Furthermore, the

simultaneous nitrification and denitrification (SND) within the biofilter was observed by Garzón (2001) after 140 days of operation. By means of a mass balance, it was shown that 30% of the nitrogen was eliminated as N_2 and 10% as N_2O. The performance of the BIOSOR^{MD} biofilter was also validated at full scale at two different locations, treating up to 12 m^3 of swine slurry daily (Dubé et al., 2005; Buelna et al., 2008).

The swine slurry can be supplied continuously or sequentially depending on the flow rate and the type of packing material. Metcalf and Eddy (2003) report hydraulic loads of 1 to 75 $m^3 \cdot m^{-2} \cdot d^{-1}$ for wastewater treatment by biofilters filled with rocks or plastic packing materials to allow microorganisms adapted to the specific pollutants to colonize the filter bed. For swine slurry treatment, a hydraulic loading rate of 0.065 $m^3 \cdot m^{-2} \cdot d^{-1}$ has already been applied to a biofilter, but due to clogging problems, values of 0.035 or 0.017 $m^3 \cdot m^{-2} \cdot d^{-1}$ are often used (Aubry et al., 2006; Garzón-Zúñiga et al., 2007). These values are much lower than the ones used for wastewater treatment because the concentrations of nutrients in swine slurry are 60 to 100 times higher than in municipal wastewater (Buelna et al., 2008).

When treating wastewater with an aerobic biofilter, a minimal air flow of approximately 18 $m^3 \cdot m^{-2} \cdot h^{-1}$ is required to maintain a proper concentration of oxygen (Metcalf and Eddy, 2003). On the other hand, Garzón-Zúñiga et al. (2007) studied air flow rates from 3.1 to 34 $m^3 \cdot m^{-2} \cdot h^{-1}$ for slurry biofiltration and determined that a value of 4.4 $m^3 \cdot m^{-2} \cdot h^{-1}$ was sufficient for complete nitrification. Furthermore, according to these authors, suspended solids must not exceed 68 $g \cdot m^{-2} \cdot d^{-1}$ and the organic loading rate must be kept below 526 $g \cdot m^{-2} \cdot d^{-1}$ as COD to avoid clogging. For this reason, solids are generally removed from the raw slurry before it is supplied to a biofilter.

Microorganisms make up the core of a biofilter's purification arsenal, acting as catalysers for the breakdown of the contaminants (Cohen, 2001). The biodegradation of the pollutants in swine slurry requires a wide range of microorganisms that can be organized according to the type of contaminant: organic matter or NH_4^+.

Organic matter

As shown in Table 1-1, organic matter is the most important group of contaminants in swine slurry. This organic matter can be classified into four fractions: readily biodegradable (S_S), slowly biodegradable (X_S), inert soluble (S_I) and inert particulate (X_I). When using the

BOD to represent slurry organic matter, only the biodegradable fractions (S_S and X_S) are taken into account. The X_S fraction is usually particulate and made up of complex organic polymers with high molecular weights or dead biomass. This fraction of the organic matter cannot be directly assimilated by microorganisms and must first be hydrolyzed to S_S, which is usually soluble and composed of smaller molecules (volatile fatty acids, monosaccharides, alcohols, etc.) (Aubry 2008). For swine slurry, the organic matter distribution among the different fractions is quite variable and depends particularly on the type of farm and the slurry storage time. The values for S_S range from 8 to 30% of the total COD, from 30 to 60% for the X_S and from 10 to 60% for the inert fractions (S_I and X_I) (Andreottola et al., 1997; Boursier et al., 2005; Aubry, 2008).

Various types of microorganisms can degrade organic matter: bacteria, protozoa and fungi. With sufficient oxygen, these microorganisms oxidize the organic matter into CO_2, water and additional biomass as in equation 1-1 (Metcalf and Eddy, 2003):

$$\text{Organic Matter} + O_2 + \text{Nutrients} \rightarrow \text{Biomass} + CO_2 + H_2O \qquad (1\text{-}1)$$

Ammonium

The biological treatment of NH_4^+ follows two distinct steps: the nitrification of NH_4^+ to NO_3^- and the denitrification of the NO_3^- to N_2. The nitrification step is carried out by strictly aerobic bacteria, usually autotrophic, and also has two steps. Ammonium is first transformed into NO_2^- by bacteria with the prefix *Nitroso* (*Nitrosomonas* for example). The second step is performed by bacteria with the prefix *Nitro* (*Nitrobacter* for example) and pushes the oxidation to NO_3^-. For a steady state and a temperature lower than 28°C, the oxidation of NH_4^+ to NO_2^- controls the kinetics and very little NO_2^- accumulates in the system, but for start-up periods and for high temperatures (>28°C), the relative kinetics change and NO_2^- can build up in the system. The two separate steps are presented in equations 1-2 and 1-3 while the combined reaction is given in equation 1-4 (Henze et al., 2002):

$$NH_4^+ + \tfrac{3}{2}O_2 \xrightarrow{\textit{Nitroso}\text{-bacteria}} NO_2^- + 2H^+ + H_2O \qquad (1\text{-}2)$$

$$NO_2^- + \tfrac{1}{2}O_2 \xrightarrow{\textit{Nitro}\text{-bacteria}} NO_3^- \qquad (1\text{-}3)$$

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + 2H^+ + H_2O \qquad (1\text{-}4)$$

The nitrification reaction in equation 1-2 generates H^+ ions that consume about 7 g of alkalinity as calcium carbonate ($CaCO_3$) per gram of N-NH_4^+ oxidized. Swine slurry naturally has an alkalinity around 6 g $CaCO_3$ per litre, but after it is treated by a biofilter that value can fall to 0.035 g $CaCO_3$ per litre (Aubry, 2008).

During the transformation of NO_3^- to N_2, many intermediate compounds are produced (NO_2^-, nitric oxide (NO) and N_2O) as shown in the following metabolic pathway (equation 1-5) (Zumft, 1997):

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2 \qquad (1\text{-}5)$$

Nitrate reduction can be either assimilatory (carried out by most bacteria; NO_3^- is used as a source of nitrogen for biomass build-up) or dissimilatory (carried out by facultatively aerobic bacteria, autotrophic or heterotrophic; NO_3^- is used as an electron acceptor when there is little oxygen in anoxic conditions). In this paper, we will use the term "denitrification" as meaning dissimilatory NO_3^- reduction. Denitrification is carried out solely by bacteria, but many genera are capable of using NO_3^-, such as *Halobacterium, Methanomonas* and *Pseudomonas.* Heterotrophic denitrification is faster than autotrophic (Modin et al., 2007) and requires a source of easily biodegradable organic carbon. With acetic acid (CH_3COOH) as a carbon source, equation 1-6 represents the denitrification reaction (Metcalf and Eddy, 2003):

$$5CH_3COOH + 8NO_3^- \rightarrow 4N_2 + 10CO_2 + 6H_2O + 8OH^- \qquad (1\text{-}6)$$

As seen in this equation, denitrification generates OH^- ions that produce 3.5 g of alkalinity as $CaCO_3$ for each gram of N-NO_3^- reduced. Part of the alkalinity used for nitrification is therefore restored by denitrification.

In wastewater treatment, the two steps of NH_4^+ treatment are generally carried out in separate reactors. However, when there are anoxic zones within an aerobic reactor, it is possible to observe SND. This phenomenon can take place within a biofilm where nitrifying microorganisms occupy the exterior of the biofilm with an excess of oxygen and denitrifying bacteria are found inside the biofilm with NO_3^- and a low concentration of oxygen (Garzón, 2001). However, so far, it has not been possible to achieve complete denitrification by treating slurry with a biofilter.

To improve nitrogen removal, Aubry (2008) studied different C/N mass ratios: 4, 9 and 17 g COD/g N-NH_4^+. The pre-treated swine slurry used had a C/N ratio of 9 while the two

other ratios were obtained by diluting the slurry or supplementing either a synthetic solution of NH_4^+ or organic carbon. The C/N ratio of 17, with the highest proportion of carbon, had the best denitrification potential and it was possible to remove more than 90% of the total nitrogen. Nevertheless, around 80% of the total nitrogen was still removed with the C/N ratios of 4 and 9. The N_2O production was similar for all three ratios tested, around 12% of the nitrogen supplied to the system. To stimulate denitrification once the concentration of organic matter in the treated slurry is low (around 30 $mgBOD_5 \cdot L^{-1}$), Dubé et al. (2008) added whey at an organic load of 0.15 $kgBOD_5 \cdot m^{-2} \cdot d^{-1}$. These authors were able to remove 90% of the residual NO_3^- that would have otherwise been released into the environment.

1.3. Greenhouse Gases

Other than aquatic pollution and odours, the piggery industry is also an important source of GHG. When released into the atmosphere, these gases retain the sun's heat near the surface of the earth (Environment Canada, 2003). In Canada, the energy sector is the main contributor to the emission of GHG with 82% of the 747 million tons of CO_2 equivalent produced in 2005 (Jaques, 2007). The agricultural sector is second with 57 million tons, equivalent to 7.6% of 2005 Canadian emissions, which is an increase of 24% since 1990. Agricultural GHG do not come from energy requirements, but rather from livestock production: 44% from enteric fermentation, 41% from agricultural land and 15% from manure management (Jaques, 2007). Enteric fermentation only occurs in ruminants such as cattle; GHG from the piggery industry are therefore associated with manure management and land-based sources.

The two most important GHG found on a pig farm are CH_4 and N_2O with respectively 49% and 51% of emissions (Jaques, 2007). Methane is the most abundant organic gas in the atmosphere (Hanson and Hanson, 1996) with a global warming potential (GWP) of 21, that is to say that its influence on the greenhouse effect in 21 times that of CO_2 (CITEPA, 2008). Nitrous oxide's effect on climate change is more powerful with a GWP of 310.

1.3.1. Sources of Greenhouse Gases in the Piggery Industry

There are many direct and indirect sources of GHG in the piggery industry. The indirect sources include fertilizer production and transportation (Clemens and Ahlgrimm, 2001), but they are generally not considered part of the agricultural sector in inventories. Direct sources consist mainly of the hogs' digestive processes, manure management and land-based emissions. However, the specific sources of CH_4 and N_2O are very different.

Methane is produced by the anaerobic digestion of organic matter by microorganisms. This process occurs predominantly (65-70%) during slurry storage, but it can also take place after the slurry is applied to land and in the large intestine of non-ruminant mammals such as pigs (Monteny et al., 2006; Haeussermann et al., 2006). During slurry storage, the anaerobic conditions combined with a high concentration of organic matter promote CH_4 production (Petersen et al., 2005). Methane biosynthesis increases with the temperature, by up to 150% between 5 and 25°C (Dinuccio et al., 2008), and with the biodegradability of the slurry, but it is inhibited by NH_4^+ and sulphides (Monteny et al., 2006). When the slurry is applied to land, anaerobic conditions can prevail for several hours or even days (Bender and Wood, 2007). Taking into account all the different sources (slurry storage, land-based and intestinal), a hog generates 4.8 kg of CH_4 per year. This value is much smaller than with dairy cattle for example, which release from 84 to 123 kg of CH_4 per animal per year (Monteny et al., 2006). But since the CH_4 from the piggery industry comes mainly from slurry management rather than enteric fermentation as in dairy cattle, it is much easier to control emissions or to treat the effluent. In Canada, in 2005, swine slurry management caused the emission of 1.6 million metric tons of CO_2 equivalent of CH_4 (Jaques, 2007).

Typical concentrations of CH_4 from pig houses vary between 5 and 100 $mg \cdot m^{-3}$ (7 and 150 ppmv) and depend essentially on the ventilation flow rate. Methane concentrations from covered slurry storages with no aeration can reach 425 $g \cdot m^{-3}$ (65% v/v), but storage covers are rarely airtight and concentrations usually vary from 0.1 to 20 $g \cdot m^{-3}$ (150 to 30600 ppmv) (Melse and van der Werf, 2005).

As previously discussed, N_2O is an intermediate compound in the denitrification of NO_3^- to N_2. No N_2O is produced during swine slurry storage (Chadwick et al., 1999) since anaerobic conditions prevail and the NH_4^+ cannot be oxidized to NO_3^-. Nitrous oxide is essentially generated once the slurry has been applied to agricultural land as a fertilizer where

both aerobic and anoxic conditions can exist (Velthof et al., 2003). The aerobic treatment of slurry and composting also offer the appropriate conditions for N_2O production where denitrification can occur simultaneously to nitrification or simply after aeration (Garzón, 2001; Monteny et al., 2006). As a comparison, emissions of N_2O are usually lower when synthetic nitrogen fertilizers are applied to land because of the lack of organic carbon necessary for denitrification (Bender and Wood, 2007; Gregorich et al., 2005).

1.3.2. Reduction and Treatment Methods

Limiting Nutrient Availability

In order to limit the piggery industry's impact on climate change, GHG emissions must either be reduced or treated. By limiting the quantity of certain key substances in the slurry, it is possible to greatly reduce GHG emissions from the piggery industry. To begin with, this can be achieved by modifying the hogs' diet. By optimizing feed, it is possible to decrease the quantity of nitrogen in the slurry, which directly impacts N_2O production (Clemens and Ahlgrimm, 2001). Velthof et al. (2005) linked the quantity of NH_4^+ in the slurry with the amount of protein in the feed. These authors also demonstrated that by lowering the crude protein content of the feed by 21%, both the emission of CH_4 from slurry storage and the land-based emission of N_2O were reduced, by up to 21% and 63% respectively. This reduction in dietary crude protein has no effect on animal performance as long as the diet is optimized and essential amino acids are supplemented to the pigs.

The slurry treatment methods previously described can also influence the release of GHG. By simply aerating the slurry and favouring aerobic microorganisms, it is possible to lower CH_4 production by 70 to 100% (Martinez et al., 2003; Boursier et al., 2004). However, this process increases the discharge of N_2O, but the sum of GHG released is still lower than without treatment, by 40 to 55% (Amon et al., 2006; Loyon et al., 2007). As for solid-liquid separation, Dinuccio et al. (2008) discovered that GHG emissions were actually higher by up to 30% with the storage of the separated fractions when compared with the storage of the untreated slurry. This phenomenon could be caused in part by the dry conditions and air-filled porosities found in the solid fractions that create a "mosaic of anaerobic and aerobic micro-sites" and therefore promote N_2O production. Of all the swine slurry treatment systems available, anaerobic digestion provides the lowest total emissions of GHG with a reduction

between 45 and 60% when compared to raw swine slurry (Pelletier et al., 2005; Amon et al., 2006). Anaerobic reactors optimize CH_4 production for use as a source of energy, which greatly reduces the CH_4-producing potential of the resulting treated slurry (Sommer et al., 2000; Insam and Wett, 2008). This type of system has no effect on nitrogen and so the risk of generating N_2O is still present. But swine slurry treated by anaerobic digestion releases up to 54% less N_2O than raw slurry (Bertora et al., 2008) since this process limits the availability of the readily biodegradable organic matter necessary for denitrification (Monteny et al., 2006).

Reducing Biological Activity

Since GHG emitted by swine slurry management are essentially produced by microorganisms, an effective way to limit production is to reduce the biological activity. This can be accomplished by cooling or acidifying the stored slurry (Clemens and Ahlgrimm, 2001; Monteny et al., 2006; Haeussermann et al., 2006).

Treatment

When GHG reduction is not sufficient, end-of-pipe treatment is another viable option. However, treatment is not feasible for diffusive sources of GHG because it is practically impossible to collect the waste gas. Therefore, the treatment methods reviewed here focus on the main point (non-diffusive) source GHG, CH_4.

The most important source of CH_4 in the piggery industry is the slurry storage pit where it is relatively easy to cover the surface and collect the gases produced. It is theoretically possible to collect the gas and burn it using a flare, but concentrations are rarely high enough for direct combustion which requires a minimal concentration of 20% v/v (Clemens and Ahlgrimm, 2001; Nikiema et al., 2007).

Another approach uses microorganisms to oxidize CH_4 into CO_2, water, salts and biomass (Nikiema et al., 2007). A few authors have studied this phenomenon in both natural and artificial slurry surface crusts. These surface crusts did show potential for CH_4 removal with oxidation rates up to 4.5 $g \cdot m^{-2} \cdot d^{-1}$, but it is difficult to control and optimize the biological reactions (Petersen et al., 2005; Petersen and Ambus, 2006; Sommer et al., 2000; Dever et al., 2007; Petersen and Miller, 2006).

1.3.3. Biofiltration of Methane

To improve control of operating parameters and to enhance the biological reactions, CH_4 can be treated by biofiltration. In a biofilter, the polluted gas passes through a bed packed with a porous humid material where microorganisms capable of degrading the specific contaminants are established (Jorio and Heitz, 1999).

For the biofiltration of gaseous pollutants, the empty bed residence time (EBRT) usually varies from a few seconds to several minutes (Delhoménie and Heitz, 2005), but they can reach a few hours for slowly biodegradable compounds such as CH_4 (Nikiema et al., 2007). A specific difficulty with the biofiltration of CH_4 is its low solubility in water ($0.022 g \cdot L^{-1}$ at 20°C) which limits its absorption in the liquid phase and hinders biodegradation (Melse and van der Werf, 2005).

Microorganisms that can use CH_4 as their only source of carbon and energy are known as methanotrophs. These microorganisms are strictly aerobic and are omnipresent in nature as they are found in all sorts of environments, such as wetlands, rivers and soil (Hanson and Hanson 1996). Most of these bacteria are obligate methanotrophs: they are incapable of metabolizing carbon to carbon bonds (Anthony, 1986). As an exception to this rule, bacteria belonging to the genus *Methylocella* are able to use longer chain carbon compounds as well (Dedysh et al. 2005). The biological oxidation of CH_4 to CO_2 involves many intermediate compounds (methanol (CH_3OH), formaldehyde (CH_2O), and formic acid (CH_2O_2)) as in the following pathway (equation 1-7) (Hanson and Hanson, 1996):

$$CH_4 \xrightarrow{MMO} CH_3OH \rightarrow CH_2O \rightarrow CH_2O_2 \rightarrow CO_2 \qquad (1\text{-}7)$$

The first step this pathway, i.e. the transformation of CH_4 to CH_3OH, requires the methane monooxygenase (MMO) enzyme. Methane biooxidation rates can usually be described by typical Michaelis-Menten kinetics for both CH_4 and oxygen (Gebert et al., 2003; Hittiarachchi et al., 2007). As with many other bacteria, methanotrophs produce exopolymeric substances (EPS) and can grow anchored to a solid surface as a biofilm. Hilger et al. (2000) suggested that EPS may protect methanotrophs against desiccation or predation, but they can also impede oxygen diffusion to the biofilm and therefore limit CH_4 biodegradation.

Several studies have been carried out on the biofiltration of CH_4 originating from sanitary landfills; Nikiema et al. (2007) conducted an extensive review on this topic.

Other studies have shown that with the use of an appropriate synthetic nutrient solution, an inorganic filter bed can outperform certain organic materials (Nikiema, 2006). For CH_4 concentrations around 7500 ppmv, a maximum conversion of 41% was obtained with an inorganic material, but only 19% with a mature compost-based filter bed at similar operating conditions. Nikiema (2008) studied the effect of different operational parameters during CH_4 biofiltration with a 15 cm diameter biofilter packed with 18 L of an inorganic filter bed: the CH_4 concentration (from 1500 to 10000 ppmv), the gas flow rate (from 1 to 7 $L \cdot min^{-1}$) and the concentration of certain compounds in the nutrient solution (NO_3^- from 0 to 1 $g\text{-}N \cdot L^{-1}$, phosphorous from 0 to 6.2 $g \cdot L^{-1}$, potassium from 0 to 3.8 $g \cdot L^{-1}$ and copper from 0 to 0.006 $g \cdot L^{-1}$). Results show that the gas flow rate has a greater influence on conversion than the CH_4 concentration. In fact, tripling the gas flow rate, from 1 to 3 $L \cdot min^{-1}$ reduced the conversion by 40% while tripling the CH_4 concentration, from 2500 to 7500 ppmv, had a negative impact of only 7%. For the nutrients, nitrogen had the greatest influence (the elimination capacity (EC) was increased by a factor of up to 4.5 at an inlet load (IL) of 95 $g \cdot m^{-3} \cdot h^{-1}$ when the NO_3^- concentration was varied from 0.14 to 0.75 $g\text{-}N \cdot L^{-1}$) (Nikiema et al., 2009), while phosphorous had a less significant effect (a change in the phosphorous concentration from 0.3 to 3.1 $g \cdot L^{-1}$ increased the EC by 35% for an IL of 75 $g \cdot m^{-3} \cdot h^{-1}$) (Nikiema et al., 2010) and potassium and copper had minor influences.

Relatively few studies have focused on CH_4 from the piggery industry. In 2006, the Canadian Pork Council produced a report on the biofiltration of CH_4 from a 3800 m^3 slurry storage reservoir equipped with a floating cover (CPC, 2006). Four different organic packing materials were tested without inoculation: mixtures of compost, wood chips, soil and peat moss. With an EBRT of about 10 minutes, the CH_4 concentrations varied from 2000 to 35000 ppmv and the average IL was 29.9 $g \cdot m^{-3} \cdot h^{-1}$. After a start-up period of 3 months, average removal efficiencies between 50 and 60% were obtained, corresponding to EC between 16 and 20 $g \cdot m^{-3} \cdot h^{-1}$. Using a biofilter packed with a mixture of compost and perlite, Melse and van der Werf (2005) treated CH_4 from a 6 m^3 pilot-scale slurry storage unit. The biofilter was inoculated with activated sludge from a wastewater treatment plant and the EBRT was varied from 1 to 80 minutes with an IL between 1 and 25 $g \cdot m^{-3} \cdot h^{-1}$. With

concentrations no higher than 8500 ppmv, up to 85% of the CH_4 was removed after a start-up phase of 25 days.

Both these studies treated CH_4 from slurry storages with relatively high CH_4 concentrations, up to 35000 ppmv, but few authors have looked at the biofiltration of CH_4 from pig houses where the concentrations are much lower, below 150 ppmv. Girard et al. (2008a, 2008b) presented some preliminary results on the biofiltration of CH_4 at concentrations from 100 to 2000 ppmv using an inorganic filter bed. These authors obtained a maximal removal efficiency and EC of 87% and 13 $g \cdot m^{-3} \cdot h^{-1}$ respectively for an IL up to 20 $g \cdot m^{-3} \cdot h^{-1}$. Furthermore, for NO_3^- concentrations in the nutrient solution between 0.05 and 0.75 $g\text{-}N \cdot L^{-1}$, no significant effect on CH_4 removal was observed.

1.4. Simultaneous Treatment of Methane and Swine Slurry by Biofiltration

When considering the simultaneous treatment of swine slurry and CH_4 from the piggery industry, few processes are available. Plasma-assisted wet oxidation has been used to treat the solid fraction of swine slurry (Laflamme et al., 2002) and could potentially treat methane with the same unit. However, since this process was developed for sludge treatment, further research is required to determine whether it can handle the high water content of slurry. Biofiltration is an interesting alternative since it can break down pollutants whether they are in liquid or gas phase. Several studies have demonstrated the effectiveness of biofiltration for both swine slurry and CH_4 when treated separately. According to our knowledge, no studies have been published with regards to the simultaneous biofiltration of swine slurry and CH_4. This concept is nevertheless very appealing since it would solve both the problems of aquatic pollution and the emission of greenhouse gases from the piggery industry.

In a biofilter designed for simultaneous treatment, the swine slurry, pre-treated to remove suspended solids, would be supplied at the top and flow through the packing material by gravity while the air contaminated with CH_4 would be fed at the base and flow counter-currently to the liquid phase. Ideally, the use of slurry would eliminate the need for a

synthetic nutrient solution for CH_4 biodegradation. Methanotrophs prefer NO_3^- as a nitrogen source (Nikiema et al., 2007), but their performance is optimal for a specific NO_3^- concentration which depends on the IL (Nikiema et al., 2005). With a synthetic solution, it is easy to control the NO_3^- concentration, but with swine slurry, the availability of NO_3^- will depend on nitrification and it will be very difficult, if not impossible, to control its concentration. In fact, NO_3^- concentrations in a biofilter treating slurry can reach values of 1000 $mg \cdot L^{-1}$ (Aubry, 2008). On the other hand, methanotrophs can also oxidize NH_4^+ with the MMO enzyme by a process called methanotrophic nitrification (Knowles, 2005). The MMO enzyme is structurally similar to the ammonium monooxygenase (AMO) enzyme in nitrifying microorganisms (Knowles, 2005) and could derive from a common molecular ancestor since both enzymes share several properties (Hanson and Hanson, 1996). However, this process is inhibitory to CH_4 biodegradation. In fact, Bronson and Mosier (1994) observed a reduction of up to 89% in the CH_4 removal efficiency when ammonium chloride (NH_4Cl) was added to the packing material at a concentration of 25 $\mu gN \cdot g^{-1}$. According to Dunfield and Knowles (1995), the inhibition mechanism of NH_4^+ can be either a simple competitive inhibition or much more complex.

Even though the SND of NH_4^+ can be observed within a biofilter treating slurry (Garzón, 2001), the denitrification is incomplete. This could be due to an elevated concentration of oxygen within the biofilm (more than 0.2 $mg \cdot L^{-1}$ according to Metcalf and Eddy (2003)) or to a lack of easily biodegradable organic carbon which is necessary for denitrification. Methanotrophs could improve both these scenarios. Despite the fact that no methanotroph known to date can reduce NO_3^- to N_2 (Modin et al., 2007), these microorganisms can assist denitrification through associated bacteria by releasing intermediate compounds, such as CH_3OH, which act as hydrogen donors for denitrification (Eisentraeger et al., 2001). Methanotrophs also consume oxygen, which creates a microenvironment better suited for denitrification (Knowles, 2005).

Preliminary laboratory-scale tests for the simultaneous biofiltration of swine slurry and CH_4 have been carried out at the Université de Sherbrooke in Quebec (Canada). A CH_4 conversion of 33% and an EC of 16 $g \cdot m^{-3} \cdot h^{-1}$ were obtained using an inorganic packing material with an EBRT of about 4 minutes and an IL of 48 $g \cdot m^{-3} \cdot h^{-1}$. As for the swine slurry, 68% of the total organic carbon and 62% of the NH_4^+ were removed (Girard et al., 2008a).

These results are very promising, but there are important challenges that must be overcome to improve performance and demonstrate the applicability of this process.

1.5. Conclusion

The goal of this paper was to review the environmental concerns associated with swine slurry and the greenhouse gases from the piggery industry as well as to explore the available mitigation technologies.

In Canada, the piggery industry is an essential part of the agricultural sector, generating an important economic impact and providing over 64 000 jobs. However, swine slurry, the main waste product of this industry, is particularly harmful to the environment. The anaerobic storage conditions and the excessive use of slurry for agricultural fertilization contribute respectively to the emission of greenhouse gases and to aquatic pollution. There are many technologies that can valorize the slurry (through agricultural fertilization), reduce GHG emissions (by limiting nutrient availability for example) or treat the effluents (such as solid/liquid separation, flaring and biological processes). One of these technologies, biofiltration, which uses microorganisms to biodegrade contaminants, has the potential to treat these two types of pollution. The biofiltration of swine slurry is well known and the treatment of methane from sanitary landfills has been widely studied, but few papers have been published on methane from the piggery industry. As for the simultaneous biofiltration of these two contaminants, results from preliminary tests are promising: 33% conversion of CH_4 and removal rates above 60% for both organic carbon and NH_4^+ from slurry.

Acknowledgements

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CHAPITRE 2. Biofiltration du méthane

Avant-propos

L'article « *Biofiltration of Methane at Low Concentrations Representative of the Piggery Industry – Influence of the Methane and Nitrogen Concentrations* » a été publié dans le Journal of Chemical Engineering en 2011 : Vol. 168, pages 151-158.

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Résumé

Au Canada, l'industrie porcine occupe une place essentielle au sein du secteur agricole, mais les conditions de stockage anaérobiques du lisier de porc causent des émissions de méthane (CH_4), un puissant gaz à effet de serre. Cette étude a examiné l'influence de la concentration de CH_4 et de la concentration d'azote sous forme de nitrate sur la performance d'un biofiltre garni d'un milieu filtrant inorganique traitant de faibles concentrations de CH_4, entre 0.16 et 2.8 $g \cdot m^{-3}$, représentatives de l'industrie porcine. Une capacité d'élimination maximale de 14.5±0.6 $g \cdot m^{-3} \cdot h^{-1}$ a été obtenue pour une charge à l'entrée de 38±1 $g \cdot m^{-3} \cdot h^{-1}$. Le biofiltre respectait une cinétique de premier ordre avec une valeur de 7.5 h^{-1} pour la constante de premier ordre. Des concentrations de nitrate de 0 à 0.5 $gN \cdot L^{-1}$ ont été testées pour une charge à l'entrée de 14 $g \cdot m^{-3} \cdot h^{-1}$ et une concentration de nitrate de 0.1 $gN \cdot L^{-1}$ s'est avérée suffisante pour assurer l'opération adéquate du biofiltre. Lorsque l'azote inorganique a été éliminé de la solution nutritive, l'efficacité d'épuration est demeurée à 18±0.7 %, suggérant la présence de méthanotrophs capables de fixer l'azote atmosphérique. Des bilans de masse sur le carbone et l'azote ont illustré que le carbone accumulé dans le biofiltre était probablement utilisé pour la production de substances exopolymériques ou de composés intracellulaires.

Abstract

In Canada, the piggery industry is an essential part of the agricultural sector, but the anaerobic storage conditions of swine slurry lead to the emission of methane (CH_4), an important greenhouse gas. This study examined the influence of the CH_4 concentration and the nitrate-nitrogen concentration in the nutrient solution on the performance of a biofilter packed with an inorganic material treating low concentrations of CH_4, between 0.16 and 2.8 $g \cdot m^{-3}$, representative of the piggery industry. A maximum elimination capacity of 14.5±0.6 $g \cdot m^{-3} \cdot h^{-1}$ was obtained for an inlet load of 38±1 $g \cdot m^{-3} \cdot h^{-1}$. The biofilter satisfied first order kinetics with a value of 7.5 h^{-1} for the first order constant. Nitrate concentrations from 0 to 0.5 $gN \cdot L^{-1}$ were tested at an inlet load of 14 $g \cdot m^{-3} \cdot h^{-1}$ and a nitrate concentration of 0.1 $gN \cdot L^{-1}$ was sufficient for proper biofilter operation. When no inorganic nitrogen was provided in the nutrient solution, the removal efficiency remained at 18±0.7 % suggesting the presence of methanotrophs capable of fixing atmospheric nitrogen. Carbon and nitrogen mass balances suggested that the carbon accumulated within the biofilter was probably used for the production of exopolymeric substances or intracellular compounds.

2.1. Introduction

In Canada, the piggery industry is an essential part of the agricultural sector, comprising more than 64 000 direct and indirect jobs (Agriculture and Agri-Food Canada, 2007). In 2009 alone, there were over 28 million hogs produced in Canada with exports worth just under 3 billion dollars (CPC, 2011). However, the main waste product of this industry, swine slurry, causes severe environmental problems. The anaerobic storage conditions of this waste product lead to the emission of methane (CH_4), an important greenhouse gas (GHG). In fact, in Canada in 2008, swine slurry management was responsible for the release of 1.3 million metric tons of carbon dioxide (CO_2) equivalent of CH_4 (Jaques, 2010). In terms of climate change, CH_4 has a global warming potential 25 times that of CO_2 for a 100 year time horizon (Solomon et al., 2007).

Methane is produced by the anaerobic digestion of organic matter by microorganisms which occurs mainly during the storage of swine slurry. Typical concentrations of CH_4 in the

polluted air from pig houses vary between 0.005 and 0.1 $g \cdot m^{-3}$ (7 and 150 ppmv) and depend essentially on the ventilation flow rate. Methane concentrations ($[CH_4]$) from covered slurry storages with no aeration can reach 425 $g \cdot m^{-3}$ (65% v/v), but storage covers are rarely airtight and concentrations usually vary from 0.1 to 20 $g \cdot m^{-3}$ (150 to 30 600 ppmv) (Melse and Van der Werf, 2005).

In order to limit the piggery industry's impact on climate change, GHG emissions must be reduced or treated. Methane emissions can be reduced by modifying the hogs' diet, treating the slurry or decreasing the slurry's biological activity (Amon et al., 2006; Monteny et al., 2006; Velthof et al., 2005). To mitigate CH_4 emissions, it is possible to collect the gas and burn it using a flare, but concentrations are rarely high enough for direct combustion which requires a minimal concentration of 130 $g \cdot m^{-3}$ (20% v/v) (Haubrichs and Widmann, 2006). An innovative approach uses microorganisms to oxidize CH_4 into CO_2, water, salts and biomass. This process can be carried out in a biofilter where the polluted gas passes through a bed packed with a porous humid material on which microorganisms capable of degrading the specific contaminants are established (Delhoménie and Heitz, 2005; Kennes and Veiga, 2001). This phenomenon has been studied in the piggery industry with both natural and artificial slurry surface crusts. These surface crusts showed potential for CH_4 removal, but it is difficult to control and optimize the biological reactions (Petersen and Ambus, 2006; Petersen et al., 2005).

Several studies have been carried out on the biofiltration of CH_4 originating from sanitary landfills; Nikiema et al. (2007) conducted an extensive review on this topic. Most of these studies used organic packing materials, but promising results have been obtained with inorganic materials (Nikiema et al., 2005; Sly et al., 1993). For relatively high $[CH_4]$s, between 1.6 and 6.5 $g \cdot m^{-3}$ (2500 and 10 000 ppmv), maximum elimination capacities (EC) of 20.8 and 29.2 $g \cdot m^{-3} \cdot h^{-1}$ were obtained for CH_4 inlet loads (IL) of 26 and 70 $g \cdot m^{-3} \cdot h^{-1}$, respectively.

For biofilters using an organic filter bed, most nutrients are available in the packing material and usually no other nutrients are provided (Philopoulos et al., 2008; Streese and Stegman, 2003). However, when using inorganic materials, essential nutrients such as nitrogen are usually not present in the filter bed and must be supplied by an exterior source. The nutrients can be incorporated directly in the packing material or supplied with a nutrient

solution. For CH_4 biofiltration, nitrate (NO_3^-) seems to be the preferred type of inorganic nitrogen (Nikiema et al., 2007) while ammonium can be a competitive inhibitor to CH_4 biodegradation (Dunfield and Knowles, 1995). Furthermore, Nikiema et al. (2009) determined that the optimal nitrogen concentration increases with the IL: 0.50 $gN \cdot L^{-1}$ for ILs between 20 and 55 $g \cdot m^{-3} \cdot h^{-1}$ and 0.75 $gN \cdot L^{-1}$ for ILs between 55 and 95 $g \cdot m^{-3} \cdot h^{-1}$.

Relatively few studies have focused on CH_4 from the piggery industry (Girard et al., 2009). In 2006, the Canadian Pork Council produced a report on the biofiltration of CH_4 from a 3800 m^3 slurry storage reservoir equipped with a floating cover (CPC, 2006). Four different organic packing materials were tested with $[CH_4]$s ranging from 1.3 to 23 $g \cdot m^{-3}$ (2000 to 35000 ppmv). Average removal efficiencies between 50 and 70% were obtained, corresponding to ECs between 16 and 20 $g \cdot m^{-3} \cdot h^{-1}$. Using a biofilter packed with a mixture of compost and perlite, Melse and van der Werf (2005) treated CH_4 from a 6 m^3 pilot-scale slurry storage unit. With concentrations no higher than 5.5 $g \cdot m^{-3}$ (8500 ppmv), up to 85% of the CH_4 was removed. According to our knowledge, no studies have been published on the biofiltration of CH_4 from the piggery industry using a filter bed composed only of inorganic materials. Even for other applications, such as landfill gas, no studies were found on the treatment of CH_4 at concentrations below 0.65 $g \cdot m^{-3}$ (1000 ppmv) using an inorganic biofilter. This type of packing material combined with low concentrations of CH_4 representative of the piggery industry present an interesting challenge with regards to the supply of nutrients, of which nitrogen is the most important.

Consequently, the objectives of this study were to examine the biofiltration of CH_4 using an inorganic filter bed at low concentrations representative of the piggery industry and to determine the influence of two key operating parameters on the performance of the biofilter:

1) the CH_4 concentration;
2) the nitrogen concentration in the nutrient solution.

2.2. Material and Methods

2.2.1. Biofilter Set-up

The biofilter used in these experiments was made of 3 sections of Plexiglas tubing with an internal diameter of 15 cm, as shown in Figure 2-1. The filter bed was composed of an entirely inorganic gravel material, evenly distributed among each section, with a total height of 1 m and a volume of 17.7 L. The gravel material used was chemically and biologically inert and had a diameter between 4 and 8 mm with a void space of 40% and an initial surface area (including the pores) estimated at 8.5 km^2/m^3 (Nikiema et al., 2008). Due to a confidentiality agreement, it is not possible to reveal the exact nature of the packing material. The temperature was maintained at ambient levels, between 20 and 25°C, throughout the entire study and the pH of the filter bed remained at near neutral values, between 6.5 and 7.5.

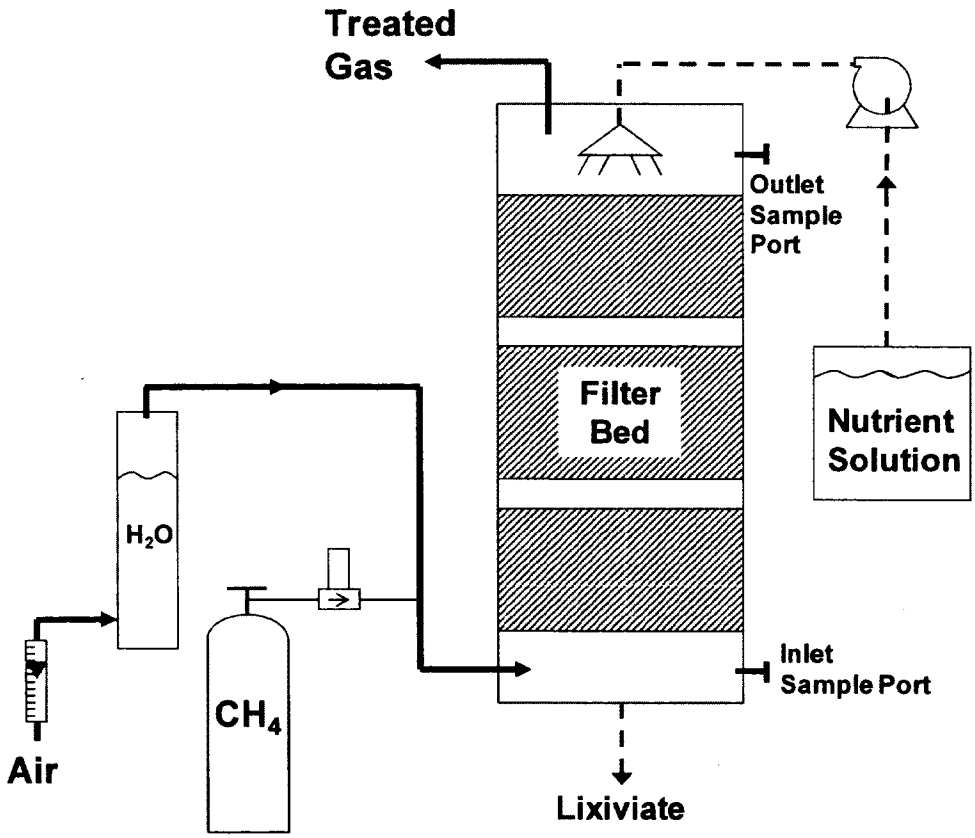

Figure 2-1: Lab-scale biofiltration system

A synthetic gas composed of humidified air (above 90% humidity (Nikiema et al., 2009)) and pure CH_4 (Praxair Inc., Canada) was injected at the base of the biofilter. The $[CH_4]$ was maintained between 0.16 and 2.8 $g \cdot m^{-3}$ (250 and 4300 ppmv) and the total gas flow rate was kept at 0.25 $m^3 \cdot h^{-1}$ (4.2 $L \cdot min^{-1}$) throughout the entire study, which corresponded to an empty bed residence time (EBRT) of 4.2 minutes. The air flow rate was controlled with an R-2-15-C volumetric flow meter while the CH_4 flow rate was controlled with a 5850S mass flow meter (both from Brooks, USA).

The inlet and outlet $[CH_4]$s were measured with an inline FIA-510 total hydrocarbon analyser equipped with a flame-ionization detector (Horiba, USA), which was calibrated daily prior to measuring. Carbon dioxide concentrations ($[CO_2]$) were measured with an Ultramat 22P gas analyser (Siemens, Germany). Detection limits for CH_4 and CO_2 were 0.5 and 10 ppmv respectively. Gas samples were extracted directly from the biofilter with vacuum pumps integrated in the CH_4 and CO_2 analysers.

Liquid samples of the nutrient solution were taken directly from the storage container while samples of the lixiviate were collected over a 24 hour period. Specific anions in the nutrient solution and lixiviate (NO_3^- and nitrite = NO_2^-) were monitored with an ICS 1000 ion chromatograph (Dionex, USA) using an AS23-4mm column and a combination of a conductivity detector and a UV detector (225 ηm). The eluent used was an aqueous solution of Na_2CO_3 at 4.5 mM and $NaHCO_3$ at 0.8 mM with a flow rate of 1 $ml \cdot min^{-1}$. The organic carbon content of the lixiviate was measured with a TOC-VE total organic carbon analyser (Shimadzu, Japan). Samples were injected in a catalyst filled combustion tube heated to 680°C and then carried to a non-dispersive infrared detector (for CO_2 analysis) by a carrier gas (purified air) at a flow rate of 150 $ml \cdot min^{-1}$. Detection limits were 0.1 $mg \cdot L^{-1}$ for NO_2^- and NO_3^- and 0.05 $mgC \cdot L^{-1}$ for total carbon.

2.2.2. Nutrient Solution

A synthetic nutrient solution was sprayed at the top of the biofilter at a rate of 1.6 $L \cdot day^{-1}$ to ensure proper filter bed moisture and to provide the nutrients necessary for microbial growth. The nutrient solution is similar to that presented by Cornish et al. (1984) and is described in detail in Table 2-1.

Table 2-1: Composition of the nutrient solution

Compound	Concentration ($g \cdot L^{-1}$)
$NaNO_3$	0 - 3.036
Na_2HPO_4	0.860
KH_2PO_4	0.530
K_2SO_4	0.170
$MgSO_4 \cdot 7H_2O$	0.037
$CaCl_2 \cdot 2H_2O$	0.007
$ZnSO_4 \cdot 7H_2O$	$5.76 * 10^{-4}$
$MnSO_4 \cdot 7H_2O$	$4.66 * 10^{-4}$
$CuSO_4 \cdot 5H_2O$	$2.50 * 10^{-4}$
KI	$1.66 * 10^{-4}$
H_3BO_3	$1.24 * 10^{-4}$
$FeSO_4 \cdot 7H_2O$	$1.12 * 10^{-4}$
$NaMoO_4 \cdot 2H_2O$	$9.6 * 10^{-5}$
$CoCl_2 \cdot 6H_2O$	$9.6 * 10^{-5}$

2.2.3. Experimental Strategy

The study was divided into two phases: (1) the effect of the $[CH_4]$ and (2) the influence of the nitrogen concentration in the nutrient solution. To determine the impact of the $[CH_4]$ on biofilter performance, the biofilter was started at a $[CH_4]$ of 1.4 $g \cdot m^{-3}$ and then the $[CH_4]$ was randomly varied between 0.16 and 2.8 $g \cdot m^{-3}$ while the NO_3^- concentration ($[NO_3^-]$) was maintained at 0.5 $gN \cdot L^{-1}$. To test the effect of the nitrogen concentration in the nutrient solution, the $[CH_4]$ was maintained at 1.0 $g \cdot m^{-3}$ (1500 ppmv) and the $[NO_3^-]$ was reduced from 0.5 to 0 $gN \cdot L^{-1}$. The biofilter was kept at each set of conditions until a steady state was reached (± 5% variation of the EC on average). Each steady state was then maintained for several days (17 days on average) in order to obtain numerous repetitions of the same conditions (8 points on average). For certain conditions at steady state, a sample of both the nutrient solution and the lixiviate were collected for carbon and anion analysis. The performance of the biofilter was evaluated using the parameters from Table 2-2.

Table 2-2 : Parameters used to evaluate biofilter performance

Parameter	Formula	Equation
Inlet Load	$IL\left(\frac{g}{m^3h}\right) = \frac{[CH_4]_{IN} * Q_{Air}}{V}$	2-1
Removal Efficiency	$RE = \frac{[CH_4]_{IN} - [CH_4]_{OUT}}{[CH_4]_{IN}}$	2-2
Elimination Capacity	$EC\left(\frac{g}{m^3h}\right) = IL * RE$	2-3
CO_2 Production Rate	$PCO_2\left(\frac{g}{m^3h}\right) = \frac{([CO_2]_{OUT} - [CO_2]_{IN}) * Q_{Air}}{V}$	2-4
Carbon Mass Balance	$C_{ACC} = C_{IN} - C_{OUT}$	2-5
	$C_{IN}\left(\frac{gC}{m^3h}\right) = \frac{\left(C_{(CH_4)IN} + C_{(CO_2)IN}\right) * Q_{Air}}{V}$	2-6
	$C_{OUT}\left(\frac{gC}{m^3h}\right) = \frac{\left(C_{(CH_4)OUT} + C_{(CO_2)OUT}\right)Q_{Air}}{V} + \frac{C_{Lix} * Q_{Lix}}{V}$	2-7
Nitrogen Mass Balance	$N_{REM} = N_{IN} - N_{OUT}$	2-8
	$N_{IN} = \frac{N_{(NO_3^-)NS} * Q_{NS}}{V}$	2-9
	$N_{OUT} = \frac{\left(N_{(NO_3^-)Lix} + N_{(NO_2^-)Lix}\right) * Q_{Lix}}{V}$	2-10

Q_{Air} is the total air flow rate ($m^3 \cdot h^{-1}$), V is the filter bed volume (m^3), $[CO_2]$ is the CO_2 concentration ($g \cdot m^{-3}$), C represents either the total carbon load (C_{IN} or C_{OUT}) or the load for a specific compound (CH_4, CO_2 or C_{Lix}) ($gC \cdot m^{-3} \cdot h^{-1}$), C_{ACC} is the accumulated carbon within the biofilter ($gC \cdot m^{-3} \cdot h^{-1}$), N is either the total nitrogen load (N_{IN} or N_{OUT}) or the load for a specific compound (NO_3^- or NO_2^-) in the nutrient solution (NS) or lixiviate (Lix) ($gN \cdot m^{-3} \cdot h^{-1}$), N_{REM} is the amount of nitrogen remaining from the partial mass balance ($gN \cdot m^{-3} \cdot h^{-1}$) and Q_{NS} and Q_{Lix} are the daily volumes of nutrient solution (subscript $_{NS}$) and lixiviate (subscript $_{Lix}$), respectively, divided by 24 hours ($m^3 \cdot h^{-1}$).

2.3. Results and Discussion

2.3.1. Influence of the Methane Concentration

Effect of the Inlet Load on the Elimination Capacity

Figure 2-2 presents the EC and removal efficiency (RE) as a function of the IL for a $[NO_3^-]$ in the nutrient solution of 0.5 $gN \cdot L^{-1}$.

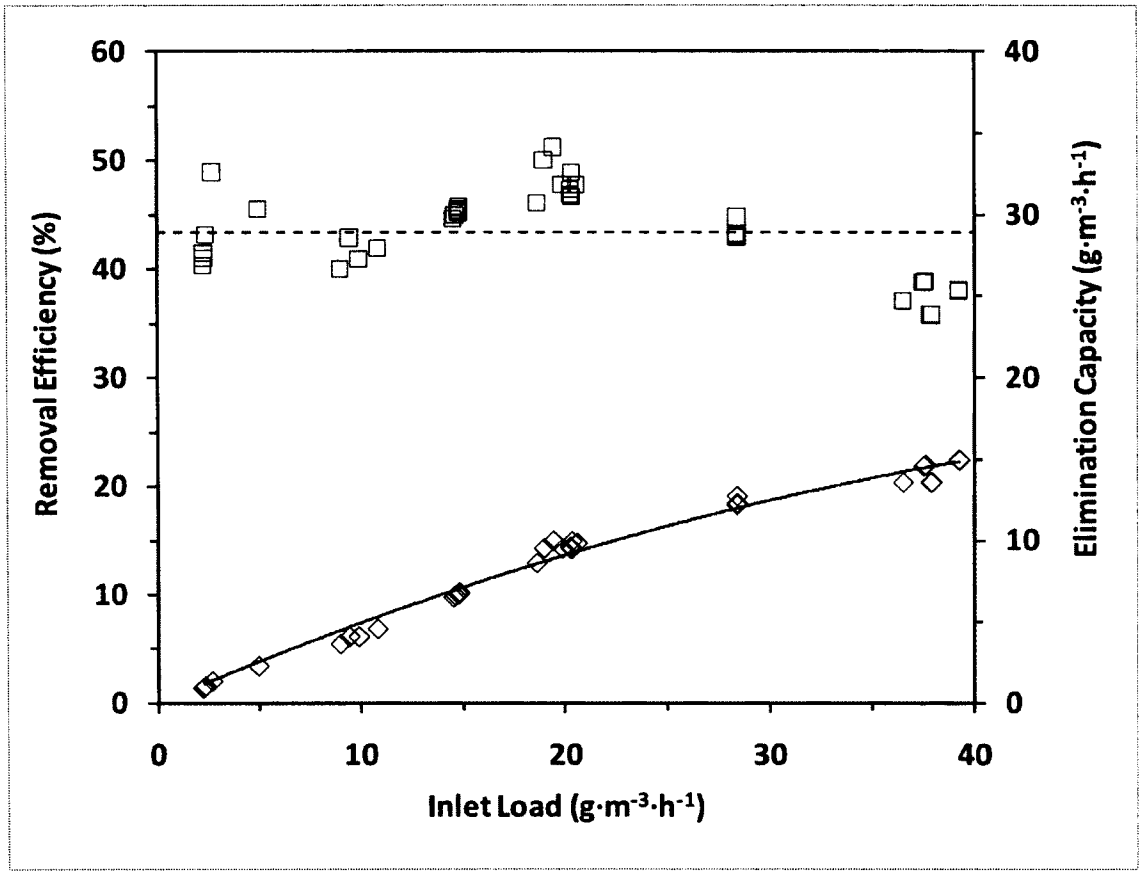

Figure 2-2: EC and RE as a function of the IL for a $[NO_3^-]$ of 0.5 $gN \cdot L^{-1}$. Experimental RE (□), average RE (_ _ _), experimental EC (◊), trend of the EC (—).

The EC increased gradually with the IL, from 1.0±0.16 $g \cdot m^{-3} \cdot h^{-1}$ for an IL of 2.4±0.18 $g \cdot m^{-3} \cdot h^{-1}$ to a maximum value of 14.5±0.6 $g \cdot m^{-3} \cdot h^{-1}$ for an IL of 38±1 $g \cdot m^{-3} \cdot h^{-1}$. In the range of ILs tested (2.4 to 38 $g \cdot m^{-3} \cdot h^{-1}$), the RE actually remained relatively stable, between 36 and 51%, with an average value of 43% and a standard deviation of ±3.7. In fact, a quarter of the average values obtained for each $[CH_4]$ were not statistically different at a

confidence level (α) of 95%. These observations can be explained if first order kinetics are assumed, where the following differential equation can be used to describe CH_4 degradation with "k" representing the first order constant:

$$\frac{d[CH_4]}{dt} = k * t \tag{2-11}$$

For plug-flow conditions, the time (t) can be calculated by dividing the void volume of the filter bed (V_{Void}) by the air flow rate (Q_{Air}). By integrating equation 2-11 between $[CH_4]_{IN}$ and $[CH_4]_{OUT}$, the following relationship is obtained:

$$RE = 1 - e^{\frac{-kV_{Void}}{Q_{Air}}} \tag{2-12}$$

According to this relationship, the RE depends solely on Q_{Air} and V_{Void}. Equation 2-12 can be rewritten to include the EC:

$$k\frac{V_{Void}}{Q_{Air}} = k * \frac{[CH_4]_{IN} - [CH_4]_{OUT}}{EC} = \ln\left(\frac{[CH_4]_{IN}}{[CH_4]_{OUT}}\right) \tag{2-13}$$

$$EC = k * \frac{[CH_4]_{IN} - [CH_4]_{OUT}}{\ln\left(\frac{[CH_4]_{IN}}{[CH_4]_{OUT}}\right)} = k * [CH_4]_{m,log} \tag{2-14}$$

By plotting the EC against $[CH_4]_{m,log}$, as shown in Figure 2-3, a linear relationship was obtained with a determination coefficient (R^2) of 0.94, which indicates that the biofilter did in fact present first order kinetics. In this study, the IL was adjusted with the $[CH_4]$ while the Q_{Air} was invariable and the V_{Void} was considered constant.

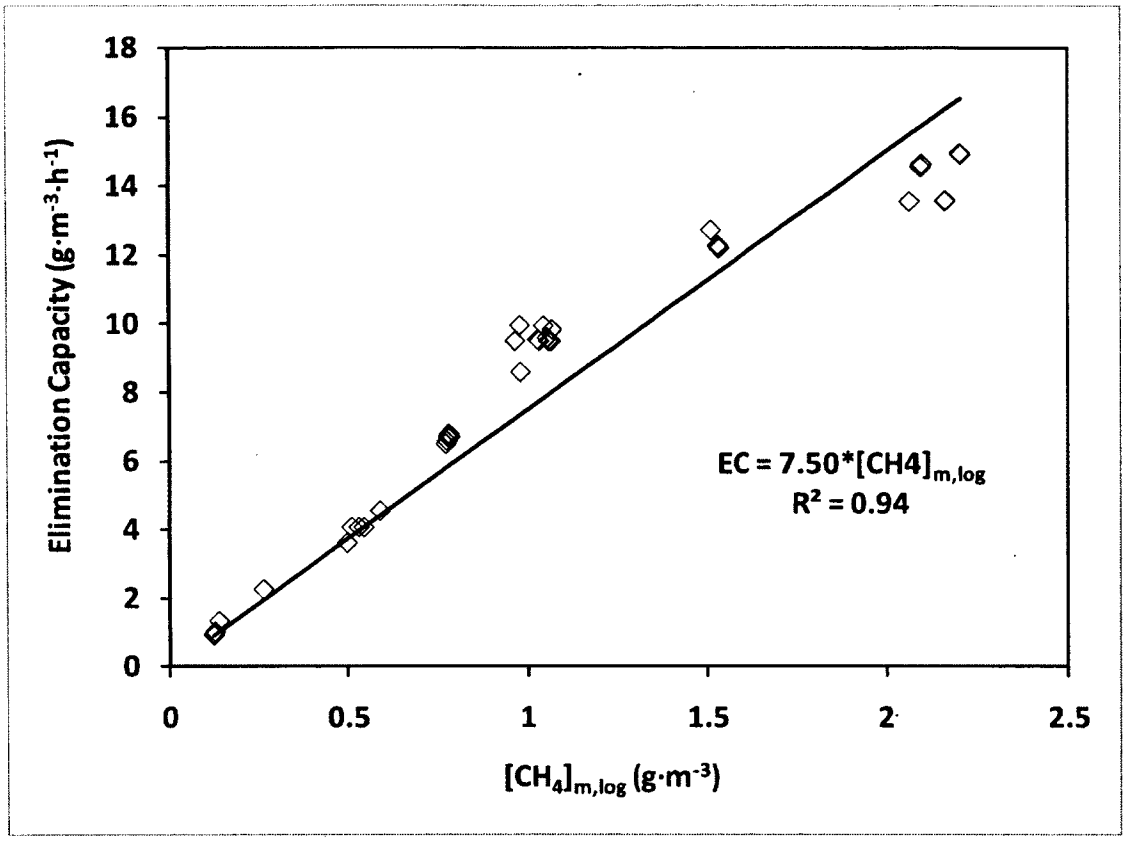

Figure 2-3: EC as a function of $[CH_4]_{m,log}$. EC (◊), linear trendline (—).

A value of 7.5 h^{-1} was obtained for the first order constant k. As shown in Table 2-3, this value is slightly higher than values obtained by other studies on the biofiltration of CH_4. While first order kinetics are respected, the higher the value of k, the closer the RE is to 100%, for constant values of Q_{Air} and V_{Void}. In this study, first order kinetics were observed for $[CH_4]$s from 0.16 to 2.8 $g \cdot m^{-3}$, but other studies have shown that first order kinetics can be maintained for $[CH_4]$s as high as 16 $g \cdot m^{-3}$ (2.5 % v/v) (Streese and Stegman, 2003). Furthermore, since the highest values of k were obtained with inorganic packing materials and a regular supply of nutrients, it seems that this type of filter bed and operating condition offer greater CH_4 removal capabilities in biofiltration than organic materials without a steady nutrient supply.

Table 2-3: Values of the first order constant, k, obtained for biofilters treating CH_4

Reference	Packing Material	Nutrient supply	k (h^{-1})
Streese and Stegman (2003)	Organic (compost, peat moss and wood chips)	None	0.98
Melse and Van der Werf (2005)	75% Organic (compost) 25% Inorganic (perlite)	Added to filter bed at start-up	2.5
Calculated from Sly et al. (1993)	Inorganic (glass beads)	Nutrient solution recycled	6.6
Present study	Inorganic (gravel)	Nutrient solution supplied daily	7.5

Table 2-4 presents some the results obtained by studies on the biofiltration of CH_4 from the piggery industry. The values obtained by the Canadian Pork Council (CPC, 2006) are up to 67% higher than the results obtained in the present study at a similar IL, but the [CH_4] was much higher, from 1.3 to 23 $g \cdot m^{-3}$. Furthermore, the EBRT used, at 10 minutes, was more than double the one used in the present study. The results obtained by Melse and van der Werf (2005) at an EBRT of 7 minutes are much lower than the results of the present study; these authors only achieved results comparable to the present study at an EBRT of 21 minutes. When compared to these studies, it seems that the biofilter used here can offer similar results at a significantly lower EBRT. This could be explained by the type of packing material since both these studies used filter beds composed mainly of organic materials: a 75:25 ratio by weight of garden compost and expanded perlite for Melse and van der Werf (2005) and mixtures of compost, peat moss, black earth and wood chips for the Canadian Pork Council (CPC, 2006). Organic packing materials are often less structurally stable than inorganic materials and filter bed compaction along with biomass growth can cause flow channelling which reduces the overall performance of the biofilter. Another important distinction lies with the nutrient supply. For the 2 previous studies, either no nutrients were added or the composition of the filter bed was adjusted at the beginning but afterwards no other nutrients were provided, while in this study, a complete nutrient solution was provided daily. A lack of readily available nutrients could also explain the lower results observed. However, a study on the biofiltration of CH_4 from landfills which compared 2 types of packing materials (mature compost and an inorganic material) found that the inorganic material performed better than the

organic material (a RE of 41% was obtained compared to 19% with the compost) even though a nutrient solution was supplied daily to both biofilters (Nikiema et al., 2005).

Table 2-4: Results obtained by studies on the biofiltration of CH_4 from the piggery industry

Reference	$[CH_4]$ ($g \cdot m^{-3}$)	EBRT (min)	IL ($g \cdot m^{-3} \cdot h^{-1}$)	EC ($g \cdot m^{-3} \cdot h^{-1}$)	RE (%)
CPC (2006)	1.3 to 23	10	29.9[a]	16[a] – 20[a]	54[a] – 67[a]
Melse and Van der Werf (2005)	up to 5.5	7	4	1.2	30
			25	5	20
		21	4	2.6	65
			15	8	53
Present study	0.16 to 2.8	4.2	5±0	2.3±0	46±0
			15±0.1	6.7±0.1	45±0.4
			28±0.1	12.3±0.2	43±0.6

[a] Average values

Carbon Dioxide Production

When dealing with the biological oxidation of CH_4, the production of CO_2 is a good indicator of the biological activity. As shown in Figure 2-4, the CO_2 production rate (PCO_2) increased with the EC, from 3.5±0.3 to 27.5±0.9 $g \cdot m^{-3} \cdot h^{-1}$. Figure 2-4 also gives the maximum amount of CO_2 that can be produced by oxidizing all the CH_4 to CO_2 if no biomass is produced, which was calculated with equation 2-15 where M_{CO2} and M_{CH4} represent the molecular weight of CO_2 and CH_4 respectively.

$$PCO_{2\,MAX} = \text{Maximum } CO_2 \text{ Production Rate}\left(\frac{g}{m^3 h}\right) = EC * \frac{M_{CO_2}}{M_{CH_4}} \qquad (2\text{-}15)$$

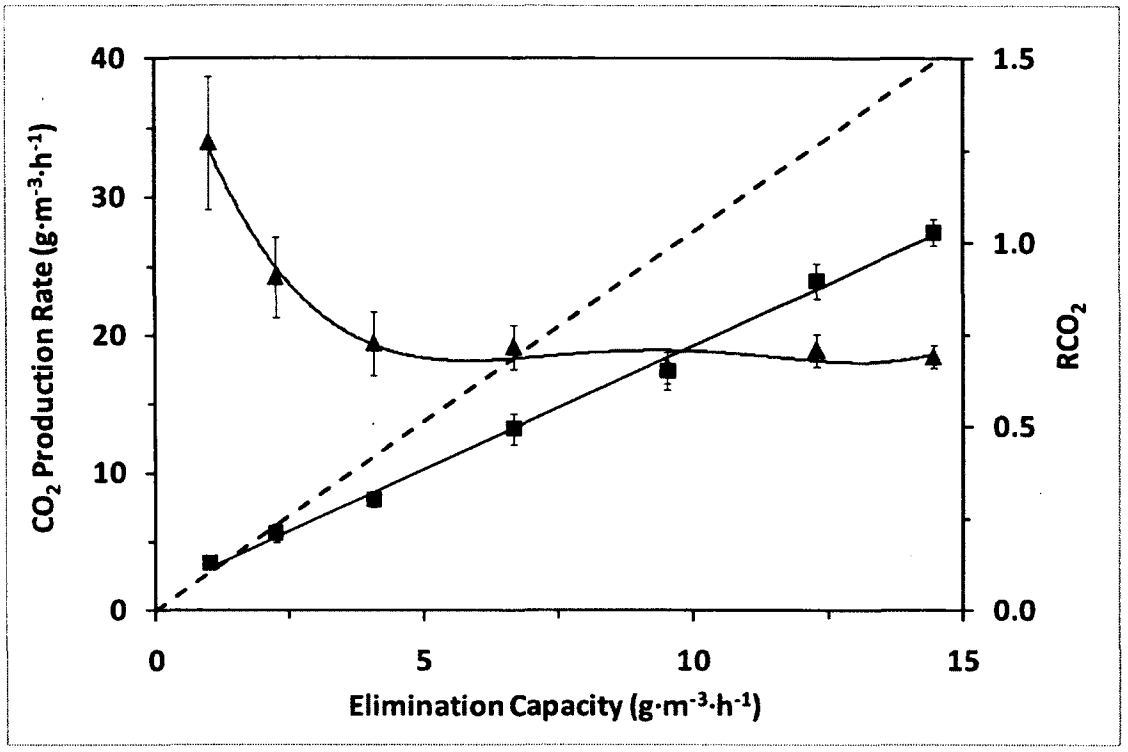

Figure 2-4: CO_2 production rate and ratio PCO_2 / $PCO_{2\,MAX}$ as a function of the EC. PCO_2 (■), RCO_2 (▲), trend of the PCO_2 and RCO_2 (—), $PCO_{2\,MAX}$ (– – –), standard deviation (vertical bars).

Since cells obtain energy by oxidizing CH_4 to CO_2 and they assimilate some carbon for biomass production, the PCO_2 should theoretically be below the maximum value. In this study, this was true for all the ECs except the lowest value, 1.0 $g \cdot m^{-3} \cdot h^{-1}$, where the PCO_2 (3.5±0.3 $g \cdot m^{-3} \cdot h^{-1}$) was slightly above the maximum (2.8 $g \cdot m^{-3} \cdot h^{-1}$). To better appreciate the difference between the actual PCO_2 and the $PCO_{2\,MAX}$, the ratio PCO_2 / $PCO_{2\,MAX}$ (RCO_2) can be calculated using equation 2-16:

$$RCO_2 = \frac{PCO_2\left(\frac{g}{m^3 h}\right)}{PCO_{2\,MAX}\left(\frac{g}{m^3 h}\right)} \qquad (2\text{-}16)$$

For ECs between 4 and 15 $g \cdot m^{-3} \cdot h^{-1}$, the RCO_2 was stable at values between 0.66±0.05 and 0.73±0.09 as shown in Figure 2-4 and no statistical difference was found between the average values (α = 95%). When the EC fell to 2.3 and then to 1.0 $g \cdot m^{-3} \cdot h^{-1}$, the value of the RCO_2 increased to 0.91±0.11 and 1.27±0.18 respectively. This means that at an EC of 1.0 $g \cdot m^{-3} \cdot h^{-1}$,

the PCO_2 was actually 27% greater than the $PCO_{2\ MAX}$. This observation can be explained according to the sequence of experiments. The biofilter was started at a relatively high IL (20 $g \cdot m^{-3} \cdot h^{-1}$ at a $[CH_4]$ of 1.4 $g \cdot m^{-3}$), where intracellular compounds (ICC), such as polysaccharides, could have been accumulated under an excess of CH_4 (Linton and Cripps, 1978). Since the filter bed was not washed between each $[CH_4]$, the microbial community could have relied on their carbon reserves to survive even though the $[CH_4]$ was reduced. With the high IL, the biofilter could also have supported a larger microbial population which might have produced CO_2 through endogenous respiration once the IL was lowered. These phenomena were observed as an overproduction of CO_2 which did not correspond to the EC. In addition, even though the performance of the biofilter was stable, the RCO_2 was quite variable for the lower ECs with standard deviations of up to ± 14% of the mean values. This indicates that the PCO_2 observed was not solely due to CH_4 oxidation.

Other studies on the biofiltration of CH_4 report values of RCO_2 between 0.17 and 0.84 (Nikiema et al., 2009; Börjesson et al., 1998; Hilger and Humer, 2003; Scheutz et al., 2009). The lowest values (0.17 and 0.36) were obtained for landfill cover soils at $[CH_4]$s from 33 to 118 $g \cdot m^{-3}$ (5 to 18% v/v). At these high $[CH_4]$s, it is possible that methanotrophs release additional metabolites, such as methanol, that can be turned into biomass by other microorganisms thereby reducing the RCO_2. An RCO_2 value of 0.59, which is close to the range of values obtained in the present study for ECs from 4 to 15 $g \cdot m^{-3} \cdot h^{-1}$, was obtained by theoretical considerations for type II methanotrophs using the serine pathway for CH_4 assimilation (Hilger and Humer, 2003). For type I methanotrophs using the ribulose monophosphate pathway, these authors suggest an RCO_2 value of 0.53. The highest RCO_2 value of 0.84 is slightly higher than the values of the present study and was obtained for an inorganic biofilter treating landfill gas at $[CH_4]$s up to 6.0 $g \cdot m^{-3}$ (Nikiema et al., 2009). This biofilter also produced values of RCO_2 greater than 1 when the EC was lowered below 10 $g \cdot m^{-3} \cdot h^{-1}$. Although occurring at an EC 10 times higher than the present study (1.0 $g \cdot m^{-3} \cdot h^{-1}$), the observation of RCO_2 values greater than 1 corroborates the explanation that the microbial community could have relied on their reserves when less CH_4 was available.

Carbon and Nitrogen Mass Balances

As previously mentioned, the carbon in CH_4 can be used as energy and end up as CO_2 or used for biomass production which can include new cells, ICC and exopolymeric substances (EPS). By performing carbon mass balances over the biofilter and determining the accumulated carbon (C_{ACC}), it was therefore possible to estimate the production of biomass as C_{ACC}. The carbon entering the biofilter (C_{IN}) includes the CH_4 introduced to the system ($C_{(CH4)IN}$) and the CO_2 naturally present in the air ($C_{(CO2)IN}$) while the carbon exiting the biofilter (C_{OUT}) was composed of the untreated CH_4 ($C_{(CH4)OUT}$), the CO_2 leaving the system ($C_{(CO2)OUT}$) and any biomass or organic material that was carried out by the lixiviate (C_{Lix}). Table 2-5 presents the carbon mass balances for the different ILs tested.

Table 2-5: Carbon mass balance for the biofilter treating CH_4 at the different ILs tested

IL ($gCH_4 \cdot m^{-3} \cdot h^{-1}$)	C_{IN} ($gC \cdot m^{-3} \cdot h^{-1}$)		C_{OUT} ($gC \cdot m^{-3} \cdot h^{-1}$)			C_{ACC} ($gC \cdot m^{-3} \cdot h^{-1}$)
	CH_4	CO_2	CH_4	CO_2	Lixiviate	Biofilter
4.96	3.72	2.20	2.04	3.59	0.032	0.26
9.03	6.77	2.78	4.06	5.08	0.028	0.38
14.8	11.11	4.78	6.09	8.78	0.082	0.94
20.3	15.19	1.87	8.00	7.01	0.061	1.99
28.4	21.30	4.03	13.25	9.46	0.054	2.57
38.6	28.94	3.23	18.25	10.87	0.055	3.00

The values presented in Table 2-5 show that the carbon accumulated within the biofilter increased with the IL, from 0.26 $gC \cdot m^{-3} \cdot h^{-1}$ at an IL of 4.96 $g \cdot m^{-3} \cdot h^{-1}$ to 3.00 $gC \cdot m^{-3} \cdot h^{-1}$ at an IL of 38.6 $g \cdot m^{-3} \cdot h^{-1}$. With more CH_4 available, the microorganisms could use more carbon for biomass production. The variations of the CO_2 in the inlet gas were simply due to changes in the atmospheric [CO_2]. The organic carbon that was found in the lixiviate was mainly composed of biomass washed out during irrigation. The values presented in Table 2-5 were relatively stable, between 0.028 and 0.082 $gC \cdot m^{-3} \cdot h^{-1}$ and no clear correlation with the IL was found. Furthermore, the carbon in the lixiviate represented only between 0.2 and 0.6% of the C_{OUT} which indicates that the C_{ACC} probably remained in the filter bed.

By measuring the inorganic forms of nitrogen (NO_2^- and NO_3^-) in the nutrient solution and the lixiviate, it was possible to perform a partial mass balance on nitrogen as shown in Table 2-6. The mass balance was only partial since the organic nitrogen in the lixiviate and the gaseous forms of nitrogen (mainly nitrous oxide - N_2O and atmospheric nitrogen - N_2) were not taken into account and several species of methanotrophs are capable of fixing atmospheric nitrogen (Auman et al., 2001). Furthermore, there are no known methanotrophs that can denitrify NO_3^- to N_2O and N_2, but there might have been other microorganisms present in the biofilter that could have accomplished this task (Eisentraeger et al., 2001). As the IL was increased from 4.96 to 38.6 $g \cdot m^{-3} \cdot h^{-1}$, the nitrogen remaining (N_{REM}) was relatively stable, varying from 0.192 to 0.385 $gN \cdot m^{-3} \cdot h^{-1}$. This demonstrates that the C_{ACC} observed in Table 2-5 was probably used for the production of EPS or ICC since they consist mainly of polysaccharides (Scheutz et al., 2009). If the C_{ACC} would have been used solely for cell synthesis, the N_{REM} would also have increased with the IL since nitrogen is required for the synthesis of proteins. This lack of microbial growth could be beneficial to the long-term operation of the biofilter by reducing the clogging of the filter bed. However, such a stable microbial population might not be capable of adapting to large variations in operating conditions, which can be observed in full-scale applications.

Table 2-6: Nitrogen mass balance for the biofilter treating CH_4 at specific ILs

IL ($gCH_4 \cdot m^{-3} \cdot h^{-1}$)	EC ($gCH_4 \cdot m^{-3} \cdot h^{-1}$)	N_{IN} ($gN \cdot m^{-3} \cdot h^{-1}$)	N_{OUT} ($gN \cdot m^{-3} \cdot h^{-1}$)	N_{REM} ($gN \cdot m^{-3} \cdot h^{-1}$)
		Nutrient solution	Lixiviate	Biofilter
4.96	2.25	1.783	1.398	0.385
9.03	3.61	1.798	1.486	0.312
20.3	9.59	1.867	1.575	0.292
38.6	14.25	2.182	1.990	0.192

2.3.2. Influence of the Nitrogen Concentration

Effect of the Nitrate Concentration in the Nutrient Solution on the Removal Efficiency

The trials to determine the influence of the nitrogen concentration in the nutrient solution were carried out at a $[CH_4]$ of 1.0 $g \cdot m^{-3}$ which corresponded to an IL of 14 $g \cdot m^{-3} \cdot h^{-1}$.

Figure 2-5 shows the RE as a function of the $[NO_3^-]$ in the nutrient solution. For $[NO_3^-]$s from 0.1 to 0.5 $gN \cdot L^{-1}$, the RE remained quite stable: the average values varied between 47±0.1 and 50±0.4 % and were statistically equivalent at an α of 95%. This observation indicates that a $[NO_3^-]$ of 0.1 $gN \cdot L^{-1}$ is sufficient for proper biofilter operation at an IL of 14 $g \cdot m^{-3} \cdot h^{-1}$. However, when the $[NO_3^-]$ was adjusted to 0.01 and 0.001 $gN \cdot L^{-1}$, the RE fell to 36±0.5 and 27.5±0.1 %, respectively. When no NO_3^- was added to the nutrient solution, the RE remained stable at 26±1 %, but the nutrient solution was prepared with municipal tap water where the $[NO_3^-]$ was approximately $1.6*10^{-4}$ $gN \cdot L^{-1}$. To eliminate all sources of NO_3^-, the nutrient solution was then prepared using distilled water. Nevertheless, the RE only dropped to 18±0.7% and remained at this value for over 8 weeks. Without proper growth conditions, such as the absence of nitrogen, methanotrophs can slow down or stop their growth and simply used CH_4 for cellular respiration and the production of EPS (Wilshusen et al., 2004). Very little nitrogen would therefore be required for microbial maintenance, which could be obtained from stored reserves, cell lysis or possibly from NO_3^- adsorbed on the filter bed. Moe and Irvine (2001) observed a reduction of up to 46% of the nitrogen content in biomass for a biofilter limited in nitrogen when compared to a biofilter with over three times the initial amount of nitrate-nitrogen. However, according to Scheutz et al. (2009), long-term depletion of nitrogen can reduce or even halt CH_4 consumption. On the other hand, several methanotrophs are capable of fixing atmospheric nitrogen. This behaviour has been shown in many type II methanotrophs and type I methanotrophs from the genus *Methylococcus* (Murrell and Dalton, 1983). In addition, a study from Auman et al. (2001) showed that nitrogen fixation capabilities are actually found in a wide range of methanotrophs. Particularly, these authors confirmed nitrogen fixation abilities in several *Methylocystis* species. This led to the hypothesis that methanotrophs with nitrogen fixing capabilities could have been present in the biofilter used here since it was inoculated with lixiviate from a biofilter where *Methylocystis parvus* was identified as the main active bacteria (Nikiema et al., 2005). The presence of nitrogen fixing methanotrophs could therefore account for the RE when no NO_3^- was provided in the nutrient solution.

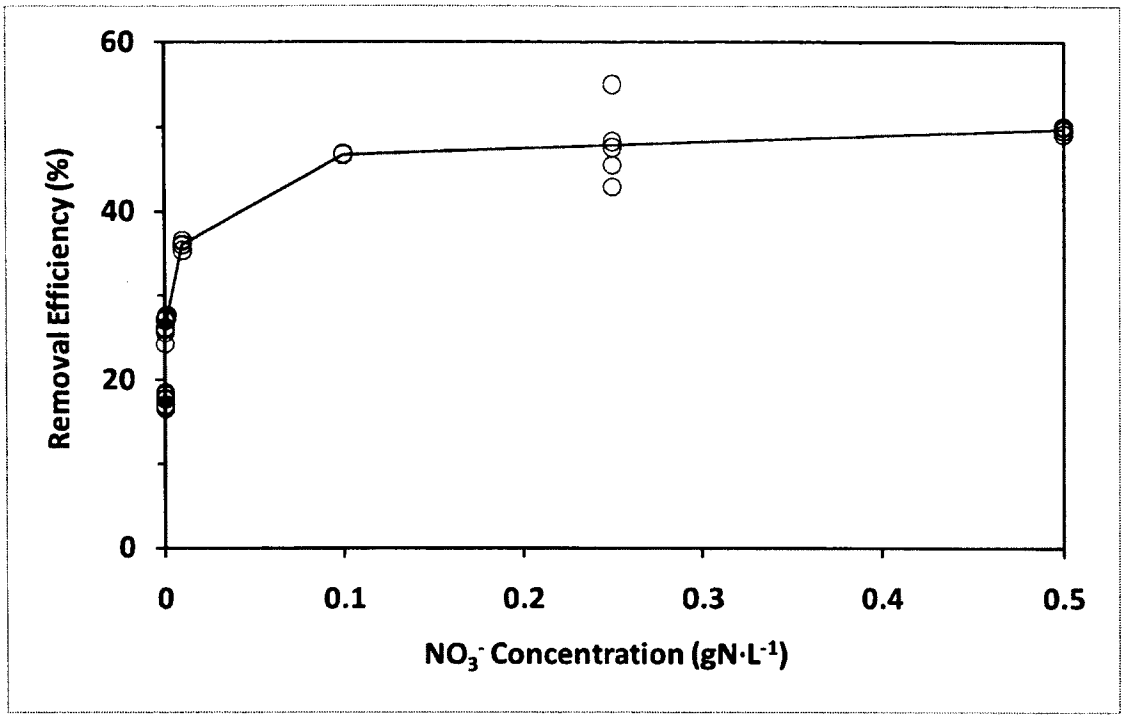

Figure 2-5: RE as a function of the [NO_3^-] in the nutrient solution for an IL of 14 $g \cdot m^{-3} \cdot h^{-1}$. Experimental RE (○), trend of the RE (—).

Using a trickling biofilter, Sly et al. (1993) tested [NO_3^-]s from 0 to 0.14 $gN \cdot L^{-1}$, but each [NO_3^-] was only maintained for a few days and no effect on CH_4 removal was observed. This indicated that a temporary lack of nitrogen should not hinder biofilter performance. With longer-term removal of nitrogen, as studied here, the reduction in CH_4 removal is clear. Nikiema et al. (2009) studied [NO_3^-]s from 0.14 to 0.75 $gN \cdot L^{-1}$ at an IL of 12 $g \cdot m^{-3} \cdot h^{-1}$, but no significant variation of biofilter performance was observed.

CO_2 Production

Figure 2-6 shows both the PCO_2 and the RCO_2 as a function of the [NO_3^-]. The PCO_2 resembled the trend of the RE in Figure 2-5; it was relatively stable (yet still statistically different at an α of 95%), between 13.8±0.6 and 14.9±0.7 $g \cdot m^{-3} \cdot h^{-1}$, for [$NO_3^-$]s from 0.1 to 0.5 $gN \cdot L^{-1}$, but it dropped once the [NO_3^-] was adjusted to 0.01 $gN \cdot L^{-1}$, reaching a value of 6.6±1 $g \cdot m^{-3} \cdot h^{-1}$ with no nitrogen in the nutrient solution. Since less CH_4 was oxidized by the microorganisms, less CO_2 was produced. However, when the PCO_2 was compared to the maximum theoretical value with the RCO_2, the average results varied only between 0.77±0.04

and 0.90±0.15 and were not statistically different at 95% confidence for all the $[NO_3^-]$s tested. This observation showed that even in the absence of inorganic nitrogen in the nutrient solution, part of the CH_4 was used other than for energy requirements. If the microorganisms only used CH_4 as an energy source for cell maintenance, the CH_4 would be entirely converted to CO_2 and the RCO_2 would have been around 1.

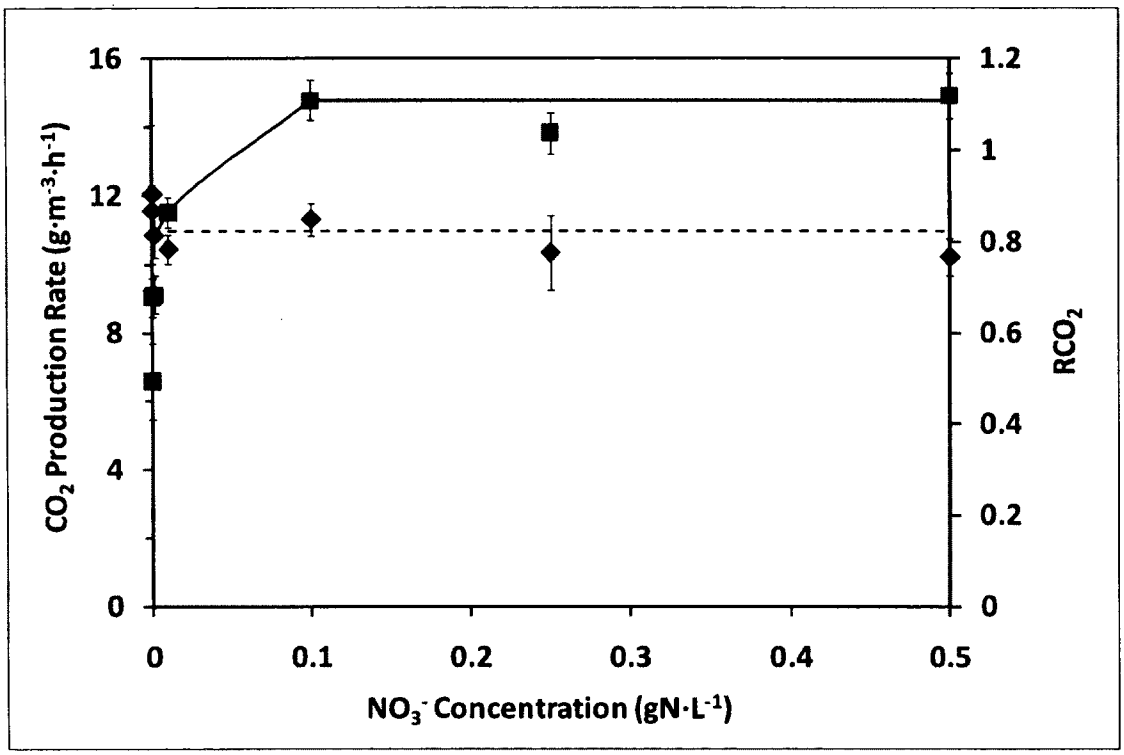

Figure 2-6: CO_2 production rate and ratio PCO_2 / $PCO_{2\,MAX}$ as a function of the $[NO_3^-]$ in the nutrient solution. PCO_2 (■), trend of the PCO_2 (—), RCO_2 (♦), average RCO_2 (_ _ _), standard deviation (vertical bars).

Carbon and Nitrogen Mass Balances

The carbon mass balances for $[NO_3^-]$s from 0 to 0.25 $gN \cdot L^{-1}$ are presented in Table 2-7 at an IL of 14 $g \cdot m^{-3} \cdot h^{-1}$. For a $[NO_3^-]$ of 0.25 $gN \cdot L^{-1}$, the C_{ACC} of 1.35 $gC \cdot m^{-3} \cdot h^{-1}$ was within the same range as the value obtained in Table 2-5, 0.94 $gC \cdot m^{-3} \cdot h^{-1}$, for an IL of 14.8 $g \cdot m^{-3} \cdot h^{-1}$ and a $[NO_3^-]$ of 0.5 $gN \cdot L^{-1}$. For $[NO_3^-]$s from $1.6*10^{-4}$ $gN \cdot L^{-1}$ (tap water) to 0.1 $gN \cdot L^{-1}$, the C_{ACC} was relatively stable at values between 0.65 and 0.91 $gC \cdot m^{-3} \cdot h^{-1}$. When distilled water was used to make the nutrient solution and no nitrogen was added, the C_{ACC} obtained was

considerably lower, at 0.15 $gC \cdot m^{-3} \cdot h^{-1}$. This was probably due to the low EC combined with the highest RCO_2 observed (0.90 from Figure 2-6). However, for all the $[NO_3^-]$s tested, there was always a significant amount of carbon accumulated in the biofilter. This observation confirms the same tendency as the RCO_2 and showed that carbon from CH_4 was still used other than for energy requirements even in the absence of inorganic nitrogen in the nutrient solution. The C_{ACC} observed could have been used for the production of EPS or ICC requiring little nitrogen. In fact, the ability of methanotrophs to produce ICC under nutrient deficiency has been used to induce the production of valuable compounds, such as poly-3-hydroxybutyrate (Zhang et al., 2008). The C_{ACC} could also have been used for cell synthesis by methanotrophs capable of fixing atmospheric nitrogen.

Table 2-7: Carbon mass balance as a function of the $[NO_3^-]$ in the nutrient solution at an IL of 14 $g \cdot m^{-3} \cdot h^{-1}$

$[NO_3^-]$ ($gN \cdot L^{-1}$)	C_{IN} ($gC \cdot m^{-3} \cdot h^{-1}$)		C_{OUT} ($gC \cdot m^{-3} \cdot h^{-1}$)			C_{ACC} ($gC \cdot m^{-3} \cdot h^{-1}$)
Nutrient Solution	CH_4	CO_2	CH_4	CO_2	Lixiviate	Biofilter
0.25	10.33	2.65	5.06	6.50	0.074	1.35
0.1	10.34	2.28	5.52	6.37	0.033	0.70
0.01	11.08	2.59	7.05	5.61	0.102	0.91
0.001	11.12	1.81	8.07	4.10	0.107	0.65
$1.6*10^{-4}$ (Tap Water)	11.07	3.23	8.07	5.28	0.086	0.86
0 (Distilled Water)	11.12	4.03	9.09	5.80	0.112	0.15

The amount of carbon found in the lixiviate for $[NO_3^-]$s of 0.1 and 0.25 $gN \cdot L^{-1}$, 0.033 and 0.074 $gC \cdot m^{-3} \cdot h^{-1}$ respectively (Table 2-7), was similar to the values obtained during the experiments on the influence of the $[CH_4]$ at a $[NO_3^-]$ of 0.5 $gN \cdot L^{-1}$, from 0.028 to 0.082 $gC \cdot m^{-3} \cdot h^{-1}$ (Table 2-5). However, for the lower $[NO_3^-]$s (0 to 0.01 $gN \cdot L^{-1}$), there was slightly more carbon in the liquid phase exiting the system. In certain microorganisms, an excess production of EPS has been linked to both nutrient imbalance and O_2 deficiency (Wrangstadh et al., 1986). In this study, some of the excess EPS produced could have been washed out with the lixiviate and explain the increased carbon content for the lower $[NO_3^-]$s. Furthermore, by

reducing the quantity of nitrogen available for the microorganisms, it is possible that cell mortality was increased therefore releasing additional carbon.

The results obtained from the nitrogen mass balances, presented in Table 2-8, show that as the quantity of nitrogen in the nutrient solution was reduced, the $[NO_3^-]$ in the lixiviate also decreased. With the partial nitrogen mass balance, about 1/4 of the nitrogen introduced to the system remained in the biofilter for inlet $[NO_3^-]$s of 0.25 and 0.1 $gN \cdot L^{-1}$, while for 0.01 $gN \cdot L^{-1}$, the N_{REM} was negative which means that nitrogen was actually rejected from the biofilter. This could simply have been due to a washing out of residual NO_3^- present in the biofilter due to the low inlet $[NO_3^-]$. However, the negative N_{REM} could also be caused by the error involved in measuring such low $[NO_3^-]$s. When the nutrient solution was prepared with tap water ($[NO_3^-] = 1.6*10^{-4}$ $gN \cdot L^{-1}$), nitrogen was once again accumulated in the system. For the test using distilled water, trace amounts on NO_3^- were still found in the nutrient solution ($4*10^{-4}$ $gN \cdot m^{-3} \cdot h^{-1}$) and about twice as much nitrogen was carried out with the lixiviate. This excess nitrogen could have come from methanotrophs capable of fixing nitrogen or from NO_3^- previously adsorbed on the filter bed. However, since the $[CH_4]$ was maintained at 1.0 $g \cdot m^{-3}$ during these experiments, the fact that the N_{REM} decreased faster than the C_{ACC} as the $[NO_3^-]$ was reduced confirms that the C_{ACC} was composed mainly of EPS or ICC which require little nitrogen. If the C_{ACC} would have been used for cell synthesis, the N_{REM} would have been relatively stable like the values of C_{ACC} in Table 2-7.

Table 2-8: Nitrogen mass balance as a function of the $[NO_3^-]$ in the nutrient solution

$[NO_3^-]$ ($gN \cdot L^{-1}$)	N_{IN} ($gN \cdot m^{-3} \cdot h^{-1}$)	N_{OUT} ($gN \cdot m^{-3} \cdot h^{-1}$)	N_{REM} ($gN \cdot m^{-3} \cdot h^{-1}$)
Nutrient Solution	Nutrient Solution	Lixiviate	Biofilter
0.25	0.938	0.726	0.212
0.1	0.386	0.292	0.094
0.01	0.056	0.094	-0.038
$1.6*10^{-4}$ (Tap Water)	0.054	0.046	0.007
0 (Distilled Water)	0.0004	0.0008	-0.0004

2.4. Conclusion

The aim of this paper was to determine the influence of the [CH_4] and the [NO_3^-] in the nutrient solution on the performance of a biofilter packed with an inorganic material treating low [CH_4]s representative of the piggery industry. A maximum EC of 14.5±0.6 $g \cdot m^{-3} \cdot h^{-1}$ was obtained for an IL of 38±1 $g \cdot m^{-3} \cdot h^{-1}$. For all the [$CH_4$]s tested, the RE remained relatively stable and the biofilter satisfied first order kinetics where the RE depends solely on the air flow rate and the void volume of the filter bed. A value of 7.5 h^{-1} was obtained for the first order constant k, which is slightly higher than other studies on the biofiltration of CH_4. Nitrate concentrations from 0 to 0.5 $gN \cdot L^{-1}$ were tested at an IL of 14 $g \cdot m^{-3} \cdot h^{-1}$. The RE was stable for [NO_3^-]s from 0.1 to 0.5 $gN \cdot L^{-1}$, but decreased significantly when the [NO_3^-] was adjusted to 0.01 $gN \cdot L^{-1}$. Therefore, a [NO_3^-] of 0.1 $gN \cdot L^{-1}$ is sufficient for proper biofilter operation at an IL of 14 $g \cdot m^{-3} \cdot h^{-1}$. When no inorganic nitrogen was provided in the nutrient solution, the RE was stable at 18±0.7 % for over 8 weeks. This observation suggested the presence of methanotrophs capable of fixing atmospheric nitrogen.

To determine the amount of carbon and nitrogen accumulated in the biofilter, mass balances were used. The C_{ACC} was found to increase with the IL which indicated an increased use of CH_4 for biomass production. However, since the N_{REM} was relatively stable with the IL, the C_{ACC} was probably used for the production of EPS or ICC requiring little nitrogen. Except for the lowest [NO_3^-], the C_{ACC} was generally stable when the [NO_3^-] was reduced even though the RE decreased. Methanotrophs have been shown to produce excess EPS or ICC when faced with a nutrient deficiency. This explanation was supported with the nitrogen balance where the N_{REM} decreased as the [NO_3^-] was reduced, indicating that the C_{ACC} was probably used for EPS or ICC production rather than for cell synthesis. However, further work is required to validate these observations and to determine the long-term trends.

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CHAPITRE 3. Traitement simultané du méthane et du lisier de porc

Avant-propos

L'article « *Simultaneous Treatment of Methane and Swine Slurry by Biofiltration* » a été soumis au Journal of Chemical Technology and Biotechnology le 1e septembre 2011. Après quelques modifications mineurs, l'article a été publié en 2012 (Volume 87(5), pages 697 à 704).

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Résumé

CONTEXTE: L'industrie porcine est importante autant à travers le monde qu'au Canada, mais la production localisée de grandes quantités de lisier de porc cause de graves problèmes environnementaux, tels que la pollution aquatique et la production de gaz à effet de serre. L'objectif principal de cette étude était de déterminer s'il est possible de traiter simultanément le méthane (CH_4) et le lisier de porc en utilisant un biofiltre avec un lit filtrant inorganique.

RÉSULTATS : Un biofiltre innovateur a été conçu pour pallier à l'inhibition de la biodégradation du CH_4 par le lisier de porc. La capacité d'élimination du CH_4 a augmentée avec la charge à l'entrée et une valeur maximale de 18.8 ± 1.0 $g \cdot m^{-3} \cdot h^{-1}$ a été obtenue pour une charge de 46.7 ± 0.9 $g \cdot m^{-3} \cdot h^{-1}$. Quatre souches pures de champignons ont été utilisées pour améliorer l'enlèvement du CH_4, mais aucun effet significatif n'a été observé. Pour des valeurs entre 0.35 et 3.4 $g \cdot m^{-3}$, la concentration de CH_4 n'a pas eu d'effet sur le traitement du lisier avec des efficacités d'épuration moyennes de $67 \pm 10\%$ pour le carbone organique total et de $70 \pm 7\%$ pour l'azote ammoniacal. L'influence de l'alimentation du lisier a été analysée et les meilleurs résultats ont été obtenus avec une alimentation de 6 doses de 50ml par jour.

CONCLUSION : Cette étude a démontré la faisabilité de traiter le CH_4 et le lisier de porc à l'aide d'un même biofiltre en utilisant un design innovateur.

Abstract

BACKGROUND: The piggery industry is important both worldwide and in Canada, but localized production of large quantities of swine slurry causes severe environmental problems such as aquatic pollution and greenhouse gas emissions. The main objective of this study was to determine whether it is possible to simultaneously treat methane (CH_4) and swine slurry using a biofilter packed with an inorganic filter bed.

RESULTS: A novel biofilter was designed to overcome the inhibition of CH_4 biodegradation by swine slurry. The CH_4 elimination capacity increased with the inlet load and a maximum value of 18.8 ± 1.0 $g \cdot m^{-3} \cdot h^{-1}$ was obtained at an inlet load of 46.7 ± 0.9 $g \cdot m^{-3} \cdot h^{-1}$. Four pure strains of fungi were used in an attempt to improve the removal of CH_4, but no significant effect was observed. For values between 0.35 and 3.4 $g \cdot m^{-3}$, the CH_4 concentration had no effect on the treatment of swine slurry with average removal efficiencies of 67 ± 10% for total organic carbon and 70 ± 7% for ammonium nitrogen. The influence of the slurry supply was analyzed and the best results were obtained with a supply method of 6 doses of 50 ml per day.

CONCLUSION: This study demonstrated the feasibility of treating CH_4 and swine slurry with the same biofilter using a novel design.

3.1. Introduction

Worldwide pork production was estimated at 1.3 billion heads in 2009 which makes it the most important meat product at 38% of total production (FAOSTAT, 2011). In Canada, 27 million hogs were produced in 2010 with exports worth over 3 billion CAN$ (CPC, 2011). However, modern pork production causes severe environmental problems, in terms of excessive fertilization and greenhouse gas (GHG) emissions. Swine slurry is often used as a fertilizer in agriculture, but fertilization above crop requirements can cause excess nutrients to leach into surface and ground waters which accelerates eutrophication (Carpenter et al., 1998; Smith et al., 2007). Furthermore, the anaerobic storage conditions of swine slurry cause the emission of methane (CH_4), a GHG 25 times more potent than carbon dioxide (CO_2) (Solomon et al., 2007). In 2008, the CH_4 released by the Canadian piggery industry was equal to 1.3 million metric tons of CO_2 equivalent (Jaques 2010).

To solve these problems, nutrient losses and GHG emissions from the piggery industry must either be reduced or the waste streams must be treated. Careful fertilization can reduce the loss of nutrients from slurry while CH_4 emissions can be reduced by adjusting the pig feed, treating the slurry or limiting the biological activity (Monteny et al. 2006). Swine slurry can also be treated by different physico-chemical methods, but biological processes, both aerobic and anaerobic, are generally used (Girard et al., 2009). Methane can be treated by flaring, but a concentration above 130 $g \cdot m^{-3}$ is required for direct combustion (Haubrichs and Widmann, 2006), which is not usually found on pig farms. Biological oxidation of CH_4 is also possible and it can be carried out directly in slurry storage reservoirs by adding a surface crust (Petersen et al., 2005). However, biofiltration, which uses microorganisms immobilized on a filter bed, has the potential to treat both swine slurry and CH_4 within the same bioreactor (Girard et al., 2009).

For the treatment of municipal and industrial wastewaters, biofiltration has been used for nearly 100 years (Metcalf and Eddy 2003), but it has only recently been applied to swine slurry (Buelna et al., 1998). The biofiltration of CH_4 has been widely studied for sanitary landfills (Nikiema et al., 2007), but there is little research for the treatment of CH_4 from the piggery industry (Melse and van der Werf, 2005). According to our knowledge, the simultaneous biofiltration of swine slurry and CH_4 has never been attempted. For the biofiltration of swine slurry or CH_4, organic packing materials are generally used due to their lower cost, but inorganic materials can offer interesting advantages. These filter beds can be washed to remove excess biomass produced during swine slurry treatment (Westerman et al., 2000) and they have shown to be more than twice as efficient as organic materials for CH_4 biofiltration (Nikiema et al., 2005).

However, there are a few substantial challenges when considering the simultaneous biofiltration of swine slurry and CH_4. The supply of nitrogen is a critical issue for the CH_4 oxidizing bacteria, methanotrophs. Swine slurry contains large amounts of ammonium (NH_4^+) which is a known inhibitor of CH_4 biodegradation (Bronson and Mosier, 1994). Thus, the methanotrophs prefer nitrate (NO_3^-) as a nitrogen source and the optimal NO_3^- concentration ($[NO_3^-]$) depends on the CH_4 inlet load (IL): 0.50 $gN \cdot L^{-1}$ for ILs up to 55 $g \cdot m^{-3} \cdot h^{-1}$ and 0.75 $gN \cdot L^{-1}$ for ILs up to 95 $g \cdot m^{-3} \cdot h^{-1}$ (Nikiema et al., 2009).

To overcome some of the challenges faced by the biofiltration of hydrophobic compounds, such as CH_4, several studies have tested the use of fungal strains either as the sole type of microorganism or as a complement to bacteria. It has been suggested that fungal biofilters perform better with hydrophobic compounds due to the aerial hyphae of filamentous fungi that improve the adsorption of these compounds by providing a larger surface area (Kennes and Veiga, 2004). For example, Arriaga and Revah (2005) found that a biofilter where fungi predominated reached an elimination capacity (EC) for hexane twice as high as a biofilter where bacteria were dominant. It has also been shown that the hydrophobicity of the fungal mycelia can increase with the presence of a hydrophobic substrate (Vergara-Fernandez et al., 2006). Moreover, Wick et al. (2007) showed that fungal mycelia could be used as a network to facilitate bacterial access to pollutants in soil. Although only methanotrophs can use CH_4 as both a carbon and energy source, fungi could grow on other compounds, such as volatile fatty acids (VFA) found in swine slurry, and potentially improve the adsorption and availability of CH_4. Furthermore, the addition of a specific VFA, acetate, has been shown to block CH_4 biodegradation by certain types of methanotrophs grown in pure cultures (Dedysh et al., 2005).

The main objective of this study was to establish the feasibility of simultaneously treating CH_4 and swine slurry using a biofilter packed with an inorganic material. Four strains of fungi capable of oxidizing VFAs were used in an attempt to improve CH_4 removal. The influence of the CH_4 concentration and of the swine slurry supply (quantity and frequency) on the removal of CH_4 and on the treatment of swine slurry was also determined.

3.2. Material and Methods

3.2.1. Biofilter Set-up

The biofilters used in this study were made of 15cm Plexiglas® tubes packed with 1 m of an inorganic gravel material. Due to a confidentiality agreement, it is not possible to reveal the exact nature of the packing material. The biofilters were separated in 3 identical sections, as shown in Figure 3-1. A mixture of humidified air and pure CH_4 (Praxair Inc., Canada) was supplied at the base of each biofilter. For biofilters B1 and B2, pre-treated swine slurry was

supplied at the surface of the bottom section. Biofilter B2 was used as control while biofilter B1 was used to test the influence of fungi on CH_4 removal. A third biofilter (B3) was used for the treatment of CH_4 alone and no slurry was supplied. The CH_4 concentration ($[CH_4]$) was adjusted to values between 0.35 and 3.4 $g \cdot m^{-3}$ which are representative of the piggery industry where the $[CH_4]$ varies from 0.005 to 20 $g \cdot m^{-3}$ (Melse and van der Werf 2005). The air flow rate was maintained at 0.25 $m^3 \cdot h^{-1}$ for the entire study, corresponding to an empty bed residence time (EBRT) of 4.2 minutes. The flow rate of pure CH_4 was controlled with a mass flow meter and the air flow rate was controlled with a volumetric flow meter (both from Brooks, United States). Masterflex peristaltic pumps (Cole-Palmer, United States) were used to supply the swine slurry to biofilters B1 and B2. The temperature of the filter bed was not controlled, but it remained at ambient levels, between 20 and 25°C.

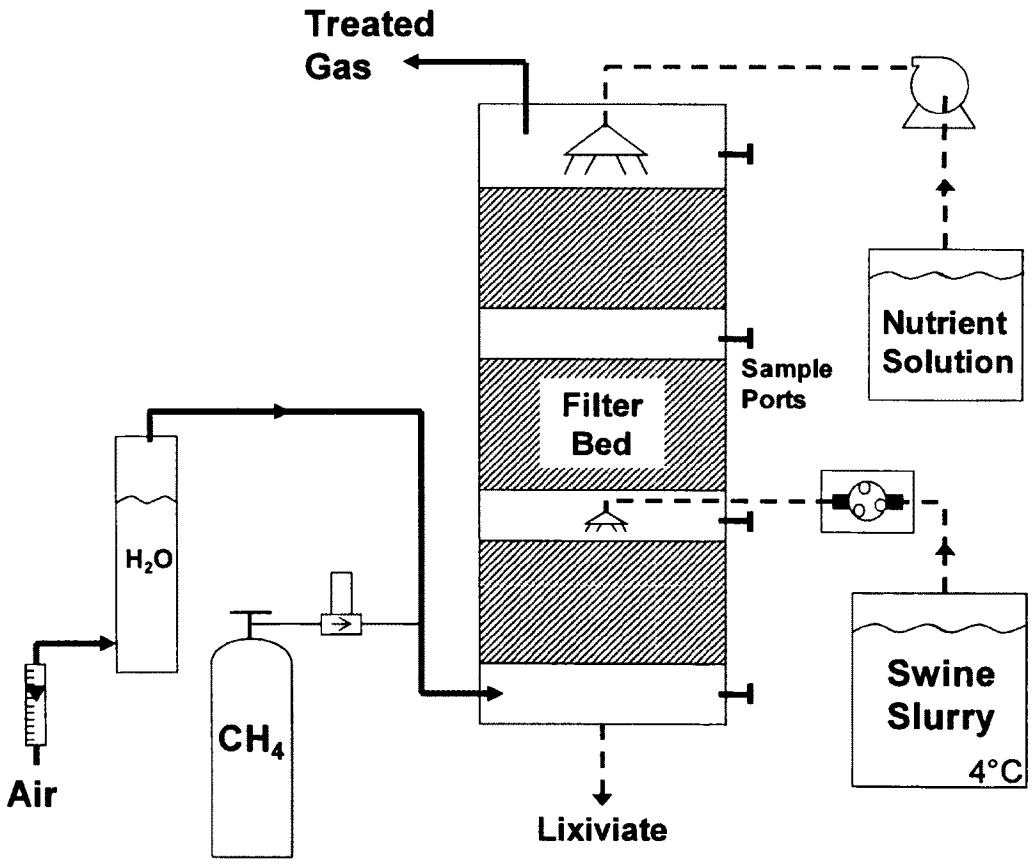

Figure 3-1: Novel biofilter design for the simultaneous treatment of CH_4 and swine slurry.

3.2.2. Analytical Methods

The [CH_4] was measured at the inlet and outlet of the biofilters as well as at the 2 intermediate sampling points with an inline FIA-510 total hydrocarbon analyzer (Horiba, USA). The FIA-510 used a flame-ionization detector with a detection limit for CH_4 of 3.3×10^{-4} $g\cdot m^{-3}$. The analyzer was calibrated prior to each set of samples and a gas sampling pump was used to extract the samples directly from the biofilters. Liquid samples of the lixiviate were collected over 24h in containers kept cool by ice whereas samples of the nutrient solution and swine slurry were collected directly from the storage containers. The organic carbon was measured with a TOC-VE total organic carbon analyzer (Shimadzu, Japan). Liquid samples of the swine slurry and the lixiviate were analyzed for NH_4^+ with an ICS 1000 ion chromatograph (Dionex, USA) using an IonPac CS12A-4mm column and a conductivity detector. The eluent used was a solution of H_2SO_4 at a concentration of 22mN and a flow rate of 1 $ml\cdot min^{-1}$. Detection limits were 0.05 $mgC\cdot L^{-1}$ for the TOC analyzer and 0.1 $mgN\text{-}NH_4^+\cdot L^{-1}$ for the ion chromatograph.

3.2.3. Nutrient Solution

To ensure proper filter bed moisture and to provide the necessary nutrients for the growth of methanotrophs, a synthetic nutrient solution was supplied at the top of the biofilters at a flow rate between 1.6 and 1.9 $L\cdot day^{-1}$. The composition of the nutrient solution is provided in detail in Girard et al. (2011), but the [NO_3^-] was maintained at 0.5 $gN\cdot L^{-1}$.

3.2.4. Swine Slurry

The swine slurry used in this study was provided by Viaporc Inc. in Saint-Isidore (Qc.), Canada. The raw swine slurry was pre-treated at the farm to reduce its solids content. The first step of the pre-treatment was carried out directly in the pig houses and consisted of a system of conveyors with perforated belts, underneath the concrete slatted floor, which separated the urine and the feces. The resulting liquid was collected in a holding tank before being pumped to a settling tank. The supernatant liquid from the settling tank was then

shipped to the laboratory and stored at 4°C before being supplied to the biofilters. The performance of the pre-treatment system is described in detail in Aubry (2008). Halfway through this study, the holding tank was by-passed and the liquid from the pig houses was pumped directly to the settling tank. Due to the natural variations in the composition of the slurry and to the modification of the pre-treatment, the concentrations of organic carbon and NH_4^+ varied from 2700 to 7100 $mgC \cdot L^{-1}$ and from 1800 to 4150 $mgN\text{-}NH_4^+ \cdot L^{-1}$ respectively.

3.2.5. Inoculation

For CH_4 removal, each biofilter was inoculated with lixiviate from biofilters that treated CH_4 for over 6 months (Girard et al., 2011). No inoculation was used for the treatment of swine slurry. Four specific fungal strains were chosen for their potential ability to degrade VFAs since these compounds represent up to 18% of the organic carbon as COD (Chemical Oxygen Demand) in swine slurry (Aubry, 2008): *Candida ingens* (ATCC 60122), *Sporotrichum pruinosum* (UAMH 4521), *Coprinus* sp. (UAMH 10067) and *Cunninghamella elegans* (UAMH 7369). Each fungal strain was first cultivated in 200ml of Wickerham's broth (*Candida ingens*) (Henry et al., 1976) or potato dextrose broth (Difco, USA) (*Sporotrichum pruinosum*, *Coprinus* sp. and *Cunninghamella elegans*) before being added to the middle section of biofilter B1 by recirculating the broth several times over the filter bed.

3.2.6. Experimental Strategy

For the first part of the study, the swine slurry supply was maintained at 3x100ml per day while the influence of the $[CH_4]$ was tested by randomly varying the $[CH_4]$ between 0.35 and 3.3 $g \cdot m^{-3}$. To test the effect of the swine slurry supply, the $[CH_4]$ was maintained at 2.0 $g \cdot m^{-3}$ while the slurry was supplied at different rates and frequencies for biofilters B1 (3x50ml, 3x100ml and 3x200ml) and B2 (1x300ml, 3x100ml and 6x50ml). Each set of conditions was maintained until a pseudo-steady state was reached (± 6% variation of the CH_4 EC on average). Then, each pseudo-steady state was maintained for an average of 24 days in order to obtain a sufficient quantity of gas and liquid samples (9 gas samples and 7 liquid samples on average). The performance of the biofilters was evaluated with the following

parameters where Q is the flow rate ($m^3 \cdot h^{-1}$), V is the filter bed volume (m^3), C is the inlet or outlet concentration (subscript IN or OUT) for each compound (CH_4, TOC and NH_4^+) ($g \cdot m^{-3}$):

$$\text{Inlet Load } \left(\frac{g}{m^3 h}\right) = \frac{C_{IN} * Q}{V} \quad (3\text{-}1)$$

$$\text{Elimination Capacity } \left(\frac{g}{m^3 h}\right) = \frac{(C_{IN} - C_{OUT}) * Q}{V} \quad (3\text{-}2)$$

$$\text{Removal Efficiency } (\%) = \frac{C_{IN} - C_{OUT}}{C_{IN}} * 100\% \quad (3\text{-}3)$$

3.2.7. Microbiological Analyses

Biofilm sampling from the middle section of biofilter B1 was performed as described by Veillette et al. (2011). DNA from the pure inoculated fungal strains and the biofilm was extracted using a FastDNA® Spin kit for soil (MP Biomedicals, USA). The extracted DNA was stored at -20 °C and quantified using a NanoDrop ND-1000 spectrophotometer (Thermo Fisher Scientific, USA). The DNA extracted from the biofilm samples and the fungal strains was used as a PCR template to amplify the full internal transcribed spacer (ITS) region for fungi, located between the genes encoding the 18S and 28S subunits of ribosomal RNA with primers PN3 and PN34 (Viaud et al., 2000). The amplification products were between 420 and 760 bp in size.

The amplified ITS sequences were ligated into a linear form of the PCR2.1 vector using the TA-cloning procedure (Invitrogen Life technologies, USA) and transferred into *Escherichia coli*. The ITS clones were then sequenced and used to construct a library. The 19 sequences obtained from the biofilm samples of biofilter B1 were compared to those obtained for the four pure strains as well as to the sequences from the GenBank database using the BLAST-N algorithm at default settings, available from the National Center for Biotechnology Information server (Altschul et al., 1990).

Microcosms were used to assess the VFA biodegradation potential of the biofilm from the middle section of biofilters B1 and B2 using ^{14}C-labelled acetic acid. Filter bed samples (20 g wet weight) were placed in 250 ml Erlenmeyer flasks with a side arm containing 0.5 M KOH to trap mineralized $^{14}CO_2$. Sterile microcosms with and without [1,2-^{14}C] acetic acid

were run to correct for [1,2-^{14}C] acetic acid volatilization. The microcosms were continuously shaken (60 rpm) at 25°C and 1 ml of KOH was sampled at 0.5, 1, 1.5, 2 and 4 hours and mixed with 6 ml of Scintiverse II Cocktail (Fisher, USA). Trapped $^{14}CO_2$ was measured by liquid scintillation counting using a Beckman LS 6000 Liquid Scintillation Counter (Beckman instruments, USA).

3.3. Results and Discussion

3.3.1. Biofilter Design

Before the novel biofilter configuration shown in Figure 3-1 was designed, preliminary tests were carried out with a standard biofilter treating CH_4 where swine slurry was used as a nutrient solution and sprayed at the top of the biofilter. It was hoped that nitrifying bacteria would oxidize sufficient NH_4^+ in the swine slurry to provide the NO_3^- necessary for methanotrophs' growth. In this way, no synthetic source of NO_3^- would be required for CH_4 biodegradation and some of the nutrients in the slurry would be removed. However, these preliminary tests were abandoned due to the poor performance of the biofilter with regards to CH_4 removal. Figure 3-2 shows the CH_4 removal efficiency (RE) during the start-up period of the standard biofilter used in the preliminary tests as well as the RE for a biofilter using the novel design. The average inlet [CH_4] was 3.3 ± 0.3 $g \cdot m^{-3}$, but after 80 days of operation, the standard biofilter using swine slurry as a nutrient solution did not show any significant removal of CH_4; the maximal RE was 4%.

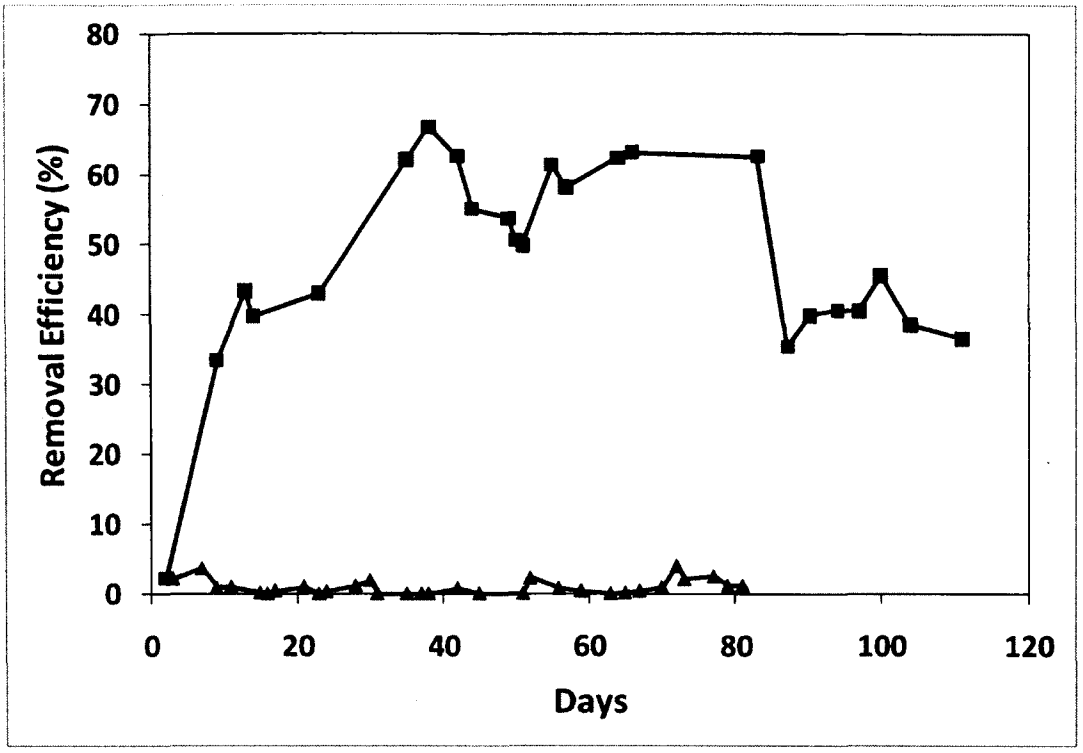

Figure 3-2: Start-up period for a standard biofilter with swine slurry used as the nutrient solution (▲) and a biofilter using the novel design (■).

This lack of CH_4 degradation was probably caused by the nitrogen supply. Methanotrophs require a significant amount of nitrogen, 0.25 moles for every mole of carbon assimilated (Scheutz et al., 2009), and since these microorganisms prefer NO_3^- as a nitrogen source, it is possible that nitrification of the NH_4^+ in the swine slurry was insufficient. However, methanotrophs can also oxidise NH_4^+ directly by a process called methanotrophic nitrification, but this process can be inhibitory to CH_4 biodegradation (Bédard and Knowles, 1989). For example, by adding NH_4^+ at a concentration of 25 $\mu gN \cdot g\ soil^{-1}$, Bronson and Mosier (1994) observed a strong inhibition of CH_4 oxidation, up to 89%. It has also been suggested that the inhibition of CH_4 oxidation by NH_4^+ can be the result of a niche competition with nitrifying bacteria (Mosier et al., 1991; Boeckx et al., 1996).

Concerning the start-up of the novel biofilter design (Figure 3-1), the system was able to reach a RE over 60% before stabilizing at around 40% after 110 days of operation, as shown in Figure 3-2. For the first 80 days of operation, the inlet [CH_4] was quite variable, at values between 1.7 and 3.3 $g \cdot m^{-3}$, which helps explain the variations of the RE. By segregating the treatment of CH_4 and swine slurry, the novel biofilter design provided a

superior performance for CH_4 removal; it was therefore this design that was selected for the remainder of this study.

3.3.2. Influence of the Methane Concentration

Effect of the Methane Inlet Load on the Elimination Capacity

The CH_4 EC for the 2 biofilters used for the simultaneous treatment (B1 and B2) and for the biofiltration of CH_4 alone (B3) is presented in Figure 3-3 as a function of the CH_4 IL. For the simultaneous treatment, the EC increased with the IL and the maximum ECs observed were 16.3 ± 1.1 $g \cdot m^{-3} \cdot h^{-1}$ for B1 and 18.8 ± 1.0 $g \cdot m^{-3} \cdot h^{-1}$ for B2 at ILs of 38.3 ± 1.7 $g \cdot m^{-3} \cdot h^{-1}$ and 46.7 ± 0.9 $g \cdot m^{-3} \cdot h^{-1}$ respectively. Both biofilters used for the simultaneous treatment showed similar ECs for most of the ILs tested; for ILs below 30 $g \cdot m^{-3} \cdot h^{-1}$, the average ECs varied by less than 17%. The main difference between biofilters B1 and B2 was observed for an IL around 45 $g \cdot m^{-3} \cdot h^{-1}$, where the average EC for B1 (13.9 ± 0.9 $g \cdot m^{-3} \cdot h^{-1}$) was 26% lower than the value for B2 (18.8 ± 1.0 $g \cdot m^{-3} \cdot h^{-1}$). No reasonable hypothesis was found to explain this observation.

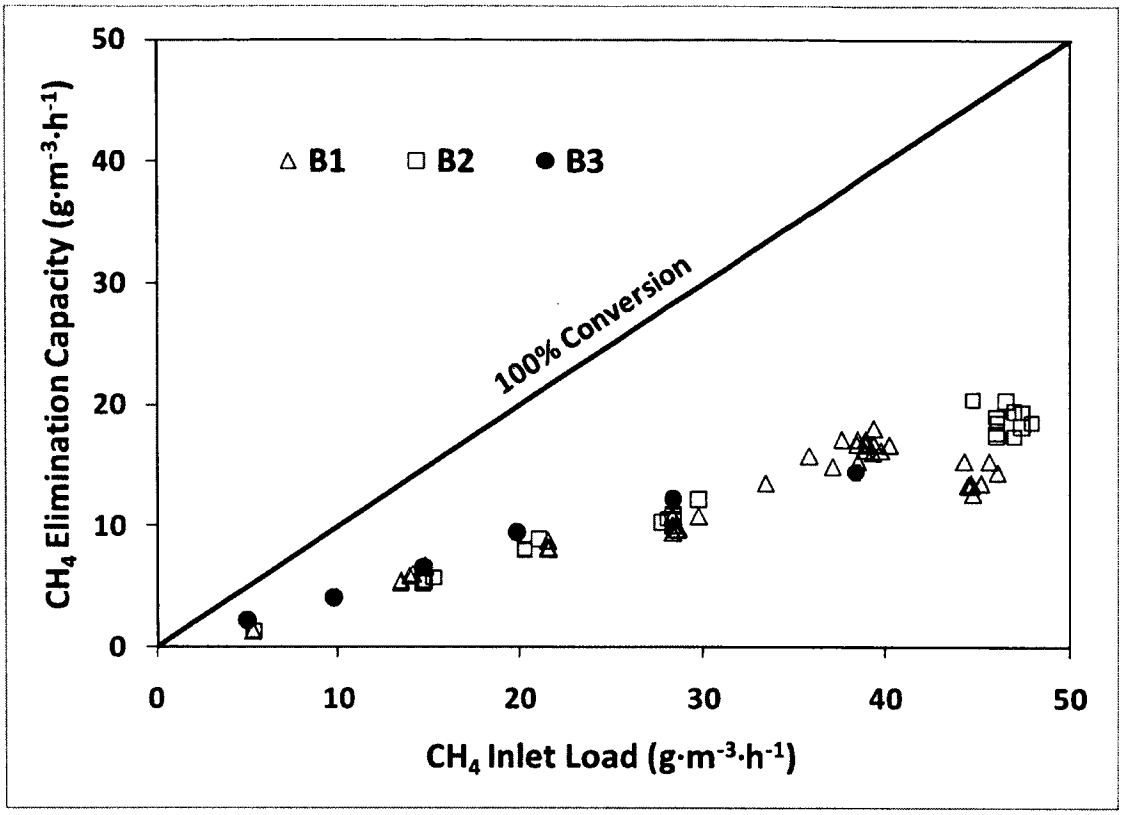

Figure 3-3: CH_4 elimination capacity as a function of the inlet load for the biofiltration of CH_4 alone (B3) and for the biofilters treating simultaneously CH_4 and swine slurry (B1 and B2).

Such similarity between the performance of biofilters B1 and B2 was not expected since it was hypothesized that at least one of the four fungal strains inoculated at the start-up of B1 would prosper and improve CH_4 elimination as previously explained. However, none of the four specific inoculated fungal strains or any other fungal species was detected from the metagenomic libraries. In fact, all 19 ITS clones from biofilter B1 corresponded to *Tubificoides fraseri* (GeneBank accession number: HM460334.1), a nematode present in the middle section of biofilter B1, with 96 to 97% similarity. This was possible since the primers used to construct the metagenomic bank may also have amplified non-fungal ITS (Viaud et al., 2000). Moreover, the microcosm tests on filter bed samples from the middle section demonstrated that both B1 and B2 were able to oxidize VFAs as shown in Figure 3-4. The results from Figure 3-4 show that the mineralization of the ^{14}C-labeled acetic acid varied between 20 and 40% after 4 hours. The four inoculated fungal strains were tested in the microcosms for control purposes and they were also able to oxidize the ^{14}C-labeled acetic

acid. It seems that the operating conditions of the biofilters had more influence over the CH_4 EC than the inoculation and that the inoculated fungal strains were overthrown by microorganisms better suited to the operating conditions.

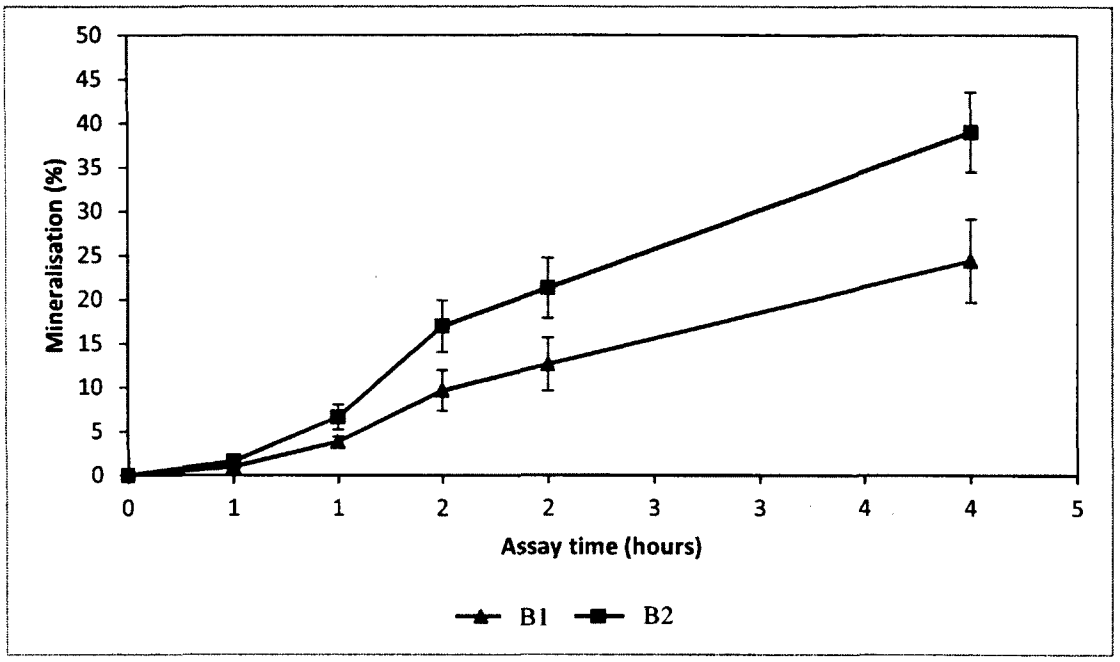

Figure 3-4: Catabolic activity of the microbial community for acetic acid in biofilters B1 and B2.

To appreciate the effect of adding swine slurry in the bottom section on the removal of CH_4, biofilters B1 and B2 were compared to biofilter B3 which was only supplied with CH_4 but had the same packing material and operating conditions. The average values of EC are presented in Figure 3-3. A maximum EC of 14.5 ± 0.6 $g \cdot m^{-3} \cdot h^{-1}$ was obtained for biofilter B3 at an IL of 38.4 ± 1.0 $g \cdot m^{-3} \cdot h^{-1}$, which is lower than the EC obtained with the B1, 16.3 ± 1.1 $g \cdot m^{-3} \cdot h^{-1}$ at an IL of 38.3 ± 1.7 $g \cdot m^{-3} \cdot h^{-1}$. For ILs lower than 30 $g \cdot m^{-3} \cdot h^{-1}$, biofilter B3 outperformed biofilters B1 and B2 which produced ECs an average of 20% lower. These differences in performance mainly originated from the bottom section where swine slurry was supplied during the simultaneous treatment. In fact, for the common ILs tested, from 5 to 38 $g \cdot m^{-3} \cdot h^{-1}$, the bottom section of the biofilter B3 consistently obtained higher CH_4 ECs than the bottom section of biofilters B1 and B2, by margins of up to 220% (data not shown). However, except for the lowest IL (5.3 $g \cdot m^{-3} \cdot h^{-1}$), the bottom section of biofilters B1 and B2 did

removed a certain amount of CH_4 and contributed up to 27% of the total EC. The supply of swine slurry therefore blocked only partially the biodegradation of CH_4 in the bottom section.

The CH_4 ECs obtained by the novel biofilter design are similar to other studies on the biofiltration of CH_4 from the piggery industry. Melse and van der Werf (2005) obtained a maximum EC of 8 $g \cdot m^{-3} \cdot h^{-1}$ for an IL of 15 $g \cdot m^{-3} \cdot h^{-1}$ with a biofilter packed with compost and perlite. At similar ILs, the biofilters used in this study obtained ECs between 5 and 7 $g \cdot m^{-3} \cdot h^{-1}$, but the EBRT was 5 times lower than the one used by Melse and van der Werf (4.2 minutes compared to 21 minutes). Higher ECs, up to 20 $g \cdot m^{-3} \cdot h^{-1}$, were achieved by the Canadian Pork Council (CCP) in 2006 for ILs up to 30 $g \cdot m^{-3} \cdot h^{-1}$ with different organic materials (mixtures of compost, peat moss, black earth and wood chips) (CCP, 2006). A similar EC was obtained in this study (18.8 ± 1.0 $g \cdot m^{-3} \cdot h^{-1}$) with an IL of 46.7 ± 0.9 $g \cdot m^{-3} \cdot h^{-1}$, but the EBRT used by the CCP (10 minutes) was twice as high as the value used in this study. Therefore, not only do the biofilters used here offer CH_4 ECs similar to other studies treating CH_4 from the piggery industry, but they do so at significantly lower EBRTs even though swine slurry was added to the bottom section of the biofilter. This could be explained by the type of packing material since inorganic materials have been shown to perform twice as better than organic materials in CH_4 biofiltration (Nikiema et al., 2005).

Effect of the Methane Concentration on Swine Slurry Treatment

The ECs for TOC and NH_4^+ in the swine slurry are given in Figure 3-5 as a function of the inlet $[CH_4]$ for biofilters B1 and B2. The swine slurry IL was quite variable over this period, ranging from 8.2 to 14.9 $gC \cdot m^{-3} \cdot h^{-1}$ for TOC and from 4.6 to 9.0 $gN \cdot m^{-3} \cdot h^{-1}$ for NH_4^+. Taking into account the results from biofilters B1 and B2, the average ECs were 7.8 ± 1.7 $gC \cdot m^{-3} \cdot h^{-1}$ for TOC and 5.0 ± 1.1 $gN \cdot m^{-3} \cdot h^{-1}$ for NH_4^+. Both the ECs for TOC and NH_4^+ were relatively stable during 16 months and no clear correlation was found with the $[CH_4]$. Biofilter B2 obtained ECs for TOC and NH_4^+ slightly higher than B1, but no significant difference was found between the average values at an α of 95%. In terms of RE, the average values for B1 and B2 were 67 ± 10 % for TOC and 70 ± 7 % for NH_4^+.

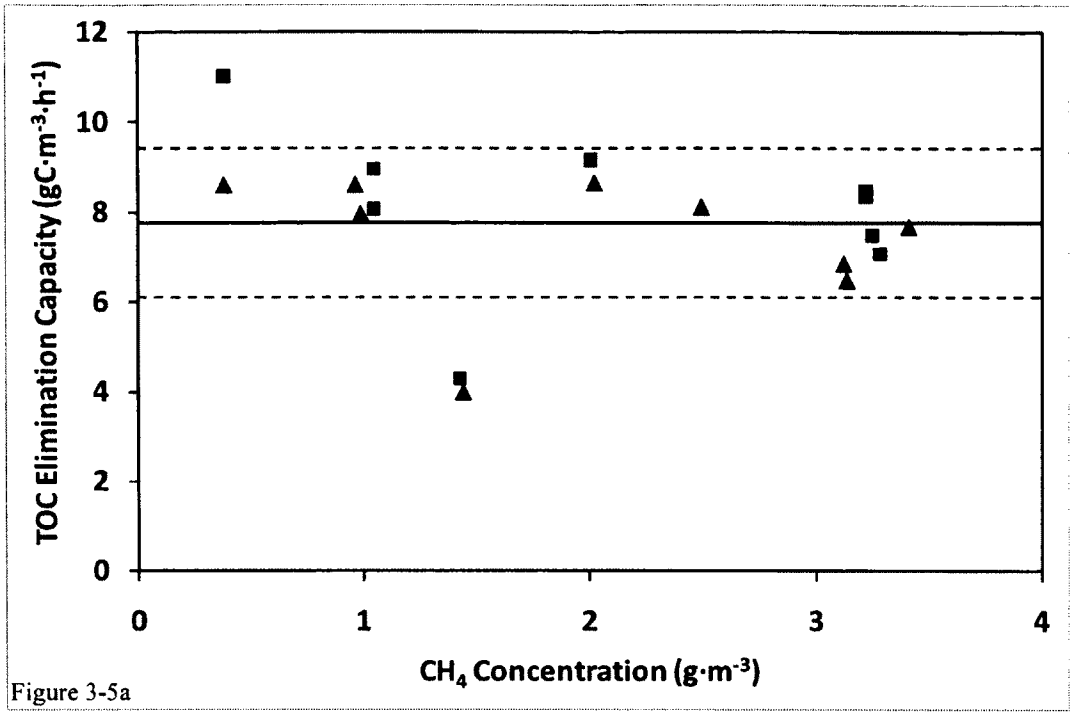

Figure 3-5a

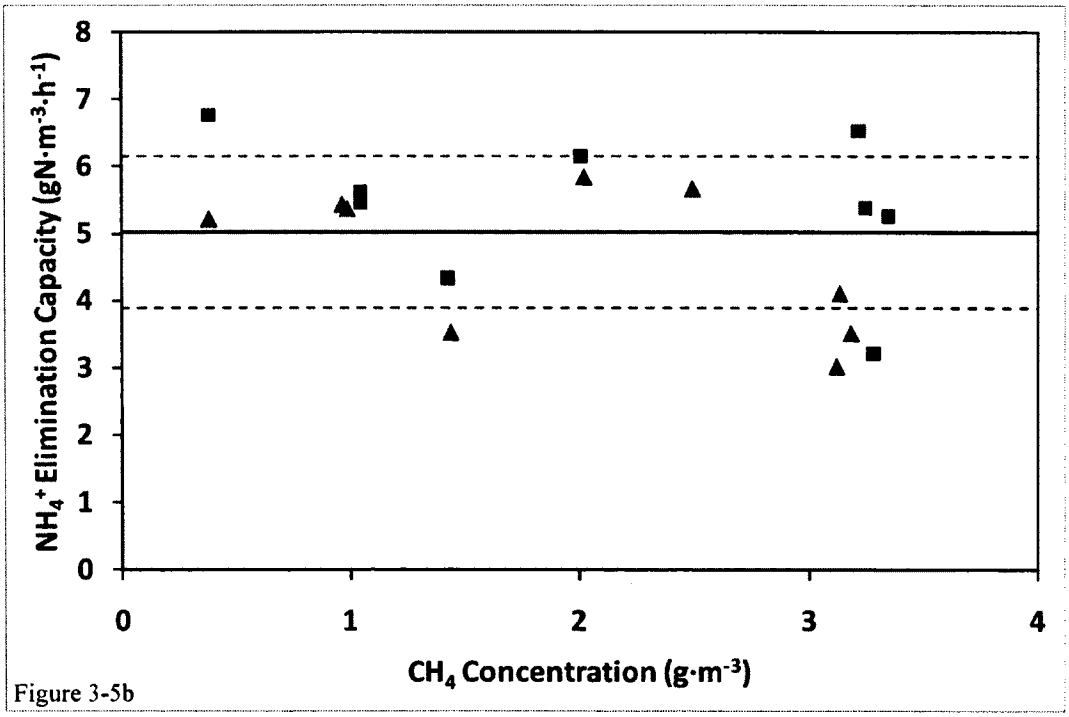

Figure 3-5b

Figure 3-5: Elimination capacity for TOC (a) and NH_4^+ (b) in swine slurry as a function of the CH_4 concentration. B1 (▲), B2 (■), average (—), standard deviation (– –).

Other studies on the biofiltration of swine slurry report REs from 59 to 99% for organic carbon as COD and NH_4^+ (Sommer et al., 2005; Westerman et al., 2000; Garzón-

Zúñiga et al., 2005; Aubry, 2008). The best results, REs of 98% for COD and 99% for NH_4^+, were obtained using a biofilter packed with wood chips and peat at a slurry IL of 0.79 $gN \cdot m^{-3} \cdot h^{-1}$ for NH_4^+ (Aubry 2008). The low IL used by Aubry (2008) provided high hydraulic residence times which increased the contact between the slurry and the microorganisms and produced very high REs. In terms of EC for NH_4^+, the values obtained by Westerman et al. (2000), up to 19 $gN \cdot m^{-3} \cdot h^{-1}$, are almost 4 times greater than those obtained in the present study (5.0 $gN \cdot m^{-3} \cdot h^{-1}$ from Figure 3-5b). However, these authors used two upflow biofilters in series packed with a plastic media with a secondary clarifier. The system was also back-washed frequently (up to 4 times a day), which is probably why it was able to support a NH_4^+ IL up to 5 times higher than the one used here without clogging (23 $gN\text{-}NH_4^+ \cdot m^{-3} \cdot h^{-1}$ as compared to values between 4.6 and 9.0 $gN\text{-}NH_4^+ \cdot m^{-3} \cdot h^{-1}$ in this study).

3.3.3. Influence of the Swine Slurry Supply

Effect of the Swine Slurry Supply on Methane Removal

To test the effect of the swine slurry supply, the [CH_4] was maintained at 2.0 $g \cdot m^{-3}$ and biofilter B1 was used to test influence of the total amount of slurry supplied while the influence of the supply frequency was tested with biofilter B2. The CH_4 EC is presented in Figure 3-6 as a function of the swine slurry supply for biofilters B1 (a) and B2 (b). With biofilter B1, the frequency was kept at 3 times per day and 3 daily volumes of slurry were tested (150, 300 and 600 ml) by adjusting the quantity of slurry supplied per dose (50, 100 and 200 ml). As shown in Figure 3-6a, the total CH_4 EC for 3x50ml and 3x100 ml were very similar at around 10 $g \cdot m^{-3} \cdot h^{-1}$ and no significant difference was found between the average values at an α of 95%. The total EC for the slurry supply of 3x200ml was up to 33% lower at 6.8 ± 0.1 $g \cdot m^{-3} \cdot h^{-1}$. Looking at the results per section, the top section was not affected by the swine slurry supply and the EC did not change significantly (α = 95%). For the bottom section, the average ECs for 3x100ml and 3x200ml were not statistically different at 1.3 ± 0.4 and 1.1 ± 0.5 $g \cdot m^{-3} \cdot h^{-1}$ respectively, but the EC for 3x50ml was more than double at 3.1 ± 0.6 $g \cdot m^{-3} \cdot h^{-1}$. The direct inhibitory effect of swine slurry on CH_4 removal was therefore reduced by decreasing the amount of slurry supplied. Observations for the middle section are a little confusing since the EC dropped from 4.2 ± 0.9 $g \cdot m^{-3} \cdot h^{-1}$ to 2.7 ± 0.8 $g \cdot m^{-3} \cdot h^{-1}$ when the slurry supply was changed from 3x100ml to 3x50ml and then to 1.6 ± 0.5 $g \cdot m^{-3} \cdot h^{-1}$ at

3x200ml. The changes in swine slurry supply could have modified the composition of the microbial community in the middle section by varying the amount of ammonia (NH_3) and VFAs emitted from the slurry. Changes in the microbial community can cause different reactions to operating conditions (De Visscher et al., 2001), such as reducing CH_4 oxidation.

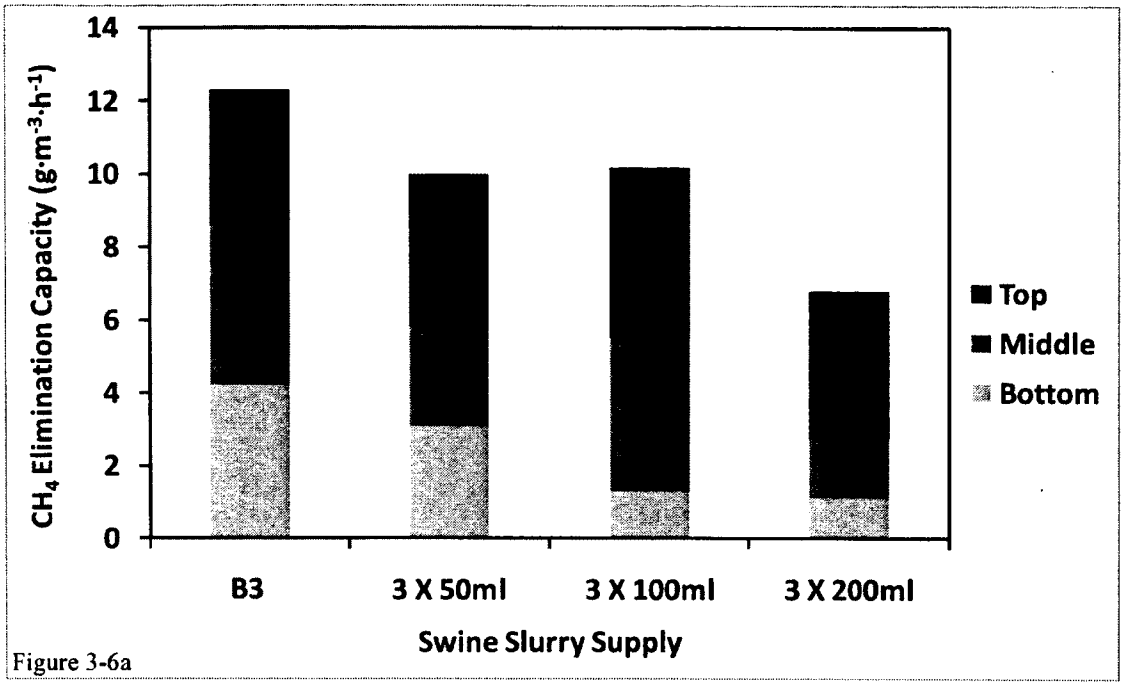

Figure 3-6a

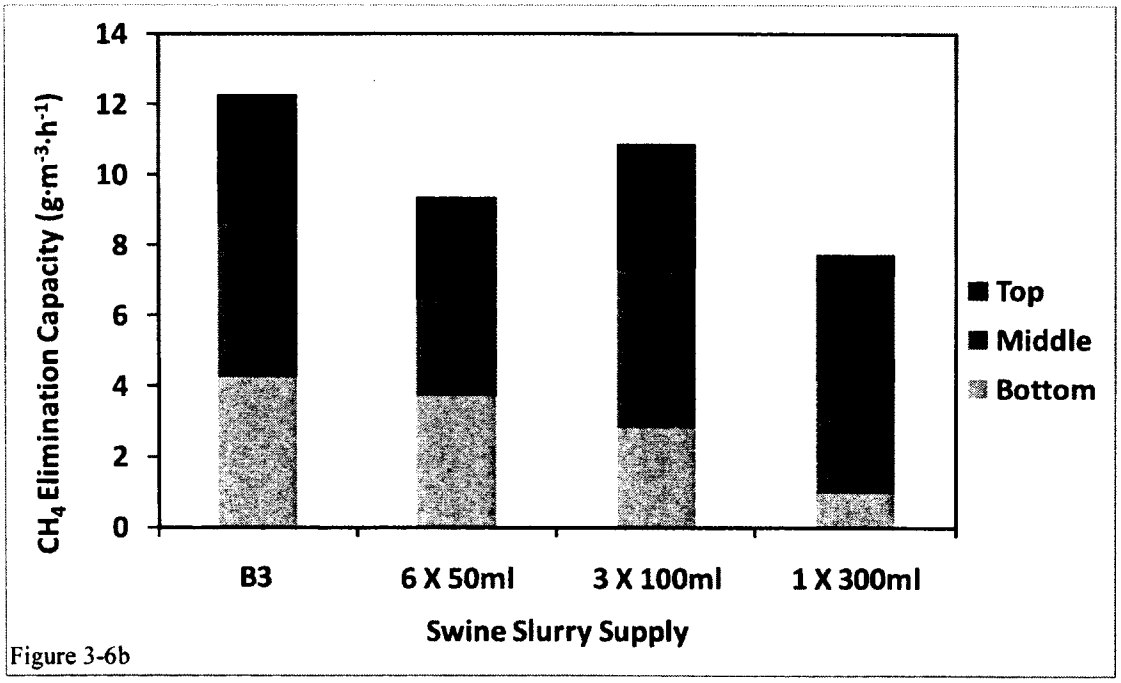

Figure 3-6b

Figure 3-6: Effect of swine slurry supply on the average CH_4 elimination capacity for each biofilter section. (a) Influence of the total quantity of slurry supplied and (b) influence of the supply frequency. Bottom section (light grey), middle section (dark grey), top section (black).

To determine the effect of the swine slurry supply frequency with biofilter B2, the amount of slurry was maintained at 300ml per day and the frequency was changed from 3x100ml per day to 1x300ml and then to 6x50ml. The results in Figure 3-6b show that the total CH_4 EC varied from 10.9 ± 0.5 $g \cdot m^{-3} \cdot h^{-1}$ at 3x100ml to 7.7 ± 0.6 $g \cdot m^{-3} \cdot h^{-1}$ and 9.4 ± 1.5 $g \cdot m^{-3} \cdot h^{-1}$ at 1x300ml and 6x50ml respectively. The supply frequency had little effect on the top section, varying only from 2.9 to 3.6 $g \cdot m^{-3} \cdot h^{-1}$. By decreasing the supply frequency from 3x100ml to 1x300ml, the CH_4 degradation decreased by 64% in the bottom section and by 29% in the middle section. When the slurry supply was adjusted from 1x300ml to 6x50ml, the EC of the bottom section increased to 3.7 ± 0.9 $g \cdot m^{-3} \cdot h^{-1}$ while the EC of the middle section decreased slightly to 2.8 ± 0.6 $g \cdot m^{-3} \cdot h^{-1}$. It seems that B2 was considerably affected when all the slurry was supplied in one dose per day at 1x300ml, but the CH_4 EC improved once the slurry supply was spread over 6 doses per day at 6x50ml. The biggest improvement was observed in the bottom section where the CH_4 EC increased from 1.0 ± 0.6 $g \cdot m^{-3} \cdot h^{-1}$ at 1x300ml to 3.7 ± 0.9 $g \cdot m^{-3} \cdot h^{-1}$ at 6x50ml. Biofilter B2 was therefore able to provide adequate CH_4 removal in the bottom section with the same amount of slurry as long as it was supplied frequently in small doses. However, the middle section did not change significantly ($\alpha = 95\%$) when the slurry supply was adjusted from 1x300ml to 6x50ml, suggesting a lasting inhibitory effect from the slurry supply of 1x300ml. As with biofilter B1, changes in the microbial community could have affected CH_4 removal in the middle section.

As a comparison with the simultaneous treatment, the CH_4 EC obtained by the biofiltration of CH_4 alone with biofilter B3 is also presented in Figure 3-6. The best CH_4 ECs obtained by biofilters B1 (10.2 $g \cdot m^{-3} \cdot h^{-1}$) and B2 (10.9 $g \cdot m^{-3} \cdot h^{-1}$) were still up to 17% lower than for biofilter B3 at 12.3 $g \cdot m^{-3} \cdot h^{-1}$. Of the 3 sections, the bottom section gave the lowest ECs for biofilters B1 and B2 because of the swine slurry supplied. In contrast, the bottom and middle sections provided the highest ECs for the biofiltration of CH_4 alone with biofilter B3. The swine slurry supply regimes of 3x200ml and 1x300ml most affected biofilters B1 and B2 with CH_4 ECs up to 45% lower than for the treatment of CH_4 alone in biofilter B3. By supplying more slurry in each dose, the quantity of NH_4^+ increased which could have enhanced the inhibitory effect on the methanotrophs. Veillette et al. (2011) studied the effect of the $[NH_4^+]$ in the nutrient solution on the biofiltration of CH_4 and found that the CH_4 RE decreased linearly with the $[NH_4^+]$, from 70 to 13% for $[NH_4^+]$ from 0.05 to 0.5 $gN \cdot L^{-1}$.

Boeckx et al. (1996) and Kravchenko (2002) also observed an increased inhibition of CH_4 oxidation rates with increasing $[NH_4^+]$ in landfill cover soils and peat.

Effect of the Swine Slurry Supply on Carbon and Ammonium Removal

The RE for TOC and NH_4^+ is presented in Figure 3-7 as a function of the swine slurry supply for biofilters B1 (a) and B2 (b). The results in Figure 3-7 show that the TOC RE decreased with the quantity of swine slurry supplied, from 78 ± 3% at 3x50ml to 57 ± 6% at 3x200ml. When the supply frequency was increased, the TOC RE also increased from 42 ± 6% at 1x300ml to 82 ± 2% at 6x50ml. By increasing the amount of slurry supplied per dose, the slurry hydraulic residence time in the biofilter was probably decreased, lowering the RE. The effect of the slurry supply on the NH_4^+ RE was similar to that of the TOC and the highest value, 90 ± 3%, was obtained for a slurry supply of 6x50ml. Increasing the total amount of slurry supplied had the greatest impact on the EC and the highest values were obtained for 3x200ml: 15.2 ± 1.6 $gTOC \cdot m^{-3} \cdot h^{-1}$ and 8.4 ± 1.4 $gN\text{-}NH_4^+ \cdot m^{-3} \cdot h^{-1}$. By supplying more slurry to the biofilter, the hydraulic residence time and the REs were lower, but the system was able to reach higher ECs. Further tests would be required to increase the EC without sacrificing the RE.

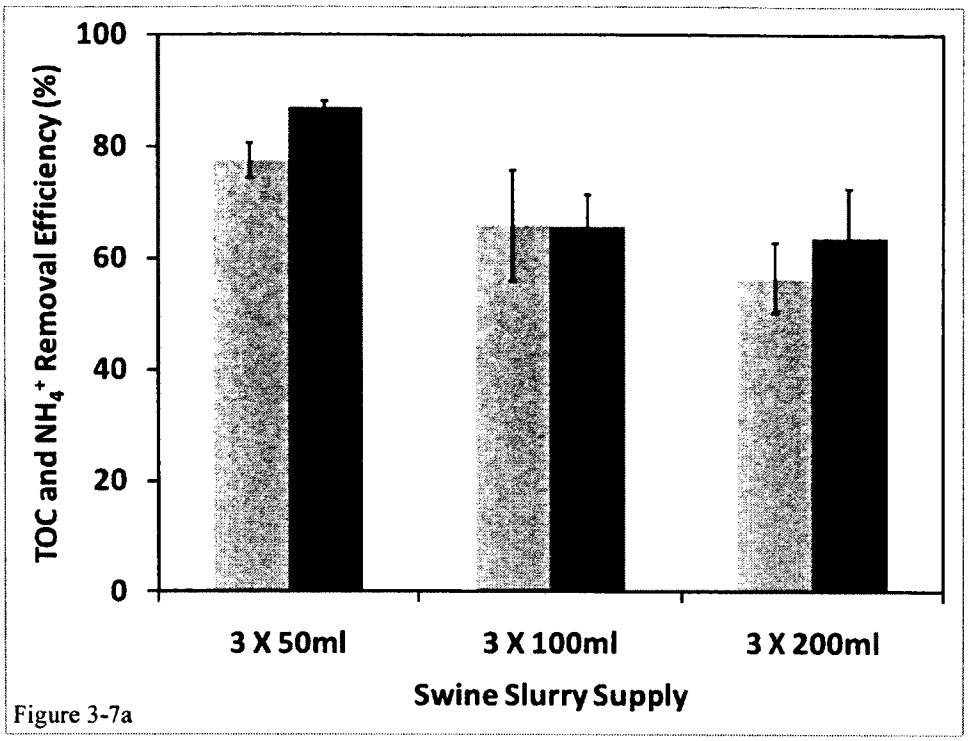

Figure 3-7a

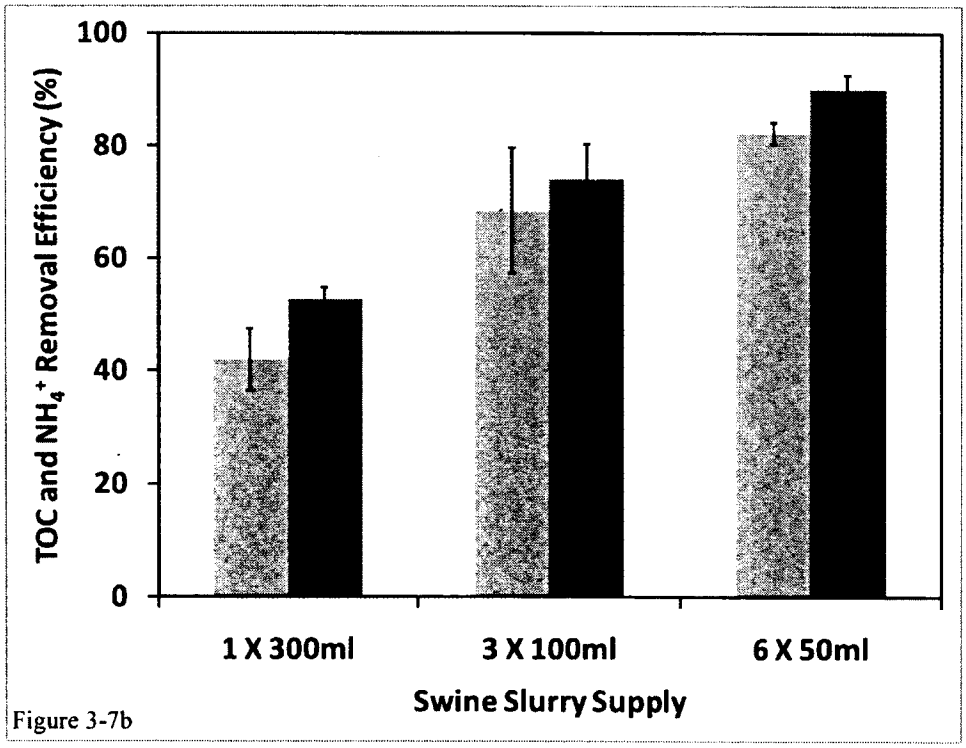

Figure 3-7b

Figure 3-7: Effect of swine slurry supply frequency (a) and volume (b) on the removal efficiency for TOC (light grey) and NH_4^+ (dark grey). Vertical bars: standard deviation.

3.4. Conclusion

This study demonstrated the feasibility of treating CH_4 and swine slurry with the same biofilter using a novel design where the slurry was supplied to the bottom section of the biofilter. The CH_4 EC increased with the IL and a maximum value of 18.8 ± 1.0 $g \cdot m^{-3} \cdot h^{-1}$ was obtained at an IL of 46.7 ± 0.9 $g \cdot m^{-3} \cdot h^{-1}$. Compared to the biofiltration of CH_4 alone, the ECs for the simultaneous treatment were 20% lower on average for ILs below 30 $g \cdot m^{-3} \cdot h^{-1}$. The strains of fungi added to the middle section of biofilter B1 did not improve CH_4 treatment and they were not found at the end of the experiments. However, the middle sections of biofilters B1 and B2 were able to oxidize VFAs. For a slurry supply of 3x100ml per day, the average REs obtained for TOC and for NH_4^+ were 67 ± 10 % and 70 ± 7 % respectively. Due to the inhibitory effect of swine slurry on CH_4 biodegradation, the CH_4 RE decreased when the quantity of slurry supplied in each dose was increased. For TOC and NH_4^+, the REs improved when the amount of slurry supplied per dose was decreased to 50ml, but the highest ECs were obtained with a slurry supply of 3x200ml: 15.2 ± 1.6 $gTOC \cdot m^{-3} \cdot h^{-1}$ and 8.4 ± 1.4 $gN\text{-}NH_4^+ \cdot m^{-3} \cdot h^{-1}$.

Taking into account both CH_4 removal and slurry treatment, the slurry supply that presented the best results was 6x50ml with a CH_4 EC of 9.4 ± 1.5 $g \cdot m^{-3} \cdot h^{-1}$ for an IL of 28.5 ± 0.4 $g \cdot m^{-3} \cdot h^{-1}$ and REs above 80% for TOC and NH_4^+. Even though it was possible to treat both CH_4 and swine slurry with the same biofilter, the results were lower than those obtained for biofilters dedicated to CH_4 only. However, this type of system used could be used as a pre-treatment for the organic carbon and NH_4^+ in swine slurry while providing a significant reduction of the GHGs released by the piggery industry.

Acknowledgements

Michèle Heitz wishes to acknowledge the Natural Sciences and Engineering Research Council of Canada (NSERC) for providing the Strategic Partnership grant that funded this study. Matthieu Girard would like to thank the NSERC and the Fonds Québécois de la Recherche sur la Nature et les Technologies for providing scholarships.

CHAPITRE 4. Essais pilotes

Avant-propos

L'article « *Biofiltration of Methane and Swine Slurry – Field Tests* » a été soumis au journal Agriculture, Ecosystems & Environment le 13 septembre 2011.

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Résumé

Traditionnellement, la biofiltration a été utilisée pour le traitement des odeurs et des composés facilement biodégradables, mais ce système peut également être appliqué au traitement du méthane (CH_4). L'objectif principal de cette recherche était d'étudier la biofiltration du CH_4 provenant de l'air de ventilation d'une bâtisse d'élevage porcin en utilisant un milieu filtrant inorganique. En ajoutant du CH_4 pur, une efficacité d'épuration moyenne de 76 ± 2% a été obtenue pour une charge à l'entrée de 8.8 ± 0.8 $g \cdot m^{-3} \cdot h^{-1}$ après une phase de démarrage de 30 jours. Pour l'air de ventilation de la porcherie, la concentration de CH_4 a varié de 75 à 323 ppmv et le biofiltre a éliminé jusqu'à 83% du CH_4 avec une capacité d'élimination moyenne de 1.0 ± 0.4 $g \cdot m^{-3} \cdot h^{-1}$ pour une charge de 1.6 ± 0.8 $g \cdot m^{-3} \cdot h^{-1}$. Du lisier de porc traité a été testé pour remplacer la solution nutritive synthétique nécessaire à la biofiltration du CH_4. Par contre, dû à la présence de composés inhibiteurs, comme l'ammonium et le nitrite, une efficacité d'épuration moyenne de seulement 12 ± 6% a été obtenue.

Le traitement simultané du CH_4 et du lisier de porc a également été démontré en injectant le lisier à l'étage du bas du biofiltre. Des efficacités d'épuration moyennes d'au moins 50% ont été obtenues pour le CH_4 ainsi que pour le carbone organique en tant que DCO (demande chimique en oxygène) et l'ammonium du lisier. En intégrant les résultats obtenus dans cette étude avec les techniques agricoles modernes, l'industrie porcine pourrait réduire ses émissions de gaz à effet de serre et traiter une partie des nutriments du lisier de porc.

Abstract

Traditionally, biofiltration has been used for the treatment of odours and easily biodegradable compounds, but it can be applied for the treatment of methane (CH_4). The main objective of this paper was to study the biofiltration of CH_4 in ventilation air from a swine house using an inorganic packing material. By supplementing pure CH_4, an average removal efficiency (RE) of 76 ± 2% was obtained for an inlet load of 8.8 ± 0.8 $g \cdot m^{-3} \cdot h^{-1}$ after a start-up period of 30 days. For piggery ventilation air, the inlet CH_4 concentration varied from 75 to 323 ppmv and the biofilter removed up to 83% of the CH_4 with an average elimination capacity of 1.0 ± 0.4 $g \cdot m^{-3} \cdot h^{-1}$ at an inlet load of 1.6 ± 0.8 $g \cdot m^{-3} \cdot h^{-1}$. Treated swine slurry was tested to replace the synthetic nutrient solution necessary for the biofiltration of CH_4. However, due to the presence of inhibitory compounds, such as ammonium and nitrite, an average RE of only 12 ± 6% was obtained.

Furthermore, the simultaneous treatment of CH_4 and swine slurry was achieved by supplying the slurry to the bottom section of the biofilter. Average REs above 50% were obtained for CH_4 as well as for the organic carbon as COD (chemical oxygen demand) and for the ammonium in swine slurry. By integrating the results obtained in this study with modern farming techniques, the piggery industry could reduce its greenhouse gas emissions and treat part of the nutrients in swine slurry.

4.1. Introduction

Biofilters are efficient and versatile biological systems that can be used for the treatment of both liquid and gas waste streams. In a biofilter, the waste fluid passes through a bed packed with a porous humid material where microorganisms capable of degrading the specific contaminants are established (Jorio and Heitz, 1999). For air pollution, biofiltration has traditionally been used for the treatment of odours and easily biodegradable volatile organic or inorganic compounds (Delhoménie and Heitz, 2005). More recently, biofiltration has been applied to slowly biodegradable compounds such as methane (CH_4), a greenhouse gas (GHG) with a global warming potential (GWP) 25 times that of carbon dioxide (CO_2) (Solomon et al., 2007). The biofiltration of CH_4 has been extensively studied for sanitary

landfills (Nikiema et al., 2007), but few studies have been published on the treatment of CH_4 from the piggery industry (Girard et al., 2009).

In 2008, the Canadian piggery industry produced over 31 million hogs, more than double the amount produced in 1984 (CPC, 2011), with CH_4 emissions totalling 1.3 million metric tons of CO_2 equivalent (Jaques, 2010). On a pig farm, CH_4 is generated by the anaerobic digestion of organic matter in swine slurry which occurs in pig houses and slurry storages. Other than CH_4, over 130 compounds have been identified in air from livestock buildings (Hartung and Phillips, 1994). These compounds can be sorted in two main categories: odorous compounds (hydrogen sulphide, ammonia - NH_3 and volatile fatty acids for example) and GHGs (CH_4, nitrous oxide - N_2O and CO_2). Specific concentrations of the different compounds depend on the type of ventilation (natural or mechanical), on the manure management system, on the temperature and, most importantly, on the ventilation flow rate.

According to our knowledge, no studies have been published on the biofiltration of CH_4 from piggery ventilation air, but some authors have studied the biofiltration of CH_4 from slurry storages. Treating CH_4 from a 6 m^3 pilot-scale slurry storage unit, Melse and van der Werf (2005) obtained removal efficiencies (RE) up to 85%. The Canadian Pork Council (CCP, 2006) studied the biofiltration of CH_4 from a 3800 m^3 slurry storage reservoir equipped with a floating cover and obtained REs up to 60%. Both these studies used biofilters packed with organic materials, but research has shown that inorganic materials can remove more than twice as much CH_4 (Nikiema et al., 2005). However, with inorganic materials, nutrients are usually not present on the filter bed and must be supplied by an exterior source. Nitrogen must be provided as nitrate (NO_3^-) since ammonium (NH_4^+) can inhibit CH_4 biodegradation (Bronson and Mosier, 1994). A synthetic solution can easily be used in a laboratory setting, but for full-scale applications, a practical alternative is required. The nitrogen in swine slurry is mainly found as NH_4^+, but by using an aerobic treatment process, the NH_4^+ can be oxidized to NO_3^- and become accessible for the CH_4 degrading bacteria, methanotrophs.

Other than generating CH_4, swine slurry itself can be harmful to the environment. In Canada, swine slurry is generally applied to land as a fertilizer, but excess nutrients can leach into aquatic ecosystems and accelerate eutrophication (Smith et al., 2007). Biofiltration can also be used to treat the nutrients found in swine slurry and solve this problem. Biofilters used for slurry treatment can be as simple as piles of straw or highly engineered systems such as

upflow biofilters (Sommer et al., 2005; Westerman et al., 2000). Since biofilters can be used to treat both CH_4 and swine slurry, an interesting concept would be to supply both waste streams to the same unit. This possibility was discussed by Girard et al. (2009).

The main objective of this study was to treat the CH_4 in piggery ventilation air using a biofilter packed with an inorganic material. Treated swine slurry was tested as a readily available nutrient solution for CH_4 biofiltration. The viability of simultaneously treating CH_4 and swine slurry with the same biofilter was also determined.

4.2. Material and Methods

4.2.1. Biofilter Set-up

This study was carried out on-site at the Viaporc Inc. pig farm in St-Isidore, Canada. The pilot-scale biofilters were made of 29 cm Plexiglas® tubing packed to a height of 1 m and separated in 3 identical sections as shown in Figure 4-1. The filter bed was composed of an inorganic gravel material, but it is not possible to reveal the exact nature of this material due to a confidentiality agreement. Piggery ventilation air was injected at the bottom of the biofilters by an extraction fan drawing air from underneath the slatted floor of a swine house containing an average of 700 weanlings. Due to the low CH_4 concentration ($[CH_4]$) in piggery ventilation air (see section 4.3.1), pure CH_4 was supplemented to the biofilters at a concentration of 1000 ppmv for the start-up period and for testing the effect of certain operational parameters. Biofilter BM was used to study the biofiltration of CH_4 alone, while biofilter BST was used to test the simultaneous treatment of CH_4 and swine slurry. The air flow rate was controlled manually with 2 inch ball valves and varied between 1.0 ± 0.2 and 2.1 ± 0.1 $m^3 \cdot h^{-1}$. The corresponding empty bed residence times (EBRT) were 4.0 and 1.9 minutes respectively. The flow rate of pure CH_4 was controlled with a volumetric flow meter (Brooks, USA). The air temperature was not controlled and varied seasonally between 5 and 26°C. Masterflex peristaltic pumps (Cole-Palmer, USA) were used to supply both the nutrient solution and the swine slurry.

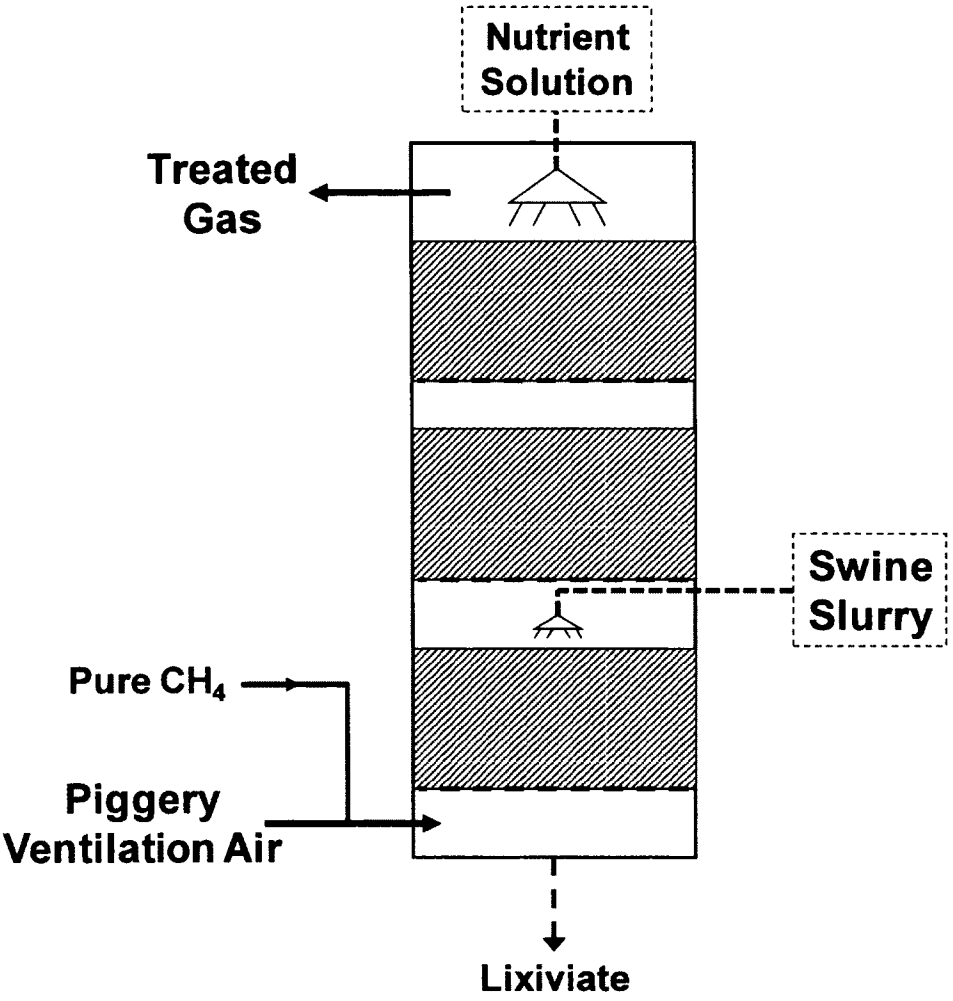

Figure 4-1: Pilot-scale biofiltration system.

4.2.2. Analytical Methods

The concentrations of CH_4, CO_2, N_2O and NH_3 were analysed at the inlet and outlet of the biofilters using a Fourier transformed infrared (FTIR) analyser (Gasmet Technologies Inc., Canada). Gas samples were collected in Tedlar® bags over a 10 minute period (more than twice the highest EBRT), brought back to the lab and analysed within 6 hours. Samples of lixiviate were collected over a period of 24 hours while samples of the nutrient solution, swine slurry and treated slurry were collected from the storage containers. Liquid samples were analysed for organic carbon as COD (Chemical Oxygen Demand) and inorganic nitrogen: NH_4^+, NO_2^- (nitrite) and NO_3^-. Analysis of the COD was carried out with the Hach test system

(Hach Company, USA): digestion vials were placed in a COD reactor for 2 hours at 150°C before being measured with a Hach spectrophotometer. Samples were analyzed for NH_4^+ using a Kjeltec 2400/2460 auto sampler system (Foss, USA). A DX-320 ionic chromatograph (Dionex, USA) using an AS14A column and a conductivity detector was used to measure the concentrations of NO_2^- and NO_3^-.

4.2.3. Nutrient Solution and Swine Slurry

The synthetic nutrient solution used in this study provided the necessary nutrients for the growth of methanotrophs and is described in detail in Girard et al. (2011). The solution had a NO_3^- concentration ($[NO_3^-]$) of 0.5 $gN \cdot L^{-1}$ and was supplied at the top of the biofilters at an average flow rate of 6.1 L per day. The treated swine slurry tested as a replacement for the synthetic nutrient solution came from a biofilter packed with peat and wood chips treating up to 5 m^3 of slurry per day at Viaporc Inc. This biofilter removed on average 99.5% of the carbon (as 5-day biological oxygen demand) and 98% of the NH_4^+ in the slurry. Most of the NH_4^+ was oxidised to NO_3^- and the treated slurry had an average $[NO_3^-]$ of 0.63 ± 0.09 $gN \cdot L^{-1}$, making it a potential nutrient solution for CH_4 biofiltration. However, the treated slurry still contained a certain amount of NH_4^+: 0.076 ± 0.025 $gN \cdot L^{-1}$. The treated slurry was extracted directly from the outlet of Viaporc's biofilter and supplied to biofilters BM and BST at flow rates between 3 and 6.2 $L \cdot day^{-1}$.

The swine slurry supplied to biofilter BST was pre-treated to remove excess solids. The pre-treatment system consisted of a conveyor with a perforated belt to separate the urine and the feces directly in the swine house followed by a settling tank. Pre-treated swine slurry was only supplied at the surface of the bottom section of biofilter BST to avoid the possible inhibition of CH_4 biodegradation by swine slurry (Girard et al., 2009). The slurry flow rate was maintained at 1.13 ± 0.03 $L \cdot day^{-1}$ (supplied in 24 doses) with average concentrations of 18.7 ± 3 $gO_2 \cdot L^{-1}$ and 3.0 ± 0.4 $gN \cdot L^{-1}$ for organic carbon as COD and NH_4^+ respectively.

4.2.4. Experimental Strategy

This study was carried out in two separate phases, from July to December, in 2009 and 2010. At the beginning of each phase, the biofilters were inoculated with lixiviate from

biofilters treating CH_4 (Girard et al., 2011) and supplied with the synthetic nutrient solution. The inlet load (IL), elimination capacity (EC) and RE were used to evaluate the performance of the biofilters and are defined as follows where C is the inlet or outlet concentration (subscript IN or OUT) for each pollutant (CH_4, organic carbon as COD and NH_4^+) ($g \cdot m^{-3}$), Q is the gas or liquid flow rate ($m^3 \cdot h^{-1}$) and V is the filter bed volume (m^3):

$$IL\left(\frac{g}{m^3 h}\right) = \frac{C_{IN} \times Q}{V} \quad (4\text{-}1)$$

$$EC\left(\frac{g}{m^3 h}\right) = \frac{(C_{IN} - C_{OUT}) \times Q}{V} \quad (4\text{-}2)$$

$$RE\ (\%) = \frac{C_{IN} - C_{OUT}}{C_{IN}} \times 100\% \quad (4\text{-}3)$$

4.3. Results and Discussion

4.3.1. Composition of the Piggery Ventilation Air

Swine houses must be properly ventilated to maintain adequate temperature, humidity and air quality. Minimal ventilation requirements vary from 12 to 144 $L \cdot s^{-1}$ per pig in summer and from 0.4 to 7 $L \cdot s^{-1}$ per pig in winter and depend essentially on the outside temperature and on the type and size of pig (sow, weanling or grower/finisher) (Prairie Swine Center Inc., 2000). The daily concentrations of CH_4 and CO_2 found in the piggery air at Viaporc Inc. from July to December in 2009 and 2010 are shown in Figure 4-2.

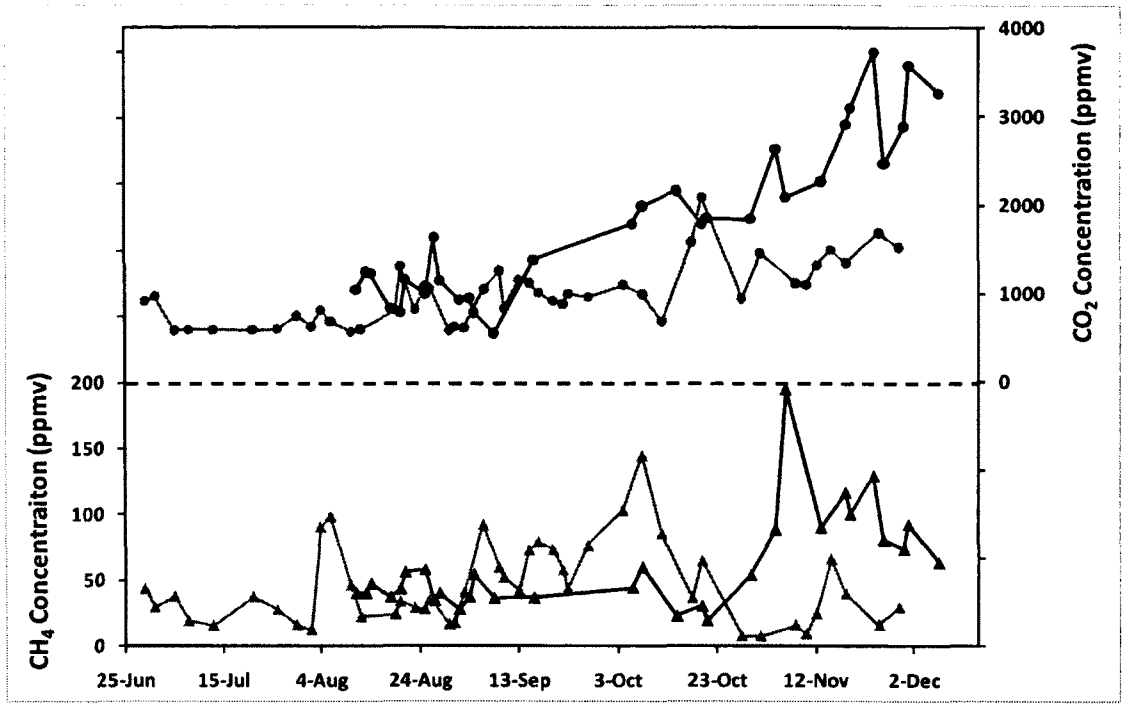

Figure 4-2: CH_4 and CO_2 Concentrations in the Ventilation Air from a Pig House from July to December. CH_4 Concentration (▲), CO_2 Concentration (•), Values for 2009 (Black), Values for 2010 (grey).

The results in Figure 4-2 show that the [CH_4] varied from 7 to 195 ppmv over the entire period of the study. During the summer months (from June to September), the [CH_4] was more stable at average concentrations of 42 ± 9 ppmv and 44 ± 25 ppmv for 2009 and 2010. No statistical difference was found between the average values at a confidence level (α) of 95%. For both years, an increase in the [CH_4] was observed when the ventilation strategy was changed because of the lower outside temperatures. In 2009, the [CH_4] increased to 195 ppmv and occurred at the beginning of November, while in 2010, the [CH_4] only increased to 145 ppmv and occurred a month earlier, in October. After this increase, the [CH_4] decreased to values lower than 100 ppmv. These observations could have been due to a combination of the ventilation flow rate and the temperature of the slurry stored in the swine house. The warmer summer temperatures provide CH_4 emission rates higher than in winter, but the increased ventilation in summer maintains low concentrations (Ni et al., 2008). The CH_4 emission rate decreases in winter but with a lower ventilation flow rate, the [CH_4] is actually higher. The range of [CH_4]s found in this study is very similar to that reported by Melse and

Van der Werf (2005) (7 to 150 ppmv at 25°C); only one value exceeded the 150 ppmv upper limit. However, other studies observed lower average [CH_4]s with little variability: 11 ppmv, 13 ppmv and 27 ppmv (Ni et al., 2008; Blanes-Vidal et al., 2008).

Concerning CO_2, the results in Figure 4-2 show that the CO_2 concentrations ([CO_2]) were relatively stable until the beginning of October at average values of 1050 ± 280 ppmv and 850 ± 220 ppmv for 2009 and 2010 respectively. Thereafter, the [CO_2] increased gradually to reach values as high as 3720 ppmv in 2009 and 2090 ppmv in 2010. This increase was caused by the propane space heaters used to heat the pig houses which make it difficult to correlate the production of CH_4 and CO_2. Ni et al. (2008) observed similar [CO_2]s from 670 to 6900 ppmv with the highest concentrations found in cold weather when space heaters were used.

For each sample of piggery air, the concentrations of NH_3 and N_2O were also measured. The NH_3 concentration ([NH_3]) varied from 1.4 to 11.3 ppmv with average values of 5.6 ± 2.2 ppmv and 4.3 ± 1.7 ppmv for 2009 and 2010 respectively (data not shown). Hayes et al. (2006) looked at [NH_3]s from different swine houses in Ireland and found values of 4.7 to 10.8 ppmv for first and second stage weaners, but the highest [NH_3], 15.2 ppmv, was obtained for a finishing barn. In Korea, Kim et al. (2007) found an average [NH_3] of 7.5 ppmv with variations from 0.8 to 21.4 ppmv depending on the type of ventilation and manure handling. The values reported by these studies are very similar to the results obtained at Viaporc Inc. and are all below the recommended value of 25 ppmv NH_3 according to Agriculture and Agri-Food Canada (AGR, 1993).

In the piggery industry, most of the N_2O is produced once the slurry has been applied to agricultural land as a fertilizer, but some N_2O can be found in air from swine houses. Concentrations of N_2O between 0.08 and 0.93 ppmv were measured at Viaporc Inc. with average values of 0.42 ± 0.17 ppmv and 0.38 ± 0.15 ppmv for 2009 and 2010 respectively (data not shown). These values seem quite low, but due to N_2O's GWP of 298, its contribution to GHG emissions from the piggery air were 7.3 ± 4.0 % on average and as high as 21%.

4.3.2. Biofiltration of Methane

Synthetic Nutrient Solution

The first part of this study focused on the biofiltration of CH_4 with biofilter BM. In 2009, the biofilter was supplied with the synthetic nutrient solution and pure CH_4 was supplemented to the piggery ventilation air for the first 143 days. During this time, the [CH_4] was maintained at 1040 ± 120 ppmv. The CH_4 IL and RE are given in Figure 4-3 over time. The stabilisation of the CH_4 RE took about 30 days once the biofilter was installed at the farm. Other studies on the biofiltration of CH_4 report start-up durations of 25 days with activated sludge as an inoculant and 3 months with no inoculation (Melse and van der Werf, 2005; CCP, 2006). As shown in Figure 4-3, the RE remained stable for over 40 days after the start-up period at an average value of 76 ± 2%, which was equivalent to an EC of 6.7 ± 0.6 $g \cdot m^{-3} \cdot h^{-1}$.

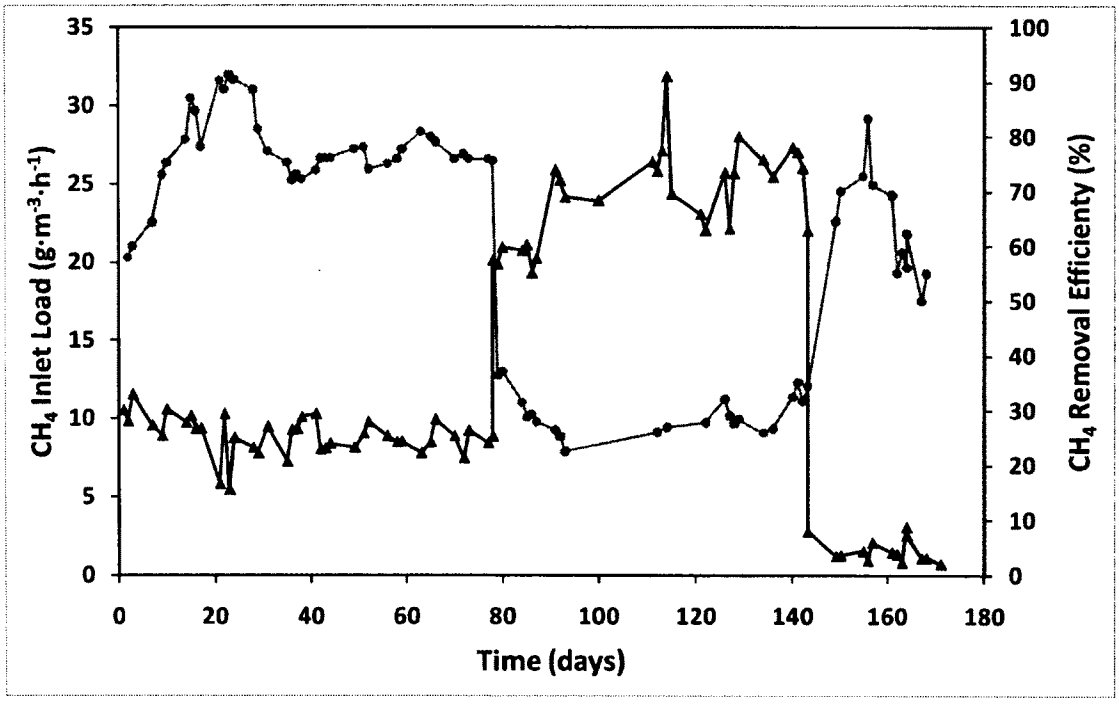

Figure 4-3: CH_4 Inlet Load and Removal Efficiency over Time for the Biofiltration of CH_4. CH_4 Inlet Load (Black ▲), CH_4 Removal Efficiency (Grey •).

The air flow was maintained at 0.92 ± 0.15 $m^3 \cdot h^{-1}$ with a CH_4 IL of 8.9 ± 1.2 $g \cdot m^{-3} \cdot h^{-1}$ for the first 77 days. On day 78, the air flow was increased to 2.1 ± 0.1 $m^3 \cdot h^{-1}$ while the [CH_4] was maintained at around 1000 ppmv, which increased the CH_4 IL to 24 ± 3 $g \cdot m^{-3} \cdot h^{-1}$. Due to

the decrease of the EBRT from 4.3 to 1.9 minutes, the CH_4 RE dropped quickly to 36% and then stabilized at 30 ± 4% with an average EC of 7.1 ± 1.1 $g \cdot m^{-3} \cdot h^{-1}$. On day 143, the air flow was returned to 1 $m^3 \cdot h^{-1}$ and the supplement of pure CH_4 was removed which caused the $[CH_4]$ to drop between 75 and 323 ppmv. The RE increased to between 50 and 83% with an average EC of 1.0 ± 0.4 $g \cdot m^{-3} \cdot h^{-1}$ for an IL of 1.6 ± 0.8 $g \cdot m^{-3} \cdot h^{-1}$.

Treating CH_4 from swine slurry storages, the Canadian Pork Council (CPC, 2006) obtained average ECs up to 20 $g \cdot m^{-3} \cdot h^{-1}$ for an IL of 30 $g \cdot m^{-3} \cdot h^{-1}$ at $[CH_4]$s between 5000 and 20000 ppmv and an EBRT of 10 minutes. Melse and van der Werf (2005) obtained a maximum EC of 8 $g \cdot m^{-3} \cdot h^{-1}$ for an IL of 15 $g \cdot m^{-3} \cdot h^{-1}$ at a $[CH_4]$ of 5.5 $g \cdot m^{-3}$ (8500 ppmv) and an EBRT of 21 minutes. The maximum EC obtained in this study, 7.1 $g \cdot m^{-3} \cdot h^{-1}$, is lower than the studies treating CH_4 from swine slurry storages, but was obtained for an average $[CH_4]$ of 1100 ppmv and an EBRT of 1.9 minutes. The higher $[CH_4]$s and EBRTs probably improved the diffusion of CH_4 from the gas phase to the biofilm (Delhoménie and Heitz, 2005), providing higher CH_4 ECs for the studies treating CH_4 from swine slurry storages. Several authors have shown that CH_4 degradation in biofilters follows first-order kinetics with values for the first-order constant, k, ranging from 0.98 to 7.5 h^{-1} (Sly et al., 1993; Streese and Stegman, 2003; Melse and van der Werf, 2005; Girard et al., 2011). By assuming first-order kinetics and plug-flow conditions, the following relationships can be obtained where $V_{Filter\ Bed}$ is the volume of the filter bed in m^3 and Q_{Air} is the air flow rate in $m^3 \cdot h^{-1}$:

$$k\frac{V_{Filter\ Bed}}{Q_{Air}} = \ln\left(\frac{[CH_4]_{IN}}{[CH_4]_{OUT}}\right) \tag{4-4}$$

$$EC = k * \frac{[CH_4]_{IN} - [CH_4]_{OUT}}{\ln\left(\frac{[CH_4]_{IN}}{[CH_4]_{OUT}}\right)} = k * [CH_4]_{m,log} \tag{4-5}$$

When the CH_4 EC was plotted against $[CH_4]_{m,log}$, a value of 13.4 h^{-1} was obtained for the first-order constant (data not shown) (with a determination coefficient (R^2) of 0.55) which is almost twice as high as some of the other values of k obtained for the biofiltration of CH_4. This demonstrates the potential of the system used in this study for the treatment of CH_4 even though ILs no higher than 24 ± 3 $g \cdot m^{-3} \cdot h^{-1}$ were tested.

Nitrogen mass balances were performed on biofilter BM by measuring the NH_3 and N_2O in the gas and the NO_3^- in the liquid. The results are presented in Table 4-1. Looking at the nitrogen in the gas, the biofilter was able to remove between 11 and 53% of the NH_3, while N_2O production was insignificant, representing only 6% of the inlet N_2O on average. When pure CH_4 was supplemented to the system (days 0-143), the nitrogen accumulated within the biofilter varied from 0.15 to 0.46 $gN \cdot day^{-1}$, which represented between 4 and 14% of the nitrogen entering the biofilter. The highest values of accumulated nitrogen were observed with the air flow rate of 2 $m^3 \cdot h^{-1}$, where the greatest CH_4 EC was measured (7.1 $g \cdot m^{-3} \cdot h^{-1}$). When the air flow was returned to 1 $m^3 \cdot h^{-1}$ with no addition of pure CH_4 on day 143, the accumulated nitrogen dropped to 0.08 and -0.31 $gN \cdot day^{-1}$. The lower CH_4 uptake at an EC of 1.0 $g \cdot m^{-3} \cdot h^{-1}$ probably reduced the nitrogen requirements, while the negative value observed on day 167 could have been caused by a washing out of excess nitrogen previously adsorbed on the filter bed. In a laboratory setting, Girard et al. (2011) studied the behaviour of nitrogen in CH_4 biofilters. At CH_4 ILs comparable to the ones used here (9 and 20 $g \cdot m^{-3} \cdot h^{-1}$), up to 17% of the inlet nitrogen was accumulated on the filter bed.

Table 4-1: Nitrogen Mass Balances during the Biofiltration of CH_4 for Biofilter BM

Time (days)	Air Flow Rate ($m^3 \cdot h^{-1}$)	IN ($gN \cdot day^{-1}$)			OUT ($gN \cdot day^{-1}$)			Accumulated Nitrogen ($gN \cdot day^{-1}$)
		Gas		Nutrient Solution	Gas		Lixiviate	
		NH_3	N_2O	NO_3^-	NH_3	N_2O	NO_3^-	
77	0.83	0.0005	0.027	3.83	0.0004	0.029	3.68	0.15
91	2.25	0.012	0.037	3.45	0.005	0.042	3.29	0.16
114	2.17	0.012	0.040	3.36	0.006	0.041	2.91	0.46
127	2.04	0.011	0.043	3.32	0.007	0.045	2.88	0.44
141	2.04	0.031	0.035	3.19	0.017	0.035	2.85	0.34
155	1.08	0.018	0.034	3.41	0.016	0.035	3.33	0.08
167	0.94	0.014	0.024	3.22	0.015	0.025	3.52	-0.31

Treated Swine Slurry as a Nutrient Solution

To test the use of treated swine slurry as a nutrient solution in 2010, biofilter BM was first started with the synthetic nutrient solution. The $[CH_4]$ was set at 1080 ± 150 ppmv for the first 50 days by supplementing pure CH_4. When the pure CH_4 was removed, the $[CH_4]$

varied between 10 and 220 ppmv. The air flow rate was maintained at 0.95 ± 0.31 $m^3 \cdot h^{-1}$ during this part of the study. The changes over time of the CH_4 IL and RE are presented in Figure 4-4 for tests carried out in 2010 with biofilter BM.

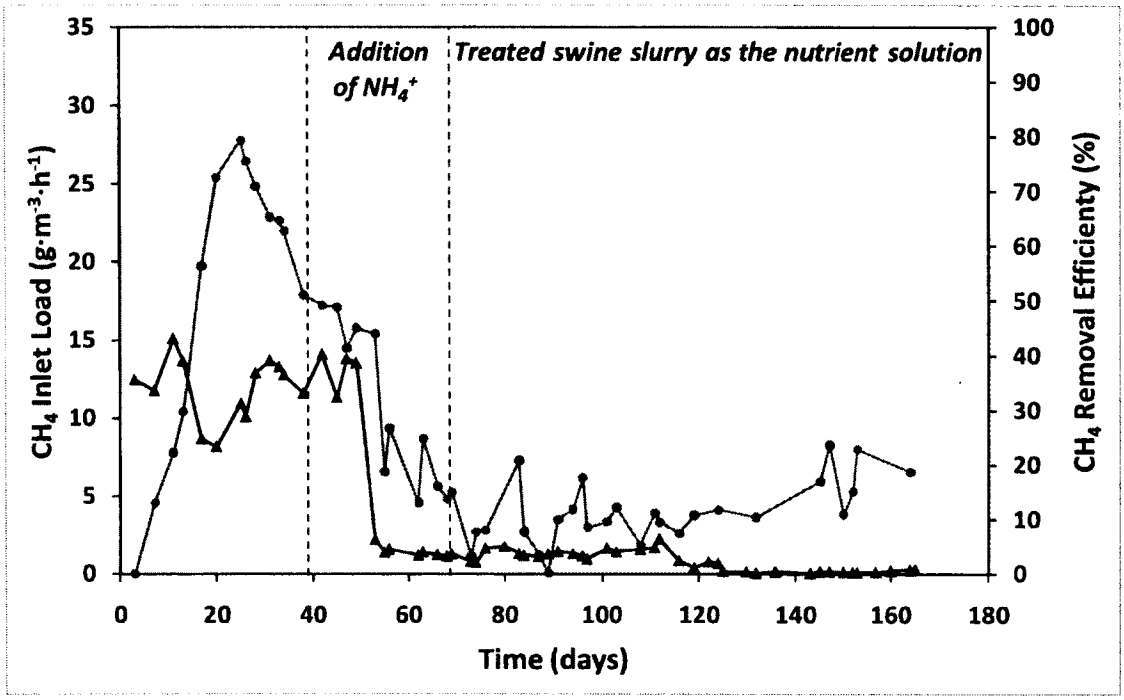

Figure 4-4: CH_4 Inlet Load and Removal Efficiency over Time for the Biofiltration of CH_4 using Treated Swine Slurry as a Nutrient Solution. CH_4 Inlet Load (Black ▲), CH_4 Removal Efficiency (Grey •).

To reduce the shock on biofilter BM before the treated slurry was used, NH_4Cl was gradually added to the synthetic nutrient solution from days 39 to 68, up to a maximum concentration of 0.05 $gN \cdot L^{-1}$. As shown in Figure 4-4, the CH_4 RE dropped quickly to 19 ± 6% on day 55 with the increase in the NH_4Cl concentration and the removal of the supplementary CH_4. The RE dropped even further, to 3%, once the synthetic nutrient solution was replaced by the treated swine slurry. Subsequently, the RE did recover and from days 80 to 165, the biofilter obtained an average RE of 12 ± 6% with a maximum value of 24%. In an attempt to improve the CH_4 RE, the biofilter was re-inoculated on day 109, but no significant effect was observed.

This lack of CH_4 removal could have been caused by the NH_4^+ in the treated swine slurry at concentrations between 0.039 and 0.109 $gN \cdot L^{-1}$. Bronson and Mosier (1994) found that CH_4 oxidation was inhibited up to 89% when NH_4^+ was added to soil at a concentration of 25×10^{-6} $gN \cdot g\ soil^{-1}$. On the other hand, Veillette et al. (2011), observed no significant decrease of the CH_4 RE in an inorganic biofilter for NH_4^+ concentrations in the nutrient solution up to 0.1 $gN \cdot L^{-1}$. Some authors have hypothesised that the inhibition of CH_4 oxidation by NH_4^+ could be caused by the partial oxidation of NH_4^+ to NO_2^-, which is a known methanotroph inhibitor (King and Schnell, 1994). The presence of NO_2^- in the treated swine slurry, at concentrations from 0.007 to 0.031 $gN \cdot L^{-1}$, could also explain the lower CH_4 REs when the treated slurry was used as a nutrient solution.

However, biofilter BM was able to remove up to 54% of the NH_4^+ in the treated swine slurry as shown in Table 4-2. The treated slurry also contained residual organic carbon, between 1.68 and 3.58 $gO_2 \cdot L^{-1}$ as COD. Most of this carbon seemed to be difficulty biodegradable since the biofilter only removed a maximum of 19% of the inlet COD.

Table 4-2: Removal Efficiencies for NH_4^+ and COD when Treated Swine Slurry was used as a Nutrient Solution for Biofilter BM

Days	NH_4^+			COD		
	Treated Slurry	Lixiviate	Removal Efficiency	Treated Slurry	Lixiviate	Removal Efficiency
	$gN \cdot day^{-1}$	$gN \cdot day^{-1}$	%	$gO_2 \cdot day^{-1}$	$gO_2 \cdot day^{-1}$	%
96	0.39	0.28	28	12.3	10.6	14
111	0.12	0.055	54	5.2	5.5	-6
124	0.24	0.37	-54	8.5	8.3	2
152	0.42	0.20	52	14.8	12.4	16
164	0.41	0.19	54	16.3	13.2	19

4.3.3. Simultaneous Biofiltration of Methane and Swine Slurry

Methane Removal

As with biofilter BM, the biofilter used for the simultaneous treatment of CH_4 and swine slurry (BST) was started at a $[CH_4]$ of about 1000 ppmv with a synthetic nutrient solution. The CH_4 IL and RE are given in Figure 4-5 as a function of time for both 2009

(Figure 4-5a) and 2010 (Figure 4-5b). For the experiment carried out in 2009, biofilter BST was started with CH_4 only before swine slurry was supplied to the bottom section on day 86. The air flow rate was maintained at 0.97 ± 0.13 $m^3 \cdot h^{-1}$ while the average [CH_4] and IL were 1050 ± 200 ppmv and 10.2 ± 2.1 $g \cdot m^{-3} \cdot h^{-1}$ respectively. After a start-up period of 30 days as shown in Figure 4-5a, the CH_4 RE became relatively stable at an average value of 58 ± 5% which corresponded to an EC of 5.6 ± 1.0 $g \cdot m^{-3} \cdot h^{-1}$. Once the swine slurry was supplied to the bottom section on day 86, the CH_4 RE quickly dropped to 38% before slowly recovering to reach an average of 53 ± 8% between days 120 to 170. The presence of NH_4^+ in the swine slurry (2.61 ± 0.35 $gN \cdot L^{-1}$) probably inhibited CH_4 biodegradation in the bottom section of the biofilter. Veillette et al. (2011) studied the effect of NH_4^+ in a synthetic nutrient solution on the biofiltration of CH_4. For a NH_4^+ concentration of 0.5 $gN \cdot L^{-1}$ (more than 5 times lower than the NH_4^+ concentration in swine slurry), these authors obtained a CH_4 RE of only 13% for an IL of 20 $g \cdot m^{-3} \cdot h^{-1}$. By supplying the swine slurry exclusively to the bottom section with the innovative design of biofilter BST, the NH_4^+ only affected the bottom section and the average RE was 5% lower than with CH_4 only (53% compared to 58%).

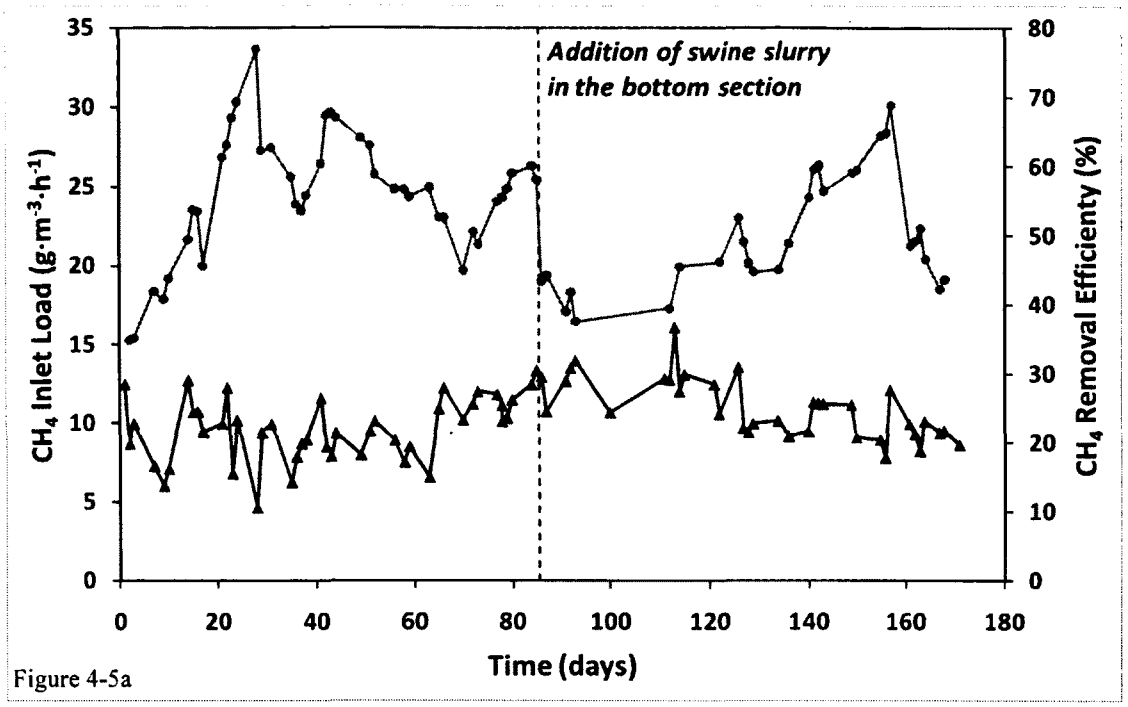

Figure 4-5a

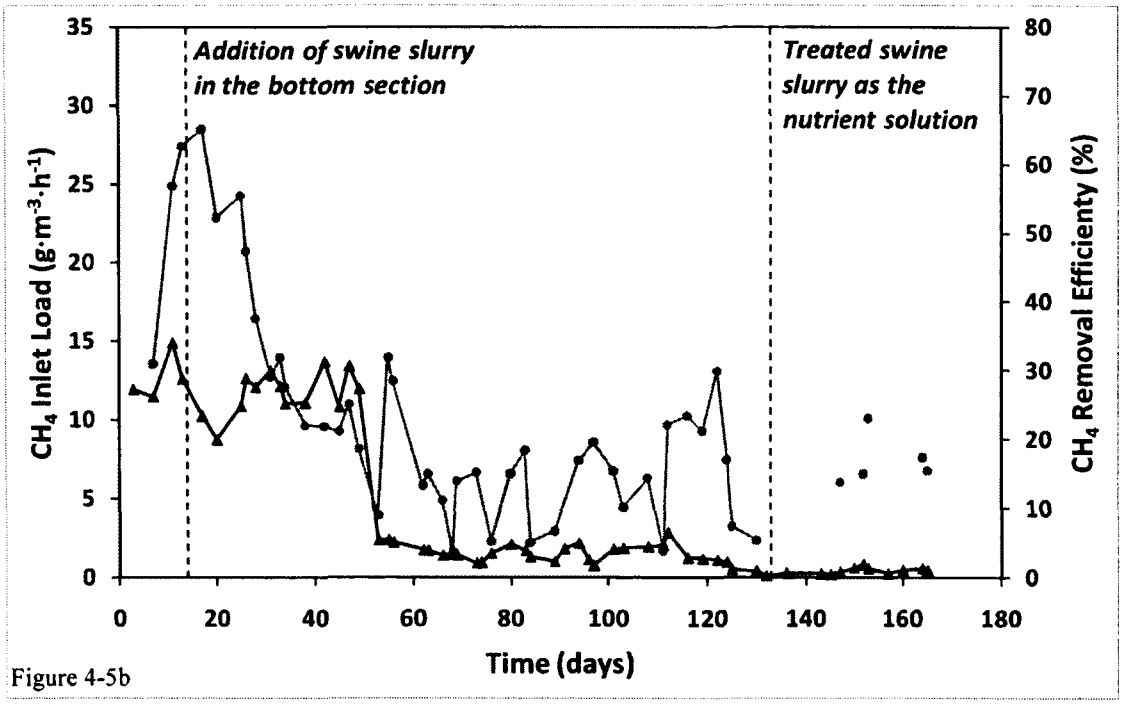

Figure 4-5b

Figure 4-5: CH_4 Inlet Load and Removal Efficiency over Time for the Simultaneous Treatment of CH_4 and Swine Slurry for 2009 (a) and 2010 (b). CH_4 Inlet Load (Black ▲), CH_4 Removal Efficiency (Grey ●).

During the tests carried out in 2010 (Figure 4-5b), the same start-up procedure was used, but the swine slurry was added on day 14 and the supplemental CH_4 was removed on day 50. The air flow rate was maintained at 1.16 ± 0.19 $m^3 \cdot h^{-1}$. With no addition of pure CH_4, the [CH_4] varied between 10 and 220 ppmv and the BST obtained an average RE of 14 ± 7%. This value is much lower than the RE obtained in 2009 with a [CH_4] of 1050 ± 200 ppmv (53 ± 8%). It seems that the addition of swine slurry in the bottom section had a greater impact on CH_4 removal when the [CH_4] was low (below 220 ppmv). On day 133, the synthetic nutrient solution was replaced by treated swine slurry. This change severely impacted CH_4 biodegradation and for several samples, more CH_4 was found in the outlet than in the inlet, up to 16 ppmv (data not shown). When the BST was able to remove some CH_4, a maximum RE of 23% was obtained. De Visscher and Van Cleemput (2003) observed similar phenomena in kinetic flask tests where the inhibitory effect of NH_4^+ on the CH_4 oxidation rate was more important at a low [CH_4]. For a [CH_4] of 250 ppmv, NH_4^+ added to soil caused a 40% inhibition of the CH_4 oxidation rate. For a high [CH_4] of 20000 ppmv (2% v/v), the effect of NH_4^+ depended on the dominant type of methanotroph and varied from a stimulation of the CH_4 oxidation rate to an inhibition.

Swine Slurry Treatment

To evaluate the treatment of swine slurry, both the organic carbon as COD and the NH_4^+ were measured. The REs for NH_4^+ and COD are presented in Figure 4-6 for 2009 and 2010. The removal of organic carbon in 2010 was slightly higher than in 2009 with average REs for COD of 60 ± 6% in 2009 and 70 ± 13% in 2010. For NH_4^+, the average RE in 2009, 24 ± 8%, was much lower than the value obtained in 2010 at 63 ± 6%. In terms of EC, the best values were obtained in 2010 with a synthetic nutrient solution at averages of 4.3 ± 0.5 $gN \cdot m^{-3} \cdot h^{-1}$ and 31 ± 5 $gO_2 \cdot m^{-3} \cdot h^{-1}$ for NH_4^+ and COD respectively at ILs of 6.9 ± 0.4 $gN \cdot m^{-3} \cdot h^{-1}$ and 41 ± 5 $gO_2 \cdot m^{-3} \cdot h^{-1}$. In 2009, biofilter BST was only supplied with swine slurry for 86 days while in 2010, the simultaneous treatment was tested for over 150 days. The low RE for NH_4^+ obtained in 2009 could therefore have been due to the relatively short time the biofilter was supplied with slurry. According to the results obtained by Garzón-Zúñiga et al. (2005) for the biofiltration of swine slurry with an organic packing material,

approximately 40 days are required before any nitrification is observed. Subsequently, these authors observed an increase in the NH_4^+ RE until a maximum value of 97% was reached after 120 days. The difference between the results for 2009 and 2010 obtained in this study was less pronounced with the organic carbon since heterotrophic microorganisms grow faster. In fact, Garzón-Zúñiga et al. (2005) observed the nearly complete removal (97%) of the biodegradable COD in only 20 days. When treated swine slurry was used as a nutrient solution in 2010, the COD RE decreased to 53%. The COD IL introduced to biofilter BST was higher with treated swine slurry as a nutrient solution (57 $gO_2 \cdot m^{-3} \cdot h^{-1}$ as compared to 41 $gO_2 \cdot m^{-3} \cdot h^{-1}$ with the synthetic nutrient solution) since the treated slurry still contained some residual COD. Given that the treated slurry had already undergone a biological treatment, the residual COD was probably poorly biodegradable, resulting in lower REs.

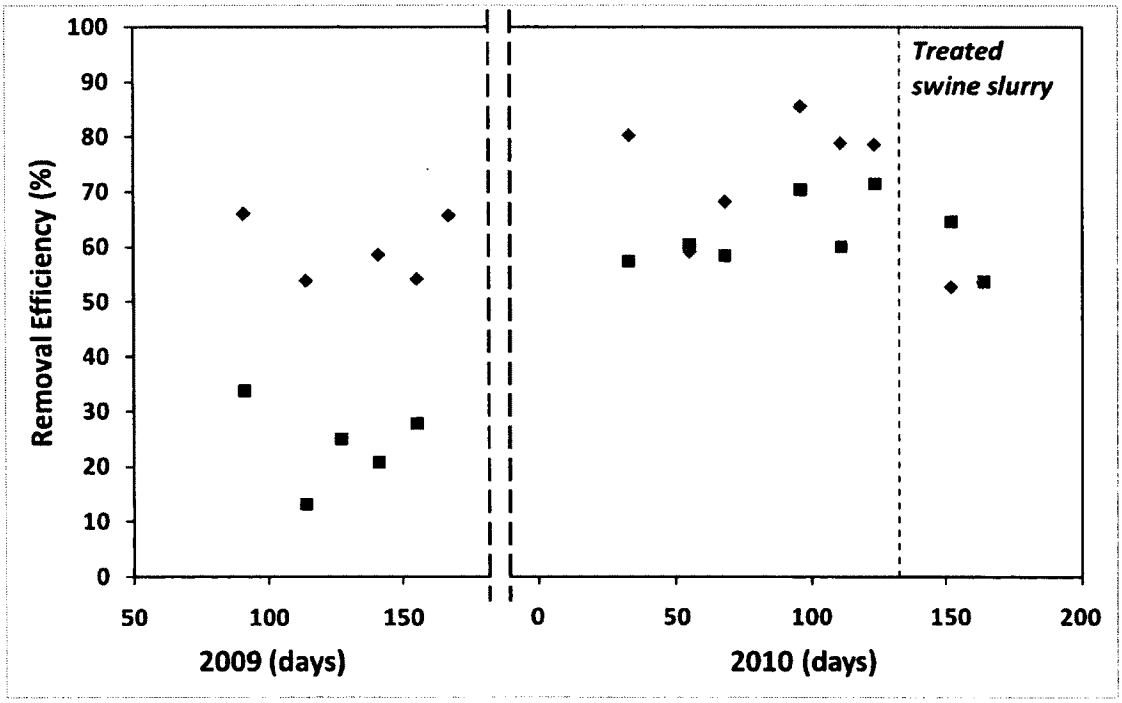

Figure 4-6: Removal Efficiency for NH_4^+ and COD over Time for the Simultaneous Treatment of CH_4 and Swine Slurry for 2009 and 2010. NH_4^+ Removal Efficiency (Black ■), COD Removal Efficiency (Grey ♦).

The REs obtained by Garzón-Zúñiga et al. (2005) are much higher than this study, but these authors used ILs of 2.4 gN- $NH_4^+ \cdot m^{-3} \cdot h^{-1}$ and 21 $gCOD \cdot m^{-3} \cdot h^{-1}$. The lower IL provided

a higher hydraulic residence time which increased the contact between the slurry and the microorganisms and produced high REs. Westerman et al. (2000) obtained REs similar to this study (values above 70% for the COD and NH_4^+) with upflow biofilters using a plastic packing material. However, by using high ILs (23 $gN\text{-}NH_4^+ \cdot m^{-3} \cdot h^{-1}$ and 275 $gCOD \cdot m^{-3} \cdot h^{-1}$), they were able to reach ECs of 19 $gN\text{-}NH_4^+ \cdot m^{-3} \cdot h^{-1}$ and 198 $gCOD \cdot m^{-3} \cdot h^{-1}$. To support such high ILs without clogging, Westerman et al. (2000) used a secondary clarifier and the system was back-washed frequently (up to 4 times a day).

Nitrogen mass balances were performed on biofilter BST by analysing NH_4^+, NO_2^- and NO_3^- in the liquid and NH_3 and N_2O in the gas. For both series of experiments, NH_4^+ volatilization to NH_3 was negligible since the concentration in the air exiting the biofilter was consistently below 2 ppmv and always lower than the concentration in the air fed to the system (4.8 ± 2.0 ppmv on average). The nitrogen remaining from the mass balances is presented over time in Figure 4-7 for the tests carried out in 2009 and 2010. Between 0.5 and 2.1 $gN \cdot day^{-1}$, which represented 7 and 26% of the inlet nitrogen, was either accumulated within the biomass or escaped the system as atmospheric nitrogen (N_2). Production of N_2 by simultaneous nitrification and denitrification has been demonstrated for biofilters treating settled swine slurry (Garzón-Zúñiga et al. 2005). For both 2009 and 2010, the remaining nitrogen increased with time, indicating an increase in biomass accumulation over time since nitrogen is required for cell synthesis. Denitrification was more important in 2010 with an average N_2O production of 6.9 ± 3.7 ppmv, while in 2009 only 1.0 ± 0.7 ppmv of N_2O on average was generated. Denitrification is suspected to take place in the deep layers of the biofilm where NO_3^- is present, but oxygen is limiting (Aubry, 2008). With swine slurry supplied for almost twice as long in 2010 as in 2009 (86 versus 151 days), the biofilm in 2010 probably offered better conditions for denitrification.

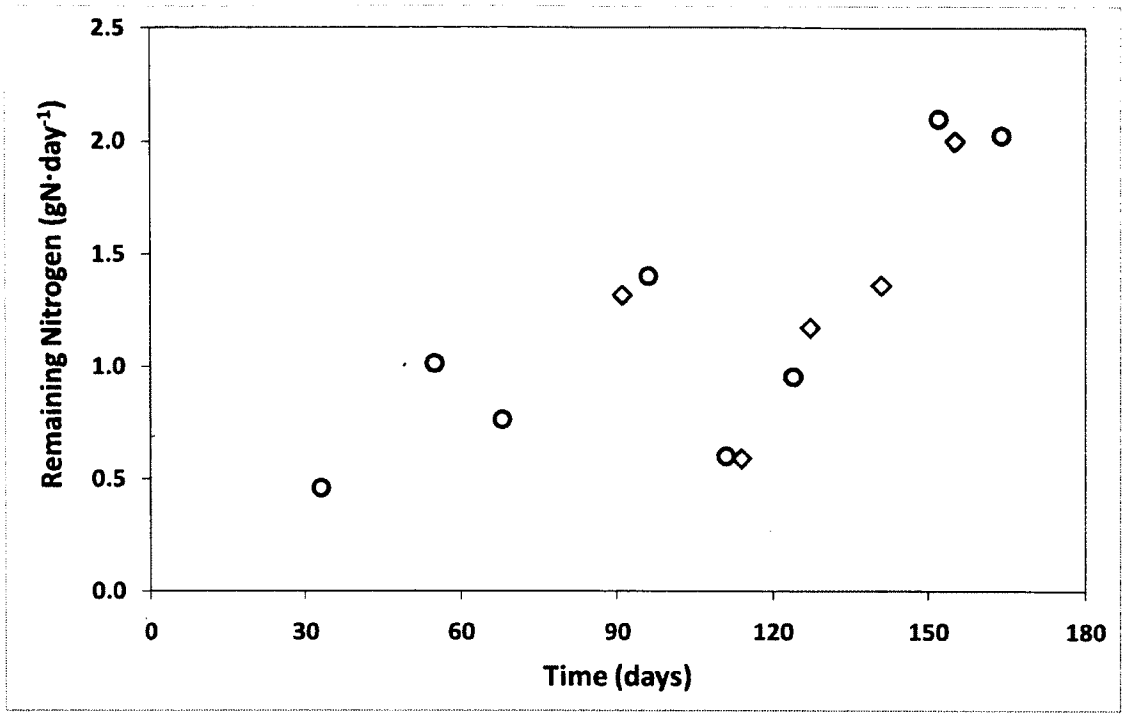

Figure 4-7: Nitrogen Remaining from Mass Balances on Biofilter BST for 2009 (Grey ◊) and 2010 (Black O).

4.4. Conclusion

The main objective of this paper was to study the biofiltration of CH_4 in piggery ventilation air using an inorganic packing material. By using lixiviate from biofilters treating CH_4 to inoculate the biofilters used in the study, the start-up period lasted 30 days before the RE stabilized. For CH_4 concentrations from 75 to 323 ppmv, the biofilters obtained REs up to 83% with an average EC of 1.0 ± 0.4 $g \cdot m^{-3} \cdot h^{-1}$. When pure CH_4 was added to the waste gas at a concentration of 1040 ± 120 ppmv, higher ECs of 6.7 ± 0.6 $g \cdot m^{-3} \cdot h^{-1}$ and 7.1 ± 1.1 $g \cdot m^{-3} \cdot h^{-1}$ with REs of 76 ± 2% and 30 ± 4% were obtained for air flows of 0.92 ± 0.15 $m^3 \cdot h^{-1}$ and 2.1 ± 0.1 $m^3 \cdot h^{-1}$ respectively. Treated swine slurry was tested as a readily available nutrient solution for the biofiltration of CH_4. However, due to the presence of inhibitory compounds in the treated slurry, such as NH_4^+ and NO_2^-, the system only reached a maximum RE of 24%. This study also demonstrated the viability of treating CH_4 and swine slurry within the same

biofilter. When swine slurry was supplied to the bottom section of the biofilter, the CH_4 RE only dropped from 58 ± 5% to 53 ± 8%. At the same time, the biofilter was able to remove up to 70 ± 13% of the COD and 63 ± 6% of the NH_4^+ in the swine slurry on average.

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CONCLUSION GÉNÉRALE

Au Québec, l'industrie porcine génère des retombées économiques importantes et fournit plusieurs emplois, ce qui lui confère une place de choix dans le secteur agroalimentaire. Par contre, le lisier de porc, sous-produit de cette industrie, est particulièrement nocif pour l'environnement. Les conditions d'entreposage et l'épandage excessif contribuent respectivement aux émissions de méthane (CH_4), un puissant gaz à effet de serre, et à la pollution de l'eau. Il existe de nombreuses techniques permettant la valorisation du lisier, la réduction des émissions de CH_4 ou le traitement des effluents. Après l'analyse des procédés de traitement disponibles, la biofiltration s'impose comme étant capable de traiter ces deux types de polluants. Ce procédé utilise différents types de microorganismes immobilisés sur un support solide pour dégrader les composés néfastes.

Les objectifs de cette thèse étaient d'étudier la biofiltration du CH_4 issu de l'industrie porcine et de traiter simultanément le CH_4 et le lisier de porc dans un même biofiltre. Des biofiltres à l'échelle laboratoire et pilote ont été utilisés pour effectuer les essais expérimentaux. Le milieu filtrant était composé d'un matériel inorganique ce qui n'avait jamais été utilisé pour traiter le CH_4 à des concentrations représentatives de l'industrie porcine. La première partie de cette étude fut consacrée à la biofiltration du CH_4 seulement. L'influence de la concentration de CH_4 et de la concentration de nitrate dans la solution nutritive a été testée. La capacité d'élimination maximale atteinte était de $14,5 \pm 0,6$ $g \cdot m^{-3} \cdot h^{-1}$ pour une charge à l'entrée de 38 ± 1 $g \cdot m^{-3} \cdot h^{-1}$. Pour des concentrations de CH_4 de 0,16 à 2,8 $g \cdot m^{-3}$, l'efficacité d'enlèvement était relativement stable et le biofiltre présentait une cinétique de premier ordre avec une valeur de 7,5 h^{-1} pour la constante cinétique. Des concentrations de nitrate de 0 à 0,5 $gN \cdot L^{-1}$ ont été testées et une concentration de 0,1 $gN \cdot L^{-1}$ s'est avérée suffisante pour assurer l'opération adéquate du biofiltre. Sans ajout d'azote inorganique, la conversion du CH_4 était stable à $18 \pm 0,7$ %, suggérant la présence de microorganismes capables de fixer l'azote atmosphérique. Des bilans de masse ont illustré que la quantité de carbone accumulé dans les biofiltres a augmenté avec la concentration de CH_4, ce qui indique une augmentation de la production de biomasse. Par contre, puisque l'azote accumulé était relativement stable, le carbone accumulé était probablement utilisé pour

la production de substances exopolymériques ou des composés intracellulaires, ce qui nécessite peu d'azote.

Le traitement simultané du CH_4 et du lisier de porc a été démontré en utilisant un design innovateur de biofiltre où le lisier était alimenté à la section du bas. D'après nos connaissances, ce type de procédé n'a jamais été utilisé auparavant et il a permis d'éviter l'inhibition de la biodégradation du CH_4 par le lisier. Pour le traitement du CH_4, la capacité d'élimination a augmenté avec la concentration de CH_4 et une valeur maximale de 18,8 ± 1,0 $g \cdot m^{-3} \cdot h^{-1}$ a été obtenue pour une concentration de 3,3 $g \cdot m^{-3}$. Les capacités d'élimination du CH_4 obtenues pour le traitement simultané étaient en moyenne 20% plus faibles que celles obtenues pour le traitement du CH_4 seul pour des charges inférieures à 30 $g \cdot m^{-3} \cdot h^{-1}$. Afin d'améliorer l'enlèvement du CH_4, quatre souches pures de champignons ont été inoculées à l'étage du milieu d'un biofiltre. Par contre, aucune augmentation significative de la conversion du CH_4 n'a été observée et les souches inoculées n'ont pas été retrouvées dans le milieu filtrant à la fin des essais. Il semblerait que les conditions d'opération du biofiltre ont eu plus d'influence que l'inoculation sur l'enlèvement du CH_4 et que les souches de champignons ont été surpassées par des microorganismes mieux adaptés aux conditions d'opération. La concentration de CH_4 n'a eu aucun effet sur le traitement du lisier avec des taux d'enlèvement moyens de 67 ± 10 % pour le carbone organique total (COT) et de 70 ± 7 % pour l'ammonium.

L'effet de l'alimentation du lisier de porc sur le traitement simultané du CH_4 et du lisier a également été analysé. En augmentant la quantité de lisier alimentée à chaque dose de 100 à 300ml, la capacité d'élimination du CH_4 a diminué jusqu'à 33%. Pour le traitement du lisier, des taux d'enlèvement supérieurs à 75% ont été obtenus pour le COT et l'ammonium en diminuant le volume de lisier alimenté à chaque dose à 50 ml. Par contre, les capacités d'élimination maximales ont été observées pour une alimentation de lisier de 3 x 200 ml par jour : 15,2 ± 1,6 $gC \cdot m^{-3} \cdot h^{-1}$ pour le COT et 8,4 ± 1,4 $gN \cdot m^{-3} \cdot h^{-1}$ pour l'ammonium. En tenant compte du traitement du CH_4 et du lisier, le mode d'alimentation optimal du lisier a été de 6 x 50ml par jour avec une capacité d'élimination du CH_4 de 9,4 ± 1,5 $g \cdot m^{-3} \cdot h^{-1}$ pour une charge de 28,5 ± 0,4 $g \cdot m^{-3} \cdot h^{-1}$ et des efficacités supérieurs à 80% pour le COT et l'ammonium. Néanmoins, la biofiltration simultané du CH_4 et du lisier de porc ne permet pas d'atteindre des performances aussi élevées qu'avec le traitement du CH_4 seulement. Ce type de système

pourrait donc servir comme prétraitement du lisier tout en éliminant une portion importante des gaz à effet de serre produits par l'industrie porcine.

Des essais à l'échelle pilote effectués directement sur une ferme porcine ont permis de valider les résultats obtenus au laboratoire pour la biofiltration du CH_4 seul ainsi que pour le traitement simultané. Les biofiltres pilotes ont été alimentés avec de l'air de ventilation des bâtiments d'élevage. En plus du CH_4, l'air de ventilation des porcheries contient entre autres de l'ammoniac et du protoxyde d'azote. En utilisant du lixiviat de biofiltres traitant le CH_4 pour inoculer les biofiltres pilotes, il a été possible d'obtenir une phase de démarrage de 30 jours. Pour le traitement du CH_4 seul, des efficacités d'épuration jusqu'à 83% ont été observées avec une capacité d'élimination moyenne de 1,0 ± 0,4 $g \cdot m^{-3} \cdot h^{-1}$ pour des concentrations de 75 à 323 ppmv. En augmentant le débit d'air de 0.92 ± 0.15 $m^3 \cdot h^{-1}$ à 2.1 ± 0.1 $m^3 \cdot h^{-1}$, la capacité d'élimination du CH_4 a augmenté de 6,7 ± 0,6 $g \cdot m^{-3} \cdot h^{-1}$ à 7,1 ± 1,1 $g \cdot m^{-3} \cdot h^{-1}$ pour une concentration de 1040 ± 120 ppmv. Pour remplacer la solution nutritive synthétique, du lisier traité a été testé puisqu'il contient les principaux nutriments nécessaires à la biofiltration du CH_4. Toutefois, l'efficacité d'enlèvement du CH_4 n'a jamais dépassé 24 %, ce qui a probablement été causé par la présence de composés inhibiteurs dans le lisier traité, tels que le nitrite et l'ammonium.

Le traitement simultané du CH_4 et du lisier de porc a également été validé par les essais pilotes. Lorsque du lisier a été alimenté à la section du bas d'un biofiltre, l'efficacité d'épuration du CH_4 a seulement diminué de 58 ± 5% à 53 ± 8%. Pour le lisier, des efficacités d'enlèvement jusqu'à 70 ± 13% pour le carbone (en terme de la demande chimique en oxygène) et jusqu'à 63 ± 6% pour l'ammonium ont été obtenus. Malgré qu'il soit possible de traiter le CH_4 et le lisier dans un même biofiltre, ce type de procédé n'est probablement pas viable à l'échelle industrielle puisqu'il faut injecter le lisier en bas de colonne. Il serait plutôt intéressant d'améliorer le traitement du lisier pour éliminer les composés inhibiteurs et d'utiliser le lisier traité comme solution nutritive naturelle pour la biofiltration du CH_4.

En somme, cette étude a permis d'améliorer la connaissance de la biofiltration du CH_4 issu de l'industrie porcine. La viabilité du traitement simultané du CH_4 et du lisier de porc a également été démontrée en utilisant un biofiltre innovateur. Finalement, en intégrant les résultats de cette étude aux techniques agricoles modernes, l'industrie porcine pourrait réduire ses émissions de gaz à effet de serre et traiter une partie des nutriments du lisier de porc.

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