ATTENUATION OF GREENHOUSE GAS EMISSIONS BY MEANS OF
METHANE BIOFILTRATION:
OPTIMIZATION OF THE OPERATING PARAMETERS

ATTÉNUATION DES ÉMISSIONS DE GAZ À EFFET DE SERRE PAR
BIOFILTRATION DU MÉTHANE:
OPTIMISATION DES PARAMÈTRES OPÉRATOIRES

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« Du haut du ciel, le Seigneur plonge son regard, Il aperçoit tous les humains. De l'endroit où il siège, il observe tous les habitants de la terre. Lui qui leur a créé à tous intelligence et volonté, il prend garde à ce qu'ils font. »

Extrait de la Bible, Psaumes 33: 13-15

« From heaven the Lord looks down and sees everyone. From his throne he watches all those who live on the earth. He creates the hearts of all people. He is aware of everything they do. »

Extracted from the Bible, Psalm 33:13-15
Abstract

The main goal of this work has been that of optimizing the operating conditions of a biofilter, intended for the control of methane, an important greenhouse gas widely emitted by older or smaller landfill installations. The specific objectives were: 1) to select a suitable packing material (of organic or inorganic type); 2) to optimize the concentrations of input nutrients, mainly consisting of nitrogen, phosphorus, potassium and copper, which are intended to be introduced via the nutrient solution; 3) to determine the optimized values of the most important design parameters, such as the methane inlet load (which depends on the air flow rate and the inlet methane concentration); and 4) to model the biofilter performance.

Firstly, the comparison of the two packing materials, one of organic type, and the other of inorganic type, has revealed that the latter was the more appropriate material for the methane biofiltration. Then, through the use of the selected packing material, the influence of each individual nutrient on the efficiency of the process has been investigated. The results obtained have shown that both nitrogen and phosphorus concentrations have to be controlled, while potassium and copper were revealed as being nutrients of only minor importance.

Secondly, the optimization of the inlet gas flow rate and of the inlet methane concentration (and consequently, of the methane inlet load also), has been performed. According to the results of the studies, these parameters require good control during methane biofiltration because a limitation in biofilter performance could otherwise be induced. In addition, it was noted that the increase in the inlet gas flow rate led generally to a greater decrease of the methane conversion than the one induced by the inlet methane concentration.

Finally, a new method, based on the use of solid extracts sampled from the methane biofilter, has been applied to the determination of methane biofilter kinetic parameters. Following this study, a steady state model of the methane biofiltration, taking into consideration the important operational parameters, as identified previously, has been developed. One particular feature of this model is that it takes into consideration the influence of the biofilter average temperature. The prediction results, obtained with the use of the model, have been successfully compared with the experimental results.

Keywords: Biofiltration; methane; landfill; packing material; nutrients; operating parameters; kinetic parameters; model
Résumé

L’objectif principal de cette thèse a été d’optimiser les conditions opératoires d’un biofiltre destiné à l’élimination du méthane, un gaz à effet de serre émis par les sites d’enfouissement sanitaire de petites tailles ou relativement âgés. Les objectifs spécifiques étaient: 1) de sélectionner un lit filtrant adapté au procédé; 2) d’optimiser les concentrations de nutriments, principalement l’azote, le phosphore, le potassium et le cuivre, fournis au biofiltre par l’intermédiaire de la solution nutritive; 3) d’identifier les valeurs optimales des paramètres de design les plus importants, notamment la charge initiale de méthane (qui dépend du débit d’air et de la concentration initiale de méthane); et 4) de modéliser les performances du biofiltre.

Dans un premier temps, la comparaison de deux lits filtrants, l’un de nature organique, et l’autre de type inorganique, a montré que le dernier lit filtrant était le plus approprié pour la biofiltration du méthane. Par la suite, l’influence de chaque nutriment sur les performances du biofiltre a été étudiée, en utilisant le lit filtrant sélectionné. Les résultats obtenus ont montré que les concentrations d’azote et de phosphore doivent être convenablement ajustées tandis que celles du potassium et du cuivre se sont révélées être de moindre importance.

Dans un deuxième temps, l’optimisation du débit d’air introduit dans le biofiltre ainsi que de la concentration initiale de méthane (et par conséquent de la charge initiale de méthane aussi), a été effectuée. Considérant les résultats de cette étude, ces deux paramètres nécessitent un bon contrôle au cours de la biofiltration du méthane, sinon une baisse de performance pourrait survenir. De plus, il a été noté que l’augmentation du débit d’air occasionne généralement une diminution de la conversion de méthane plus importante que celle causée par l’augmentation de la concentration initiale du méthane.

Finalement, une nouvelle méthode utilisant des échantillons de lits filtrants, prélevés directement dans le biofiltre traitant le méthane, a permis la détermination des paramètres cinétiques de la biofiltration du méthane. Par la suite, un modèle décrivant le fonctionnement du biofiltre en régime permanent, et prenant en compte les principaux paramètres opératoires préalablement identifiés, a été développé. Une caractéristique importante de ce modèle est qu’il intègre la température moyenne dans le biofiltre. Les résultats prédits à partir de ce modèle se sont révélés satisfying lors comparés aux données expérimentales.

Mots-clés: Biofiltration; méthane; enfouissement sanitaire; lit filtrant; nutriments; paramètres opératoires; paramètres cinétiques; modèle
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GENERAL PRESENTATION

An airborne pollutant is a substance that has a negative influence on human health and/or contributes to the degradation of animal and vegetal lives, and also of the associated water and soil resources, etc. According to Environment Canada, the main types of airborne pollutants can be grouped within 4 categories; these are: 1) criteria air contaminants and related pollutants, being responsible for both smog formation and acid rains, and which include various pollutants such as particulate matter, volatile organic compounds (VOCs) and oxides of nitrogen and sulphur; 2) persistent organic pollutants, such as the polychlorinated biphenyls (PCBs), dioxins, furans, and various pesticides; these semi-volatile organic molecules having the property of accumulating in those living organisms contacting with them; 3) heavy metals, such as mercury, cadmium and lead; these elements being generally emitted in association with the fine particles, i.e. with particle diameters of ≤ 2.5 μm, and 4) toxic pollutants, i.e. those pollutants listed under the Canadian Environmental Protection Act, 1999 (Schedule 1), such as methanol, benzene and several others (Environment Canada, 2008a).

In addition to this listing, one also has the greenhouse gases (GHG) category. This grouping includes those substances that are not necessarily toxic for either animals or the general environment, but otherwise facilitates the shortwave and the solar radiation to reach the earth, leading to an increase in the earth’s superficial temperature. Among the anthropogenic GHG are: water vapor, carbon dioxide (CO₂), nitrous oxide (N₂O) and methane (CH₄). The concentration of this latter GHG has increased by some 150 %, on average, over the most recent 250 years (as compared with 31 % and 17 % for CO₂ and N₂O, respectively) (Environment Canada, 2008b).

The main anthropogenic CH₄ emissions are linked with various agricultural practices (e.g. livestock, flooded rice cultivation, etc.), with a proportion of 25 %, the energy (i.e. mainly through coal mining and fuel gas delivery systems) with a proportion of 50 %, and organic wastes decomposition, mainly taking place within landfills, and with a proportion of 25 %. According to Environment Canada, a reduction of some 8 % of the total emissions is
necessary in order to hold the present increase of the CH₄ concentration in the atmosphere (Environment Canada, 2008c).

The first chapter of this present thesis begins with a description of sanitary landfills and how the resulting product biogas is obtained, following the wastes' disposal. Then, the biogas processing is presented: i.e. detailing its composition and describing possible valorization and elimination techniques that may be applied. Among the latter is the biofiltration method, which has been the subject of much detailed attention. As a consequence, the configuration of the biofilter, the types of micro-organisms involved and the major operating parameters (e.g. filter bed material selection, pH and moisture content of the filter bed, nutrients, operating temperature and inlet loads of methane) that require control during CH₄ biodegradation are discussed.

In Chapters 2 and 3, the influences of the input nitrogen and of the inlet load, on the methane biofilter, are presented. Two filter bed material types have been considered and compared: i.e. an organic compost material and an inorganic gravel material. Following this comparative study, the inorganic filter bed has been selected and a further study has been undertaken on the influence of the phosphorus concentration during the methane biofiltration. It is important to note that this has been the first study performed having the aim of determining the influence of the input phosphorus nutrient during the overall methane biofiltration process. The particular behavior and response, induced by the presence or abundance of phosphorus, is also discussed, taking into account the inlet load applied at the biofilter entry point.

In Chapter 4, the main interest examined is that of the influence of the total gas flow rate on the methane biofiltration. Indeed, this parameter affects the mass transfer of the pollutant methane, this in turn therefore has an effect on the overall biofilter performance.

In order to model the biofilter performance, it is necessary to determine the values of the microkinetic parameters. This matter has formed the subject of Chapter 5. It is to be noted that the determination of the kinetic parameters has never been effected (according to our knowledge) for application of methane biodegradation into air biofilters.
Finally, Chapter 6 presents the steady state model, as developed to estimate the performance of the methane treating biofilter, in terms of the conversion, elimination capacity and carbon dioxide production parameters, and which also integrates the main results obtained previously during methane biofiltration studies.
1.1. Abstract

The production of biogas in landfills, its composition and the problems resulting from its generation are all reviewed. Biofiltration is a promising option for the control of emissions to atmosphere of the methane contained in biogas issued from the smaller and/or older landfills. A detailed review of the methane biofiltration literature is presented. The micro-organisms, mainly the methanotrophs, involved in the methane biodegradation process, and their needs in terms of oxygen and carbon dioxide utilisation, are described. Moreover, the influence of nutrients such as copper, nitrogen and phosphorus, and the process operating conditions such as temperature, pH and moisture content of the biofilter bed, are also presented. Finally, the performance of various filter beds, in terms of their elimination capacities, is presented for laboratory scale biofilters and landfill covers.

Résumé

La production du biogaz dans les sites d’enfouissement sanitaire, sa composition de même que les problèmes résultant de sa génération sont étudiés dans le présent article. La biofiltration est un procédé prometteur, utilisable pour le contrôle des émissions atmosphériques du méthane contenu dans le biogaz généré dans les petits et/ou vieux sites d’enfouissement sanitaire. Une revue détaillée de la biofiltration du méthane est présentée. De plus, les micro-organismes intervenant dans la biodégradation du méthane, principalement les methanotrophes, et leurs
besoins en oxygène et en dioxyde de carbone sont également décrits. Par ailleurs, l'influence des nutriments tels le cuivre, l'azote et le phosphore, ainsi que des paramètres opératoires du procédé tels la température, le pH et l'humidité du lit filtrant est également discutée. Enfin, la performance de divers lits filtrant, en termes de capacités d'élimination, pour des essais à l'échelle laboratoire et pour les sols de couverture des sites d'enfouissement sanitaire est présentée.

1.2. Introduction

Biogas results from the anaerobic degradation of organic wastes. Every year, thousands of tons of the greenhouse gas (GHG), methane (CH₄), are produced in landfills, some of which escapes directly to the atmosphere. Even if GHG emissions associated with landfills represent only a small percentage (3.4 % for Canada) of the national total of GHG emissions from all sectors, it is important to note that landfills generally constitute the most important sources of anthropogenic CH₄. For example, in Canada and the United States, around 25 % and 34 % respectively, of the total methane emissions are directly related to landfill installations (Environnement Canada, 2006; EPA, 2006). About 10000 landfills presently exist in Canada and the average waste production per inhabitant in yr. 2000 was 1020 kg, of which some 73.2 % was discarded to landfills. The wastes have generated in yr. 2001 GHG emissions, mainly in the form of CH₄, at a level around 25.10⁶ metric tons, when expressed as the carbon dioxide (CO₂) equivalent (Environnement Canada, 2006). The recent ratification by Canada of the Kyoto protocol forces this country, along with several others, to find new alternatives for the control of CH₄ emissions. Indeed, Canada has committed itself to reduce its GHG emissions by 6 %, compared to the 1990 level, during the period from 2008 to 2012, by targeting some particular gaseous compounds, such as CH₄, for major attention (Kyoto protocol, 1998).

Methane, as a GHG, is some 21 to 25 times more detrimental to the environment than CO₂ and its lifespan in the atmosphere is around 12 years (Hiutsch et al., 1994; Goossens, 1996; Hettiaratichi and Stein, 2001; Kumar et al., 2004). Various technologies such as combustion can be used to control the CH₄ emissions issued from landfills but, for the older and/or smaller
landfills, traditional technologies are not very applicable and thus the biofiltration approach could be a promising solution. This process is one of the oldest of biotechnologies used in the treatment of polluted air. In the beginning, the process was employed only for the elimination of odors (Marsh, 1994). Thereafter, biofiltration, applied to contaminated air, proved to be also reliable for the elimination of volatile organic compounds (VOCs) and volatile inorganic compounds (VICs) (Jorio et al., 2003; Delhoménie and Heitz, 2005).

The idea of using biofiltration for CH\textsubscript{4} elimination derives from the fact that some bacterial species are able to degrade CH\textsubscript{4} while generating oxidation by-products such as water (H\textsubscript{2}O), CO\textsubscript{2}, salts and biomass, all products much less harmful for the environment than the initial substrate. On an annual basis, at least 10 to 25 % of the total CH\textsubscript{4} emitted from landfills is oxidized by micro-organisms (Nozhevnikova et al., 1993; Mancinelli, 1995; Chanton and Liptay, 2000; Christoffersen et al., 2000; EPA, 2005; Stralis-Pavese et al., 2006). Moreover, biofiltration creates environmental problems (such as CO\textsubscript{2} production) to a lesser extent, in comparison with regular chemical oxidation processes. Also, biofiltration often offers the advantage of being performed at normal atmospheric pressure and temperature, thus resulting in lower ranges operational costs than traditional technologies (Ottengraf, 1986).

### 1.3. Sanitary landfills

A sanitary landfill is an installation arranged to receive wastes and to retain the products of their decomposition so that they cease to constitute a threat for human or animal health (Popov, 2005; Zamorano et al., 2007). Several types of landfills presently exist, some, known as closed-landfills, prevent the migration of liquid phase species from these sites towards the exterior environment. They are often used for the long term storage of dangerous wastes. However, the majority of landfills are only partially closed, thereby allowing the collection and treatment of the leachate, or kept open, leading to the gradual migration and dispersal of the leachate within the immediate ecosystem (Warmer Bulletin, 2000; Nikiema et al., 2004a; Zamorano et al., 2007). Sanitary landfills can receive and process, over the period of their active life, more than a million metric tons of wastes (Desideri et al., 2003; Zamorano et al., 2007; Spokas et al., 2006). For small cities and towns of less than 35000 inhabitants, a
municipal landfill of 20-30 m in depth is able to receive up to 200000 m$^3$ of waste during its lifetime and is classified as a small landfill (Börjesson et al., 2001; Park et al., 2004). The choice of a suitable site must be the subject of quite detailed attention. Factors commonly taken into account are; the long term availability of the site, which will be devoted to this exclusive use over a period of at least thirty (30) years; its geological stability and characteristics. The site must also be of suitable size, and be located as far as possible from both residential and commercial areas, though remaining of easy access and servicing (Gielecki, 1997).

Wastes, after their arrival on the site, are dehumidified if necessary, and moderately compacted, generally using bulldozers, to reduce their density to values bordering on 0.7 to 0.9 m$^3$ per metric ton before storage (Warmer Bulletin, 2000; Zamorano et al., 2007). At the end of each day’s operations, the densified wastes are covered with an inert layer: e.g. compacted mineral material, such as clay soil, of about 0.15 m height, in order to control the harmful effects of waste’s decomposition (such as odors) and losses, and to reduce the risk of fires. When an operational section of the site is completely filled, a final cover, composed of 0.6-1.0 m of clay and 0.2-0.6 m of soil, is applied to isolate it. The goal of this operation is thus to limit and even prevent the infiltration of H$_2$O into the thus deposited wastes (Zamorano et al., 2007).

### 1.4. Biogas

#### 1.4.1. Biogas composition

Once stored in landfills, wastes degrade biologically, thereby generating biogas (Popov, 2005). This biogas contains mainly CH$_4$, a colorless and odorless GHG, explosive when its concentration lies in the range 5 % to 15 % V/V in air (Perry et al., 1997; Tagaris et al., 2003), and CO$_2$, able to cause respiratory problems when its concentration is greater than 0.5 % V/V for a prolonged exposure (Toutant, 1994; Reginster, 1999; Nikiema et al., 2004a). The CH$_4$ concentrations in biogas, as mentioned in the literature, generally vary from 30 % V/V to 70 % V/V while the CO$_2$ concentration varies between 20-50 % V/V (Humer and Lechner,
In the bio gas, some sulfur compounds are present in small proportions (typically less than 0.2 % V/V), such as hydrogen sulphide (H$_2$S), mercaptans and thiols. These are responsible for the unpleasant odors that often emerge from poorly maintained landfills and can cause to humans and animals nausea, illness and in extreme cases death (Ma et al., 1996; Reginster, 1999; Warmer Bulletin, 2000). The biogas also generally contains some chlorinated compounds (less than 40 ppmv), among which are vinyl chloride, dichloromethane and tetrachloroethylene, all carcinogenic for humans and animals (Brosseau and Heitz, 1994; Reginster, 1999; Warmer Bulletin, 2000; Scheutz et al., 2000; Zamorano et al., 2007).

Biogas can also contain trace amounts of various VOCs (less than 70 ppmv), such as benzene, a carcinogenic compound, toluene and the xylenes. Hydrogen (H$_2$), a by-product of the waste decomposition, can also be found in biogas at small concentrations, < 0.2 % V/V, along with nitrogen (< 5 % V/V) and sometimes oxygen (O$_2$) (< 1 % V/V) (Reginster, 1999; Warmer Bulletin, 2000; ZWA, 2006). Moreover, biogas is generally water saturated (Warmer Bulletin, 2000; Spokas et al., 2006). Even when all of these compounds are found in biogas of various origins, their concentrations can be very variable and depend on the type of the stored waste and the age of the landfill. Table 1-1 presents typical concentrations for several compounds generally found in biogas.

### 1.4.2. Biogas production

One metric ton of municipal waste can generate between 135 and 375 m$^3$ of biogas (Humer and Lechner, 1999b; Warmer Bulletin, 2000; Aye and Widjaya, 2006; Murphy and McCarthy, 2005; Zamorano et al., 2007). Many parameters influence the quantity and the rate of biogas production over time (Goossens, 1996; Ozkaya et al., 2007). First, the age of the site is a determining factor in the production of biogas, due to commencement of waste decomposition, which can begin approximately three months after the waste storage installation and is subsequently spread over some 20 to 50 years (Bajic and Zeiss, 2001; Zamorano et al., 2007). During the early years of a sanitary landfill’s life (when it is being
established and filled), the rate of generated biogas released increases rapidly, from 0 to 11 m\(^3\) metric ton\(^{-1}\) year\(^{-1}\) (Reginster, 1999; Kumar et al., 2004) and thereafter, a slow and continuous decline in the gas emission follows. After some 30 to 50 years, rates of biogas production become very low and almost cease (Reginster, 1999).

TABLE 1-1: TYPICAL COMPOSITION RANGES FOR BIOGAS PRODUCED IN A LANDFILL

(Reginster 1999; Humer and Lechner 1999b; ZWA 2006; Tsai 2006)

<table>
<thead>
<tr>
<th>Important Compounds</th>
<th>Percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>30-70</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>20-50</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>1-5</td>
</tr>
<tr>
<td>Oxygen</td>
<td>0.1-1.0</td>
</tr>
<tr>
<td>Ammonia</td>
<td>0.1-1.0</td>
</tr>
<tr>
<td>Sulfur compounds</td>
<td>0-0.2</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>0-0.2</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>0-0.2</td>
</tr>
<tr>
<td>Other trace compounds</td>
<td>0.01-0.6</td>
</tr>
</tbody>
</table>

*These concentrations are expressed on a dry weight basis

The rate of biogas production also depends on the waste bed internal temperature and, to a lesser extent, on the external climatic conditions, such as the ambient temperature (Kumar et al., 2004). The optimal temperature for the production of biogas is 35-37°C (Kettunen and Rintala, 1997). The lowering of the temperature to 24°C in a controlled environment, such as within a digester, causes a reduction in the rate of biogas production of nearly 50 % (Crill, 1991; Nguyen et al., 2006). On the other hand, according to Chanton and Liptay (2000), variations in the production of biogas from an older landfill, as caused by seasonal temperature changes, are weak because the composting reactions of the organic wastes, located inside the deeper installed beds, ensures a near constant year round temperature of around 50°C (Straka et al., 1999; Hudgins and Green, 2000).
Another important parameter is the waste's moisture content that should ideally remain between 50 and 60% wt/wt. This factor can be controlled during the wastes' initial compaction, i.e. just before their placement in the long-term storage. The wetter the wastes, the greater their rate of degradation. However, a waste bed that is excessively wet (i.e. more than 65 % wt/wt moisture content) may cause settlement in the site material and produces substantial amounts of leachate needing to be handled. On the other hand, when wastes are not wet enough (less than 30 % wt/wt moisture content), they degrade more slowly because the microbial activity is inhibited. Therefore, it results in an increase of the lifespan of the wastes. However, the mechanical stability of the landfill is good, reducing the risk of safety hazards generation (Reinhart and Al-Yousfi, 1996; Warmer Bulletin, 2000; Hudgins and Green, 2000).

The type of waste stored in the landfill can also influence both the composition and the quantities of the generated biogas produced. Organic wastes produce a biogas principally containing CH₄ and CO₂, in contrast to synthetic wastes that can be practically inert, like glass, or introduce into the biogas specific substances such as H₂S, in the case of certain plastics degradation (Brosseau and Heitz, 1994). Finally, the physical characteristics of the landfill, e.g. the bed depth, and its chemical characteristics, such as the pH, also play important roles in determining the production rate of the biogas. For maximum biogas production, the bed must be of sufficient depth to ensure that its interior regions provide for an anaerobic environment in which the relevant micro-organisms can thrive, and the pH must also generally be close to neutral, i.e., between 6.8 and 7.2 (Yongzhi and Hu, 2002; Kettunen and Rintala, 1997).

1.4.3. Methane in the biogas

Methane, the atomically simplest and most stable hydrocarbon, is one of the important components in biogas. Its synthesis in organic waste beds is performed in three steps. Initially, polymers of the organic matter are hydrolyzed by the heterotrophic bacteria to form monomers. These molecules are then subject to fermentation which leads to the production of the organic and soluble products, composed mainly of acetates, formates and alcohols. By-products arising during this process step are CO₂ and H₂ (Le Mer and Roger, 2001). These by-
products are then converted to acetate in the presence of acetogenic bacteria, with simultaneous acidification, according to the following reaction:

\[ 2 \text{CO}_2 + 4 \text{H}_2 \rightarrow \text{CH}_3\text{COO}^- + \text{H}^+ + 2 \text{H}_2\text{O} \quad \text{(Eq. 1-1)} \]

All of these steps are strictly anaerobic. Acetate and other organic acids are then decomposed to \( \text{CH}_4 \) and \( \text{CO}_2 \) by the methanogenic micro-organisms, all belonging to the domain Archaea (Hudgins and Green, 2000; Le Mer and Roger, 2001; Ozkaya et al., 2007). These micro-organisms are strictly anaerobic (i.e. the tolerated dissolved oxygen concentrations do not exceed the low micromolar range) and they are widely found in various environments such as anaerobic digestors, anoxic sediments, flooded soils and landfills. The acidification and methane generation steps are synchronized and mutualistic associations of micro-organisms belonging to different genera are often observed at this late stage of methanogenesis, creating reciprocally favorable conditions, each moving the reaction equilibrium of the other in the most favorable direction (Whitman et al., 1999; Le Mer and Roger, 2001).

### 1.4.4. Biogas valorization

Some landfills have active biogas collection systems (made as gas wells) but even in these cases, the quantities of recovered gases are usually only between 40 % and 60 % of the actually produced gas quantities (Humer and Lechner, 1999a, b; Bajic and Zeiss, 2001; Christophersen and Kjeldsen, 2001; Popov, 2005; Zamorano et al., 2007; Spokas et al., 2006). Newer more efficient techniques, including the use of synthetic cover materials, now allow for up to 90 % gas collection effectiveness to be reached (Spokas et al., 2006). The biogas thus collected can subsequently be used in a variety of processes.

Combustion: This option is applicable only if the generated \( \text{CH}_4 \) concentration in the biogas and the overall biogas quantities are important, i.e. more than 30 % (which occurs during the first 25 years of the landfill) and 50 m\(^3\).h\(^{-1}\), respectively (Reginster, 1999; Bajic and Zeiss, 2001; Streese et al., 2001; Haubrichs and Widmann, 2006). The calorific value of biogas is typically around 20000 kJ.m\(^{-3}\), i.e. about half that of the calorific value of natural gas and thus, the hot gases generated from biogas combustion can be best used as an energy source for the
production of electricity and/or to generate hot water or steam (Goossens, 1996; Desideri et al., 2003; Tsai, 2006; Zamorano et al., 2007; Spokas et al., 2006). This valorization process allows at least, the partial meeting of the energy demand for the wastes processing site and for other clients located in its neighborhood. The investment cost required to install and operate such technology, considering a global collection and energy recovery efficiency of 50%, in a landfill, already equipped with biogas collection systems, is 3.1 $ US/ton CO₂ equivalent of CH₄ eliminated (Ayalon et al., 2001). Estimates made by the Environmental Protection Agency (EPA) in 1996 indicated that the recovered energy from biogas, issued from the landfills across the whole USA, could be used to meet the needs of some 2.3 million homes (Goossens, 1996). However, this solution is not universally economic at present because of the low cost of natural gas. Moreover, the addition of biogas to the natural gas network may deteriorate the quality and lifetime of the latter (Brosseau and Heitz, 1994; Ewall, 1999).

Other alternatives: A catalytic flow reversal reactor technology concept was developed by Natural Resources Canada (USDE, 2005). The main goal of this process is the elimination of CH₄ when its concentration in air lies between the values of 0.1 to 1 % V/V. The methane is oxidized in a packed bed reactor, the exit product gases having a temperature ranging from 600 to 800°C. Heat can then be recovered from it, either to produce electricity or to satisfy various local heating needs. Another alternative for the CH₄ content in biogas valorization consists of transforming this compound into methanol. This latter product can then be sold to chemical processors (Ewall, 1999; Popov, 2005).

1.4.5. Biogas elimination

Flaring: Sometimes, collected biogas is simply burned in flares. This CH₄ elimination method is done with minimal facilities and without energy recuperation, the objective being to avoid the risk of explosion caused by the presence of CH₄ in the air. However, this disposal method can be environmentally harmful, when dangerous compounds, such as dioxins, are generated during the combustion and are released to the atmosphere (Gielecki, 1997; Jaffrin et al., 2003). Flaring of landfill biogas requires about 1.2 $ US/ton eq CO₂ of CH₄ eliminated (Ayalon et al., 2001). This treatment process can be used only when the amounts of biogas to
be treated exceed 10-15 m³.h⁻¹, while the biogas CH₄ concentration remains greater than 20 % V/V (Haubrichs and Widmann, 2006).

Biological oxidation: Many landfill installations are, even today, still deprived of collection systems for the biogas produced. And even where such systems are in place, it is still difficult, and usually uneconomic, to utilize traditional valorization techniques for the older or smaller landfills (Bajic and Zeiss, 2001). In these cases, other processes may need to be used to eliminate the dangers created by the CH₄ presence in the atmosphere-released biogas. A possible solution is the use of biofiltration, a biological oxidation process. This idea comes from the fact that some bacteria are able to degrade air pollution compounds, such as CH₄. This process already provides for the elimination of some 10 to 100 % of the CH₄ escaping from the upper layers of landfills, depending on local climatic conditions (Nozhevnikova et al., 1993; Kightley et al., 1995; Czepiel et al., 1996; Chanton et al., 1999; Christophersen et al., 2000; Bajic and Zeiss, 2001; EPA, 2005; Stralis-Pavese et al., 2006).

1.5. Methane Biofiltration

1.5.1. Configuration

A biofilter is a three-phase bioreactor: the filter bed constitutes the solid phase, the biofilm, the liquid phase and the gaseous pollutants, the gas phase. Contact between the microorganisms and the polluting CH₄ takes place in the biofilm, immobilized on the filter bed. The majority of biofilters, as used in lab-scale experiments, are closed systems. The air supply is ensured by a forced ventilation system. Gases circulation in the biofilter can be effected from either top to bottom or conversely. Closed biofilters are compact systems that can be assembled from several stages. Different performance parameters like inlet load (IL), elimination capacity (EC) and conversion (X) used in biofiltration are defined in Table 1-2. Maintaining the operational parameters unchanged in a closed biofilter is also a relatively easy practice, resulting in good performance, with CH₄ X values as high as 90 % (Dammann et al., 1999; Streese et al., 2001; Gebert et al., 2001; du Plessis et al., 2003; Nikiema et al., 2005). The biofilter can also be an open system generally organised within the landfill covers.
### TABLE 1-2: PERFORMANCE PARAMETERS USED IN BIOFILTRATION

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Calculation</th>
</tr>
</thead>
<tbody>
<tr>
<td>IL: Surfacic inlet load (g.m(\text{m}^2).d(^{-1}))</td>
<td>IL = (\frac{C(\text{CH}_4) \text{in} \times Q}{S})</td>
</tr>
<tr>
<td>IL: Volumetric inlet load (g.m(^3).d(^{-1}))</td>
<td>IL = (\frac{C(\text{CH}_4) \text{in} \times Q}{V})</td>
</tr>
<tr>
<td>X: Conversion (%)</td>
<td>X = (\frac{C(\text{CH}_4) \text{in} - C(\text{CH}_4) \text{out}}{C(\text{CH}_4) \text{in}} \times 100)</td>
</tr>
<tr>
<td>EC: Elimination capacity (g.m(^2).d(^{-1}) or g.m(^3).d(^{-1}))</td>
<td>EC = IL \times (\frac{X}{100})</td>
</tr>
</tbody>
</table>

Where \(C(\text{CH}_4)\): Methane concentration in g.m\(^3\); Q: Volumetric flow rate of gases in m\(^3\).d\(^{-1}\); S: Biofilter bed cross-section in m\(^2\) and V: Biofilter bed volume in m\(^3\).

Usually, in this case, the flow of the polluted gas in the bed proceeds upwards, while the O\(_2\) diffuses from the ambient air into the bed (passive ventilation). The main disadvantage of this process lies in the difficulty of controlling the operational parameters, such as the temperature and moisture levels. Moreover, transfer of O\(_2\) to the bed’s lowest layers is a very important limiting factor for the overall performance (Kjeldsen et al., 1997; Gebert et al., 2001). For example, removal efficiencies of up to 60 \% can be obtained, when the empty bed residence times (EBRT) is at least an hour, with an open biofilter, installed on a landfill site (du Plessis et al., 2003; Gebert and Groengroeft, 2006a, b).

Laboratory-scale experiments, using a forced ventilation at the top of the biofilter in order to simulate the natural behavior of landfill covers, have been reported by several authors (Hilger et al., 2000a, b; Hettiaratchi and Stein, 2001; Stein and Hettiaratchi, 2001). The best EC obtained with this operational mode was achieved in the range of 325 and 400 g.m\(^2\).d\(^{-1}\) (Hettiaratchi and Stein, 2001). The IL of CH\(_4\) is another important parameter. Various ILs have been tested at the laboratory scale and are reported in the literature, as presented in Table 1-3, ranging from 200 to 1700 g.m\(^2\).d\(^{-1}\). For an IL close to 300 g.m\(^2\).d\(^{-1}\), a conversion of 50 \%
<table>
<thead>
<tr>
<th>Filter bed</th>
<th>Operating conditions</th>
<th>Inlet load</th>
<th>Elimination capacity or conversion</th>
<th>Authors</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compost and soil</td>
<td>Aerated at the top</td>
<td>IL = 202 g.m⁻².d⁻¹</td>
<td>EC = 80-90 g.m⁻².d⁻¹</td>
<td>Bajic and Zeiss, 2001</td>
</tr>
<tr>
<td>Clay and landfill cover soil</td>
<td>Mixture 45 % V/V CH₄, 45 % V/V CO₂</td>
<td></td>
<td>EC = 40-50 g.m⁻².d⁻¹</td>
<td>Berger et al., 2005</td>
</tr>
<tr>
<td>Soil and sand</td>
<td>Optimal water content for all experiments</td>
<td></td>
<td>EC = 15-20 g.m⁻².d⁻¹</td>
<td>De Visscher et al., 1999</td>
</tr>
<tr>
<td>Soil</td>
<td></td>
<td></td>
<td>EC = 5-7 g.m⁻².d⁻¹</td>
<td></td>
</tr>
<tr>
<td>Multi-layers: Compost + sand (0.9 m)</td>
<td>Aerated at the top</td>
<td>IL = 288 g.m⁻².d⁻¹</td>
<td>EC = 164-283 g.m⁻².d⁻¹</td>
<td>du Plessis et al., 2003</td>
</tr>
<tr>
<td>Agricultural soil</td>
<td>Mixture 50 % V/V CH₄, 50 % V/V CO₂</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Landfill cover soil</td>
<td></td>
<td>IL = 214 g.m⁻².d⁻¹</td>
<td>EC = 171 g.m⁻².d⁻¹</td>
<td></td>
</tr>
<tr>
<td>Compost of pine bark</td>
<td>Aerated at the top</td>
<td>IL = &lt; 420 g.m⁻².d⁻¹</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Multi-layers (from top to bottom):</td>
<td>Pilot-scale open biofilter</td>
<td>IL = 0-6000 g.m⁻².d⁻¹</td>
<td>EC ≤ 1900 g.m⁻³.d⁻¹</td>
<td>Gebert and Groengroeft, 2006a</td>
</tr>
<tr>
<td>Humic topsoil (0.1 m) + sand (0.02 m) + clay (0.67 m) + gravel (0.1-0.3 m)</td>
<td>AERATED AT THE BOTTOM</td>
<td>IL = 590 g.m⁻².d⁻¹</td>
<td>X ≥ 70 %</td>
<td>Huttaratchi and Stein, 2001</td>
</tr>
<tr>
<td>Compost</td>
<td></td>
<td>IL = 105 g.m⁻².d⁻¹</td>
<td>EC = 47 g.m⁻³.d⁻¹</td>
<td>Wilshusen et al., 2004</td>
</tr>
<tr>
<td>Recycling paper pellets</td>
<td>Mixture 30 % V/V CH₄, 70 % V/V CO₂</td>
<td>IL = 105-485 g.m⁻².d⁻¹</td>
<td>EC = 47 g.m⁻³.d⁻¹</td>
<td></td>
</tr>
<tr>
<td>Compost + recycling paper pellets</td>
<td></td>
<td>IL = 485 g.m⁻².d⁻¹</td>
<td>EC = 475 g.m⁻³.d⁻¹</td>
<td></td>
</tr>
<tr>
<td>Compost of wood chips</td>
<td></td>
<td>IL = 160-320 g.m⁻².d⁻¹</td>
<td>EC &lt; 186 g.m⁻³.d⁻¹</td>
<td>Huttaratchi et al., 2000</td>
</tr>
<tr>
<td>Compost of municipal waste</td>
<td></td>
<td>IL = 95 g.m⁻².d⁻¹</td>
<td>EC = 62 g.m⁻³.d⁻¹</td>
<td></td>
</tr>
<tr>
<td>Compost of garden residues</td>
<td></td>
<td>IL = 345 g.m⁻².d⁻¹</td>
<td>EC = 121 g.m⁻³.d⁻¹</td>
<td></td>
</tr>
<tr>
<td>Compost of wood ships</td>
<td></td>
<td>IL = 95 g.m⁻².d⁻¹</td>
<td>EC = 49 g.m⁻³.d⁻¹</td>
<td></td>
</tr>
<tr>
<td>Peat</td>
<td></td>
<td>IL = 435 g.m⁻².d⁻¹</td>
<td>EC = 87 g.m⁻³.d⁻¹</td>
<td></td>
</tr>
<tr>
<td>Soil 1 (Sand 70 %, clay 15 %, silica 15% wt/wt)</td>
<td>Aerated at the top</td>
<td>IL = 95 g.m⁻².d⁻¹</td>
<td>EC = 62 g.m⁻³.d⁻¹</td>
<td>Huttaratchi et al., 2000</td>
</tr>
<tr>
<td>Soil 2 (Sand 70 %, clay 25 %, silica 5 % wt/wt)</td>
<td></td>
<td>IL = 345 g.m⁻².d⁻¹</td>
<td>EC = 121 g.m⁻³.d⁻¹</td>
<td></td>
</tr>
<tr>
<td>Landfill cover soil</td>
<td>Aerated at the top</td>
<td>IL = 281 g.m⁻².d⁻¹</td>
<td>EC = 125-140 g.m⁻³.d⁻¹ (Peak)</td>
<td>Hilger et al., 2000a, b</td>
</tr>
<tr>
<td>Water content: 15 % wt/wt</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mixture: 50 % V/V CH₄, 50 % V/V CO₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Filter bed</td>
<td>Operating conditions</td>
<td>Inlet load</td>
<td>Elimination capacity or conversion</td>
<td>Authors</td>
</tr>
<tr>
<td>----------------------------------------</td>
<td>---------------------------</td>
<td>----------------------------</td>
<td>-----------------------------------------------------------------------------------------------------</td>
<td>--------------------------</td>
</tr>
<tr>
<td>Fresh compost</td>
<td>Aerated at the top</td>
<td>IL = 135-170 g.m⁻².d⁻¹</td>
<td>X = 60 % from day 25 to day 50</td>
<td>Humer and Lechner, 1999b</td>
</tr>
<tr>
<td></td>
<td>Temperature: 18°C</td>
<td>Q = 4.5 mL.min⁻¹</td>
<td>X = 100 % after 55 days</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>X = 100 % after 15 days</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>X = 30-40% from day 10 to day 50</td>
<td></td>
</tr>
<tr>
<td>Mature compost</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Soil</td>
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</tr>
<tr>
<td>Compost of municipal waste</td>
<td>Aerated at the top</td>
<td>IL = ~ 235 g.m⁻².d⁻¹</td>
<td>X = 100 %</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Temperature: 18-20°C</td>
<td>Q = 4.7 mL.min⁻¹</td>
<td></td>
<td></td>
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<tr>
<td>Compost of clarification sludge</td>
<td></td>
<td></td>
<td></td>
<td>Humer and Lechner, 2001</td>
</tr>
<tr>
<td>Soil</td>
<td></td>
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<tr>
<td>Landfill cover soil</td>
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<tr>
<td>Garden soil</td>
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<tr>
<td>Mature compost</td>
<td>In situ</td>
<td>2400 L biogas.m⁻².d⁻¹</td>
<td>X = 100 %</td>
<td>Hupe et al., 1998</td>
</tr>
<tr>
<td>Inorganic material</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Compost</td>
<td>Aerated at the bottom</td>
<td>IL = ~ 1700 g.m⁻².d⁻¹</td>
<td>X = 100 %</td>
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</tr>
<tr>
<td></td>
<td>7000-7500 ppmv CH₄</td>
<td></td>
<td></td>
<td>Nikiema et al., 2004b</td>
</tr>
<tr>
<td>Soil</td>
<td></td>
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<tr>
<td>Landfill cover soil</td>
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<tr>
<td>Agricultural soil</td>
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<tr>
<td>Compost + landfill cover material</td>
<td>In situ open biofilter</td>
<td>IL = 18500-42800 g.m⁻³.d⁻¹</td>
<td>X ≥ 90 %</td>
<td>Straka et al., 1999</td>
</tr>
<tr>
<td>Compost</td>
<td>Bench-scale open biofilter</td>
<td>IL = 288-3120 g.m⁻³.d⁻¹</td>
<td>X = 100 %</td>
<td></td>
</tr>
<tr>
<td>Compost + peat + wood fibers</td>
<td>Large-scale open biofilter</td>
<td>IL = 288-3120 g.m⁻³.d⁻¹</td>
<td>X = 100 %</td>
<td></td>
</tr>
<tr>
<td>Multi-layers</td>
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<tr>
<td>Compost</td>
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<td></td>
</tr>
<tr>
<td>Compost + peat + wood fibers</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soil 1</td>
<td>Aerated at the top</td>
<td>(not available)</td>
<td>X = 40-100 g.m⁻³.d⁻¹</td>
<td>Visvanathan et al., 1999</td>
</tr>
<tr>
<td>Soil 2</td>
<td>Mixture 60 % V/V CH₄, 40 % V/V CO₂</td>
<td>(not available)</td>
<td>X = 75-100 g.m⁻³.d⁻¹</td>
<td></td>
</tr>
</tbody>
</table>

*: This EC was the maximal value obtained. After 5 months of operation, the CH₄ oxidation rate in the biofilter decrease.
was obtained, as against 100% when the IL was only of 186 g.m\(^{-2}\).d\(^{-1}\) (Hettiaratchi et al., 2000). An experiment reported by Humer and Lechner (1999b) on a sandy soil bed, showed the same tendency. However, according to Humer and Lechner (1999b), a flow rate of too low value could lead to poor performance if the filter bed porosity is not high enough.

In the case of methane biooxidation, EBRTs are typically between a few minutes to several hours, due to methane's low-biodegradability (Dammann et al., 1999; Hettiaratchi and Stein, 2001; du Plessis et al., 2003; Nikiema et al., 2004b; Nikiema et al., 2005). In contrast, for VOCs and VICs biofiltration, EBRTs are in general, between 30 and 120 seconds (Jorio and Heitz, 1999). The required operating volumes can reach as much as 100 times those used for treating the same amount of odors (Streese and Stegmann, 2003). Indeed, the size of the biofilter should be at a scale of at least 1 m\(^3\) of filter bed for achieving flow rates of CH\(_4\) in the range of 0.01 m\(^3\).h\(^{-1}\) to 2.5 m\(^3\).h\(^{-1}\) (Straka et al., 1999; Streese and Stegmann, 2003; Haubrichs and Widmann, 2006). The height of the open biofilters with passive ventilation, used for CH\(_4\) elimination, must also be lower than 1 m (Kjeldsen et al., 1997; Boeckx and Van Cleemput, 2000; Stein and Hettiaratchi, 2001; Stein et al., 2001; Park et al., 2002; Tagaris et al., 2003). Open systems are usually less expensive, at least 15%, than closed systems. In 2001, for the non-easily degradable, volatile organic pollutants, the costs for the installation of open biofilters were between 0.25 and 0.4 $ for each m\(^3\).d\(^{-1}\) of polluted gas to be treated (we assume this cost will probably be similar to that for CH\(_4\)). In addition, the industry consensus on capital and operating costs must be considered, and recently, these costs were 0.5-1.8 $ and 0.07-0.1 $ per m\(^3\).d\(^{-1}\) of polluted gas, respectively (Janni et al., 2001).

### 1.5.2. Micro-organisms

**Methanotrophs**

The specific bacteria responsible for the decomposition of CH\(_4\) are known as methanotrophs and constitute a sub-group of the methylotrophs, i.e. bacteria specialized in the degradation of those compounds having only one carbon atom. Earlier, methanotrophs were identified only according to their morphology, their intracytoplasmic membranes structure and some of their
physiological characteristics. Since then, DNA analysis has aided the identification of the genera of methanotrophs (Hanson and Hanson, 1996; Lidstrom, 2001).

There are three basic steps in the decomposition of CH₄. The first reaction step consists of the oxidation of CH₄ to methanol, utilizing the enzyme MMO (Hanson and Hanson, 1996; Auman et al., 2002). The methanol thus obtained is transformed into formaldehyde. The latter compound can be subsequently used in a dissimilatory pathway (i.e., being oxidized to CO₂, with formate as an intermediate) or via several types of assimilatory pathways, leading to the synthesis of cell components, necessary for the growth of methanotrophs (Hanson and Hanson, 1996).

The genera of methanotrophs are grouped into three main types. The genera *Methylomonas, Methylomicrobium, Methylobacter, Methylocaldum, Methylophaga, Methylosarcina, Methylothermus, Methylohalobiuss* and *Methylosphaera* belong to type I. They assimilate formaldehyde by the ribulose monophosphate pathway and their cellular membranes are mainly made up of fatty acids with 16, or sometimes 14 atoms of carbon (Hanson and Hanson, 1996; Tsubota et al., 2005, Kalyuzhnaya et al., 2005; Heyer et al., 2005; Stralis-Pavese et al., 2006). *Methylocystis, Methylocella, Methylocapsa* and *Methylosinus* constitute the type II and they use the serine pathway for their formaldehyde assimilation. Their cellular membranes contain fatty acids of 18 carbons, arranged around the cell periphery (Hanson and Hanson, 1996; Börjesson et al., 1998; Dedysh et al., 2000; Dedysh et al., 2002; Nikiema et al., 2005). *Methylococcus*, known as type X, combines the properties of types I and II i.e. fatty acids with 16 carbons and the assimilation of formaldehyde through both the ribulose monophosphate cycle and the serine pathway. The recently completed genomic sequence of *Methylococcus capsulatus* confirmed the presence of genes directing both pathways (Hanson and Hanson, 1996; Wise et al., 1999; Kelly et al., 2005). Aerobic methanotrophic bacteria are essentially unable to grow on substrates containing C-C bonds as the only carbon source and thus can be considered as obligate C₁ metabolizers. The genus *Methylocella* seems however to be an exception to this rule, being able to use compounds such as acetate, pyruvate, succinate, malate, and ethanol (Dedysh et al., 2005; Horz et al., 2005).
Methylococcus (type X), Methylothermus and Methylocaldum (type I) are moderately thermophilic and their optimal growth temperatures vary from 42°C, for the majority, to 62°C. Methylocaldum, Methylobacter and Methylosphaera, all of type I, are psychrophilic, developing over a range of temperatures, from 5 to 15°C (Trotsenko and Khmelenina, 2002). Methylobacter, type I bacteria, have an optimum growth temperature of around 6°C, while Methylosphaera develop better, between 10 and 13°C, in sea water (Berestovskaya et al., 2002). Mention is made that several methanotrophic communities have the capability of adapting to various temperatures, as long as these lie between 0 and 55°C. However, at temperatures lower than 0°C, the multiplication of the bacteria stops (Humer and Lechner, 1999b). Methylocystis and Methylosinus, bacteria composing type II, are acidophilic. They exhibit a maximum growth rate in acidic media, in the pH range from 5 to 5.5. Methylocystis (type I bacteria) are distributed between the group of halophilic, being at ease in saline media having sodium chloride concentrations ranging from 0.5 to 5.6 % wt/wt, and that of the alcaliphilic, for which the optimal pH ranges between 7.5 and 10 (Trotsenko and Khmelenina, 2002).

★ Methane monooxygenase enzyme

A specific enzyme known as methane monooxygenase or MMO characterizes the methanotrophs. The MMO is the key enzyme allowing methanotrophs to perform the decomposition of CH₄ (Hanson and Hanson, 1996). This enzyme exists in two forms: particulate MMO (pMMO) and soluble MMO (sMMO). The pMMO enzyme can be both found in and synthesized by all methanotrophs, except Methylocella, but the sMMO is almost always present in bacteria of type II and X. However, some Methylococcus strains (type I), possessing the sMMO enzyme, have already been found (Auman et al., 2002).

It is known that methanotrophs containing pMMO (mainly type I) grow more rapidly and are more specific to CH₄ than those having the sMMO (type II and X) (Henckel et al., 2000; Reay and Nedwell, 2004). These differences are noticed when the CH₄ concentration is lower than 1000 ppmv of CH₄ (Segers, 1998). Thus, type I bacteria with pMMO develop quickly when the experimental conditions permit and become dominant in environments when such rapid growth is allowed (Henckel et al., 2000). However, they are sensitive to variations in nutrients
availability, mainly the nitrogen and copper, and in the CH₄ concentrations. On the other hand, populations of type II and X bacteria, having the sMMO, are quasi-steady and very stable in various environments, such as the landfill covers (Henckel et al., 2000; Crossman et al., 2004). In addition, sMMO also has affinities for a variety of compounds, such as methanol, several chlorinated compounds and hydrocarbons, among which are the alkanes, olefinic hydrocarbons and aromatic compounds (Hanson and Hanson, 1996; Dunfield et al., 1999; Vorholt, 2002; Hilger and Humer, 2003; Erwin et al., 2005; Hesselsoe et al., 2005; Lindner et al., 2005).

Oxygen and carbon dioxide needs of methanotrophs

All of the methanotrophs species can be found in small quantities in any environments exposed simultaneously to significant amounts of CH₄ and O₂ (Börjesson et al., 1998; Dammann et al., 1999). For example, *Methylomonas* and *Methyllobacter* (type I), *Methylocystis* and *Methylosinus* (type II) as well as *Methylococcus* (type X) have already been isolated from the cover soils of several landfills (Börjesson et al., 1998). However, the distribution of methanotrophs within a filtering material is not a random process since each type of bacteria develops preferentially in that portion offering the most advantageous conditions for its growth (Henckel et al., 2000; Gebert et al., 2003). An O₂ concentration of 21% V/V, associated with a CH₄ concentration less than 1000 ppmv better supports the growth of type I bacteria. On the other hand, when the CH₄ concentration is superior to 1% V/V and the concentration of O₂ is low (about 1% V/V), type II bacteria develop better (Hanson and Hanson, 1996; Henckel et al., 2000; Crossman et al., 2004). However, there are exceptions to this scheme and some type I bacteria have their growth stimulated only in the presence of an appreciable concentration of CH₄ (> 1% V/V), and correspondingly, a low amount of O₂ (< 1% V/V) (Henckel et al., 2000; Erwin et al., 2005). Bender and Conrad (1994), Czepiel et al. (1996) and Stein and Hettiaratchi (2001) have shown that, by increasing the O₂ concentration from 3 to 20% V/V in the gas mixture, the CH₄ conversion varies only slightly (less than 10%). However, a decrease of O₂ concentrations from 3 to 1% causes the fall off of CH₄ oxidation of more than 50%. However, during the experiments of Stein and Hettiaratchi
(2001), the maximal CH$_4$ elimination was obtained at O$_2$ concentration between 0.75 and 1.6%.

The presence of CO$_2$ in a biofilter at the same time as the CH$_4$ can modify the behavior of the micro-organisms present. According to Acha et al. (2002), the activity of the methanotrophs, using the serine pathway for the assimilation of formaldehyde obtained during the decomposition process of CH$_4$, requires some CO$_2$ input (partial pressure of CO$_2$ around 11.6 kPa) (Acha et al., 2002).

- **Non-methanotrophic bacteria**

Nitrifying bacteria, responsible for the decomposition of ammonia (NH$_3$), can also degrade CH$_4$, but their performance rate is less than 5% that of the pure methanotrophic populations (Hanson and Hanson, 1996; Bodelier and Frenzel, 1999). Also, some bacteria involved in the decomposition of methanol are also capable of degrading CH$_4$, but only if the CH$_4$ concentrations remain below 10% V/V. The optimal growth temperature for these bacteria is around 35°C (Hughes et al., 2002). There are also certain anaerobic bacteria that are able to degrade CH$_4$. Such bacteria are active when immersed in aqueous media. These bacteria work in tandem with those involved in reducing sulphates, the reaction requiring additional sources of carbon such as acetate or lactate (Hanson and Hanson, 1996; Kotelnikova, 2002; Valentine, 2002). The minimal sulphate concentration in the system must be approximately 1 mmol.L$^{-1}$ (Segers, 1998). The hypothesis of coupling between sulphate reduction and anaerobic methane oxidation is also supported by studies on a landfill-leachate plume (Grossman et al., 2002) and in ground water (Van Stempvoort et al., 2005). However, experiments to isolate these anaerobic bacteria remain unsuccessful to date (Conrad, 1996; Segers, 1998; Kotelnikova, 2002). Recently, a microbial consortium has been isolated, found to be performing methane oxidation, coupled to nitrate reduction, in the absence of oxygen. The consortium includes two micro-organisms: a bacterium and an archaeon, belonging to as yet an unknown species (Raghoebarsing et al., 2006).
1.5.3. Inoculation and incubation

When contact is created between methanotrophs and CH\textsubscript{4} in a biofilter, an induction step, during which X is weak (0-10 % of the steady state conversion), always precedes the optimal system functioning. This lag phase is due to the activation and growth of the methanotrophic bacteria (Bender and Conrad, 1995; Henckel et al., 2000) and its duration is determined by the operating conditions (CH\textsubscript{4} concentration, temperature and moisture of the filter bed). During the experiments carried out by Henckel et al. (2000) in microcosms maintained under a CH\textsubscript{4} continuous flow environment, some 6 and 19 days were required to reach steady X, respectively for high (10000 ppmv) and low (1000 ppmv) CH\textsubscript{4} concentrations. In order to aid the establishment of the specific and competitive methanotrophic population in the filter bed, inoculation of the bed by selected methanotrophic bacteria is usually performed, even if the success of this practice is not guaranteed.

At the laboratory scale, another common practice involves incubation, consisting of a prolonged exposure (several days or weeks) of the filter bed to significant CH\textsubscript{4} concentrations, ranging between 1000 ppmv and 200000 ppmv. The higher the CH\textsubscript{4} concentration, the more the growth of the methanotrophs is promoted. The consequence then is a rapid increase in the oxidation rate (Bender and Conrad, 1995; Hanson and Hanson, 1996; Henckel et al., 2000; Le Mer and Roger, 2001; Crossman et al., 2004; Mor et al., 2006). For example, the oxidation rate for a CH\textsubscript{4} at initial concentration of 100000 ppmv is around 0.8 g CH\textsubscript{4}.kg soil\textsuperscript{-1}.d\textsuperscript{-1} which is 10 times higher than the value observed for a CH\textsubscript{4} initial concentration of 10000 ppmv (Bender and Conrad, 1995). Since all bacteria do not develop within the same range of CH\textsubscript{4} concentrations, the choice of the incubation parameters must be made judiciously. At the end of the induction phase, a peak value in the conversion up to 3 times that obtained for a steady operation (e.g. X = 64 %) can be noted (Hettiaratchi and Stein, 2001; Abichou et al., 2006a).
1.5.4. Parameters

○ Filter bed

The filter bed is the solid phase on which the biofilm containing the micro-organisms is to be formed. It must present sufficient space for the development of micro-organisms and it should also have a texture providing a great moisture-holding capacity, in addition to appropriate bacteriological and mechanical properties. It must also be inexpensive (Humer and Lechner, 1999a, b; Bajic and Zeiss, 2001; Nikiema et al., 2004b). Various experiments, conducted at the laboratory scale, have been performed to test various filter bed structures, using natural materials such as soils and composts or synthetic materials. The results obtained are presented in Table 1-3 and will be expressed in terms of the IL, EC and X. Composts of various origins (solid wastes, vegetable wastes, clarification sludges...) were tested during the CH₄ biofiltration. Compost, made from mature yard wastes yielded the best results with EC up to 590 g.m⁻².d⁻¹ and at values for X of between 90 and 100 %, during more than 100 days of continuous filter operation (Haubrichs and Widmann, 2006). Compost, made from dead leaves, also yielded good results (Hettiaratchi and Stein, 2001; Wilshusen et al., 2004). In addition, the time required to reach 100 %, conversion is less for the mature compost than that for freshly generated compost, being some 15 days and 55 days respectively. This result makes the mature compost a preferred framework for the biofiltration of CH₄ (Humer and Lechner, 1999b).

The soils most often employed are those of landfills covers (Hettiaratchi et al., 2000; Hilger et al., 2000a), but agricultural soils, soils derived from mountains, forests and rice plantations, peat bogs and swamps, have also been tested in CH₄ biofiltration (Dobbie and Smith, 1996; Hütsch, 1998b; Del Grosso et al., 2000; Hettiaratchi et al., 2000; Cai and Mosier, 2000; Nozhevnikova et al., 2001; Stein and Hettiaratchi, 2001; Novikov and Stepanov, 2002; Kravchenko, 2002). All of these soils contain different proportions of sand, clay, silica and organic matter. The most effective soils for CH₄ elimination are those taken directly from the upper layers of landfill covers. An EC of 435 g.m⁻².d⁻¹, corresponding to an X value of greater than 80 %, has been reported in the literature (Park et al., 2002). The addition to a soil of organic residues, such as vegetable residues (beet leaves, wheat straw), clarification sludge or
composts, can improve its CH₄ elimination. The EC values, reported from these modifications (100 to 200 g.m⁻².d⁻¹), correspond to some 40% to 100% of CH₄ conversion, and remain below the EC's obtained during similar experiments with compost-based beds (Börjesson et al., 1998; De Visscher et al., 1999; Humer and Lechner, 1999b; Park et al., 2002). The mean size of the soil particles must preferably lie between 0.5 and 2 mm (Bender and Conrad, 1995; Kightley et al., 1995; Börjesson et al., 1998; Hettiaratchi et al., 2000; Min et al., 2002). Indeed, when particle sizes are less than 0.02 mm, the bed tends to become packed, preventing the effective diffusion of pollutants in the gas phase and then negatively affecting the conversion (Bender and Conrad, 1995; Le Mer and Roger, 2001; Min et al., 2002).

With either synthetic or inert filter materials, a few interesting results were obtained during the CH₄ biofiltration. An experiment, involving biofiltration by percolation with glass particles, has been reported (Sly et al., 1993). For a residence time of 20 min. and an IL of around 200 g.m⁻².d⁻¹, more than 95% of CH₄ conversion was achieved. But the best EC reported in the literature is 700 g.m⁻².d⁻¹, obtained by Nikiema et al. (2004b) during their experiments with an inorganic-packed bed biofilter of 0.018 m³, the gas flow rate being 6 m³.d⁻¹ and the CH₄ concentration maintained at between 7000 and 7500 ppmv.

○ Nutrients

Nutrients such as copper, nitrogen and phosphorus are strong determining factors for the success of CH₄ biofiltration, since they are necessary for the growth of the micro-organisms (Trotsenko and Khmelenina, 2002). These nutrients, unless already present in the filter bed in a bioavailable form, must be added to the solution used to humidify the filter bed (Nikiema et al., 2005).

★ Copper

It has been shown that, while copper inhibits the sMMO enzyme at concentrations superior to 1μmol.L⁻¹, it supports the synthesis of the pMMO for concentrations between 1 and 5 μmol.L⁻¹ (Hanson and Hanson, 1996). Thus, by adjusting the bed copper concentration, it is possible, in various cases, to develop a medium rich in bacteria of types I or II (Wise et al.,
1999; Erwin et al., 2005). It has also been noted that, in adding around 0.02 g of copper, in the form of CuCl₂, per kg of paddy soil, CH₄ oxidation is slightly stimulated (an increase of around 5 %) (Mohanty et al., 2000).

* Nitrogen compounds

Nitrogen element is an important nutrient for the methanotrophic bacteria. This element is usually provided to micro-organisms in an inorganic form: e.g. nitrate (NO₃⁻), ammonium (NH₄⁺) or nitrite (NO₂⁻) ions. Various tests have been performed and described in the literature to determine the influence of each of these compounds. Usually, they were undertaken with soils from various environmental sites, such as landfills, rice paddies, containing indigenous populations of micro-organisms. The influence of NH₄⁺ and NO₃⁻ seems to be variable (Hütsch, 1998a, b; Bodelier and Laanbroek, 2004; Reay and Nedwell, 2004). The sources of NH₄⁺ most frequently tested are ammonium chloride, ammonium sulfate and urea. For NO₃⁻, sodium nitrate and potassium nitrate are the most studied. On some occasions, ammonium nitrate was used as a nitrogen source (Kightley et al., 1995; Hettiaratchi et al., 2000). Hettiaratchi et al. (2000) reported an example of improvement of CH₄ elimination by some 100 %, following the addition of nitrogen (25 mg N per kg soil) in the form of NH₄⁺ or NO₃⁻. But, according to Chiemchaisri et al. (2001a), 30 mg N per kg soil or more, added in the form of NH₄⁺ or NO₃⁻ inhibit the CH₄ elimination. In the case of NH₄⁺, many authors also report the risk of competition between CH₄ and NH₄⁺ when the latter was provided as a nitrogen source (Mancinelli, 1995; Boecks and Van Cleemput, 1996; Humer and Lechner, 1999b; Sitaula et al., 2000; Novikov and Stepanov, 2002). Indeed, methanotrophs can convert NH₄⁺ to NO₂⁻. During the experiments conducted by Novikov and Stepanov (2002), 12 to 28 % of the methanotrophic population was dedicated to a nitrification step instead of the CH₄ oxidation. In soils however, the decrease of CH₄ elimination rate was observed only after the nitrogen concentration reached 10-200 mg N-NH₄⁺.kg soil⁻¹ (Bronson and Mosier, 1994; Cai and Mosier, 2000; Hettiaratchi et al., 2000; Novikov and Stepanov, 2002; Park et al., 2004). But, the importance of this inhibition depends on the type of soil (Novikov and Stepanov, 2002; Wang and Ineson, 2003; Reay and Nedwell, 2004) and can be further accentuated if other operating conditions, such as moisture content, are not satisfactory (Cai and Mosier, 2000).
Generally, an increase of the N-NH$_4^+$ concentration results in a higher percentage of inhibition at constant CH$_4$ concentration. Conversely, an increase of CH$_4$ concentration results in a lower percentage of inhibition at constant N-NH$_4^+$ content (De Visscher et al., 1999; Cai and Mosier, 2000; Kravchenko, 2002). Therefore, the inhibitory effect of NH$_4^+$ could be minimized if higher CH$_4$ concentrations were continuously provided to the filter media.

For the case of equal nitrogen supply, NH$_4^+$ will be less inhibiting than NO$_3^-$ (Kravchenko, 2002; Wang and Ineson, 2003). But, according to Mancinelli (1995), NO$_3^-$ instead of NH$_4^+$ is the preferred source of fixed nitrogen for the methanotrophs. Le Mer and Roger (2001) stated that the presence of NO$_3^-$ can improve CH$_4$ elimination. Potassium nitrate has been used for the culture of methanotrophs since 1970 as a component of the "nitrogen minimal salt" (NMS) nutrient solution, which includes 0.14 g of N-NO$_3^-$ per liter (Whittenbury et al., 1970). During experiments with an inorganic filter material, conducted by Nikiema et al. (2005), the authors noted that increasing nitrogen content supplied as sodium nitrate, from 0.14 g-N.L$^{-1}$ to 0.75 g-N.L$^{-1}$ in the nutrient solution, led to 5 times increase in the EC, from 130 to 700 g.m$^{-2}$.d$^{-1}$. However, a further increase of nitrogen content (> 0.75 g-N.L$^{-1}$) resulted in a decrease of the CH$_4$ oxidation conversion. During other experiments in soils, variations in the nitrogen supply between 25 and 100 mg N-NO$_3^-$:kg soil$^{-1}$ did not show any noticeable influence on the biological elimination of CH$_4$ (Boecks and Van Cleemput, 1996; Park et al., 2002). A NO$_3^-$ inhibition in soils was reported for high concentrations of around 2500 mg N:kg soil$^{-1}$ (Kumaraswamy et al., 2001).

Nitrite is well known as an inhibiting compound for methane elimination by methanotrophs (King and Schnell, 1994; Mancinelli, 1995; Boecks and Van Cleemput, 1996; Hanson and Hanson, 1996). This compound can be generated when incomplete nitrification processes occurs in the filter media (Dunfield and Knowles, 1995; Kravchenko, 2002).

Sometimes, the inhibitory effect associated with the nitrogen content is otherwise caused by the salt effect. Indeed, the addition of salts containing inorganic nitrogen can change the overall ionic content of the soil (Hanson and Hanson, 1996; King and Schnell, 1998; Kravchenko, 2002). Also, the influence of the nitrogen content is noticeable, especially in the case of low CH$_4$ concentrations, less than 100 ppmv (King and Schnell, 1994).
Finally, it is important to mention that some methanotrophs are capable of N$_2$ fixation and express nitrogenase (Murrell and Dalton, 1983; Kim and Graham, 2001; Dedysh et al., 2002; Bodelier and Laanbroek, 2004). Until recently, only type II methanotrophs and type X Methylococcus were thought to be capable of nitrogen fixation (Oakley and Murrell, 1988; Dedysh et al., 2000). More recent work has revealed nitrogenase activity by the acetylene reduction route, and the presence of nifH genes generated by polymerase chain reaction amplification in a variety of methanotrophic species, belonging to both types I and II (Auman et al., 2001; Boulygina et al., 2002). These data suggest that methanotrophs can play a significant role in nitrogen fixation in several natural environments, such as freshwater lakes (Zani et al., 2000). However the importance of N$_2$ fixation during biofiltration of methane remains to be assessed.

★ Phosphorus

Generally speaking, phosphorus is of universal importance in promoting the growth of bacteria. However, despite its evident importance, it appears (from a close examination of the relevant literature) that only Kightley et al. (1995) have tried to obtain basic understanding of this element’s contribution to the CH$_4$ biofiltration process. In their published studies, they have shown that the addition of a quantity of clarification sludge nutrient to an ordinary soil-based filter bed (final nutrient concentrations present in the soil: 0.1g P per kg and 0.1 g N per kg) increased the rate of conversion of CH$_4$ by ~ 26 %. On the other hand however, the addition of some 0.1 g of P-K$_2$HPO$_4$ nutrient per kg of the same soil did not result in any noticeable effect on promoting the CH$_4$ elimination property of the soil (Kightley et al., 1995; Hettiaratchi et al., 2000; Le Mer and Roger, 2001). Thus, the role and activity of phosphorus, in the above described circumstances, remains unclear and further investigations will therefore be required to elucidate the mechanisms leading eventually to either the promotion of the bacterial growth or to its inhibition.

★ Other elements

Potassium sulphate or manganese oxide increases the oxidation of CH$_4$ (Kumaraswamy et al., 2001). Addition of lime provides a soil-based bed with a neutral pH and thus appears to be
interesting for CH₄ biofiltration (Hilger et al., 2000b). Excessive concentrations of sodium chloride and potassium chloride are both CH₄ elimination inhibitors (Cai and Yan, 1999; Kravchenko, 2002; Gebert et al., 2003), probably due to their osmotic effects.

○ Operating conditions

★ Temperature

Methane oxidation is exothermic and, theoretically releases about 880 kJ per mole CH₄. In case of bio-oxidation, the larger portion of this energy is used for the anabolic reactions during CH₄ biodegradation. The other portion is transferred to both the filtering material and to the mixture of gases that traverses it. The reaction heat released creates a temperature gradient in the biofilter, between its lower and upper surfaces (Humer and Lechner, 1999b; Nikiema et al., 2004b; Nikiema et al., 2005). The significance of this thermal gradient depends on the input gas flow rate, the conversion, the type of filtering material and various other influential parameters. For example, a temperature change of around 4°C is noted for an inlet gases flow rate of 3.6 m³.d⁻¹, when the volumetric EC in a compost-based biofilter is 840 g CH₄.m⁻³.d⁻¹ (Streese et al., 2001). With an inorganic material, Nikiema et al. (2004b, 2005) did not observe any temperature gradient in the biofilter.

Tests on the influence of temperature during CH₄ biofiltration were conducted with common filter materials, such as soils and composts. In general, the optimal bed temperature is usually found to lie between 29°C and 30°C for composts (Dammann et al., 1999; Streese et al., 2001; Mor et al., 2006) and between 25°C and 36°C for soils (Whalen et al., 1990; Bender and Conrad, 1995; Hanson and Hanson, 1996; Boeckx and Van Cleemput, 1996; Visvanathan et al., 1999; Cai and Yan, 1999; Christophersen et al., 2000; Min et al., 2002; Mingxing and Jing, 2002; Park et al., 2004). Apart from these intervals, the decrease in the conversion was important. For example, it fell by around 50% when the temperature was reduced from 30°C to 20°C or from 29°C to 24°C (Dammann et al., 1999; Streese et al., 2001). Between -5°C and 10°C as the ambient temperature, the biological elimination of CH₄ in an opened biofilter system (landfill cover soil) is considerably decreased, i.e., more than 80% compared to the value at 15°C (Christophersen et al., 2000; Le Mer and Roger, 2001). Therefore, the influence
of temperature on the biological process constitutes the major limit for open biofilters, mainly
during the winter season, when temperature falls to values lower than the limit that can be
tolerated by the micro-organisms consuming the CH$_4$ (Humer and Lechner, 1999b).

On the other hand, if higher temperatures (> 35°C) stimulate the activity of some
methanotrophs, it should be noted that in such cases, the biofilter beds dry more quickly; this
in turn leading to a decrease in the conversion rate (Visvanathan et al., 1999).

★ pH of the filter bed

From a practical viewpoint, the pH of the filter bed is a parameter of lesser importance
because the biodegradation of CH$_4$ does not generate intermediate or final products capable of
influencing significantly the pH. The optimal pH values for the oxidation of CH$_4$ are in fact
the same as those promoting the growth in the majority of methanotrophs bacteria. These are,
in general, neutrophiles but they can, according to Hanson and Hanson (1996), tolerate pH
values between 5.5 and 8.5. However, abrupt variations in the pH are adverse to methane
elimination. A permanent inhibition was noted when the pH of the soil was changed by
around 2 units, from 6.8 to 4.7 or from 6.8 to 9.0. This inhibition was partial for a unit
variation, from 6.8 to 5.9 or 6.8 to 7.7, over the same operating conditions. This observation
brought these present authors to propose a more restricted range of operating pH values, being
that from 5.9 to 7.7 (Arif et al., 1996). In soil-based filter beds, the optimum pH ranges
between the values of 6.7 and 8.1 (Bender and Conrad, 1995) while for peat, the range lies
between 5 and 6.5 (Le Mer and Roger, 2001).

★ Filter bed moisture

The filter bed moisture content is another key factor that determines the performance of the
biofilter (Börjesson et al., 1998). When the moisture is too high, it acts as a rate-limiting factor
by preventing the flow and transfer of CH$_4$ and O$_2$ (Humer and Lechner, 1999b; Cai and Yan,
1999; McLain, 2000; Mingxing and Jing, 2002; McLain et al., 2002; Park et al., 2002). The
optimal filter bed water content depends on both the gas flow rate and the type of filter bed
(soil, compost or other material employed) (Christophersen et al., 2000). Table 1-4 presents
some typical water contents suggested in the literature. Optimal moisture content of soil materials (from the upper layers of landfills) ideally lies between 13 and 15.5 % wt/wt, on a dry basis (Whalen and Reeburgh, 1996; Boeckx and Van Cleemput, 1996; Chiemchaisri et al., 2001b; Stein and Hettiaratchi, 2001; Jäckel et al., 2001; Park et al., 2002; Park et al., 2004). However, Giani et al. (2002) reported a case for which the optimal moisture content of the landfill cover soil, used for biofiltration, was 25-30 % wt/wt on a dry basis (at moisture values lower than 15 %, the EC of CH₄ was reduced by 50 % or more, compared to the maximal value). For composts or biological residues, optimal bed moisture lies between 25 % and 50 % wt/wt (Humer and Lechner, 1999b). Methane conversion levels in soils that are less wet than the optimum level are lower than those attained in greater moisture content soils (Boeckx and Van Cleemput, 1996; Cai and Yan, 1999; Stein and Hettiaratchi, 2001). Indeed, for a moisture content of around 745 g.kg paddy soil⁻¹, i.e. approximately 265 % of the optimal moisture (280 g.kg paddy soil⁻¹), the conversion was only 24 % of the maximum conversion. When the moisture content of the same material was changed to around 150 g.kg soil⁻¹, the conversion fell to only 1 % of that of the soil at its optimal moisture conversion (Cai and Yan, 1999).

### TABLE 1-4: OPTIMAL WATER CONTENT FOR SOME FILTER BEDS USED FOR METHANE ELIMINATION

<table>
<thead>
<tr>
<th>Filter bed</th>
<th>Water content: % wt/wt</th>
<th>Authors</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compost</td>
<td>25-50</td>
<td>Humer and Lechner, 1999b</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Boeckx and Van Cleemput, 1996</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Park et al., 2002</td>
</tr>
<tr>
<td>Landfill cover soil</td>
<td>13-30</td>
<td>Stein and Hettiaratchi, 2001</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Visvanathan et al., 1999</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Giani et al., 2002</td>
</tr>
<tr>
<td>Meadow soil</td>
<td>30-50</td>
<td>Mingxing and Jing, 2002</td>
</tr>
<tr>
<td>Woodland soil</td>
<td>18-33</td>
<td>Mingxing and Jing, 2002</td>
</tr>
<tr>
<td>Various soils</td>
<td>11-35</td>
<td>Bender and Conrad, 1995</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Christophersen et al., 2000</td>
</tr>
</tbody>
</table>
1.6. Landfill covers

Open biofilters are an attractive alternative for the older or smaller landfills, when gas collection systems cannot be installed for biogas valorization or elimination (du Plessis et al., 2003; Berger et al., 2005). To our knowledge, there are no industrial applications related to the \( \text{CH}_4 \) biofiltration process in North America at the present time. However, at least the subjects of 3 patents registered worldwide, are more or less related to landfill biogas treatment, using in situ filters (Bergmann et al., 1998; Lee et al., 2002; Contec and Landkeis, 2004). Landfill covers that permit a natural biological elimination of \( \text{CH}_4 \) could be considered as natural open biofilters. These covers are usually made of soils, sand or clay and represent the daily and final cover of the wastes in the landfill. Methane elimination in such covers is caused by the presence of methanotrophic populations. The behavior of a landfill cover is similar to that of an open biofilter equipped with passive aeration, except that the IL is usually low. Indeed, the mean IL of \( \text{CH}_4 \) in landfills covers generally lie between 50 and 340 g \( \text{CH}_4 \).m\(^{-2}\).d\(^{-1}\) (Jones and Nedwell, 1993; Bogner et al., 1997; Humer and Lechner, 2001; Perera et al., 2002; De Visscher and Van Cleemput, 2003; Park et al., 2004; Gebert and Groengroeft, 2006a; Abichou et al., 2006a, b). Börjesson and Svensson (1997) have noted that diurnal \( \text{CH}_4 \) emissions are up to 100% higher than the daily values, depending on the ambient temperature and air pressure. Also, \( \text{CH}_4 \) fluxes are themselves very variable and are usually not evenly distributed (Börjesson et al., 1998; Segers, 1998; Gebert et al., 2001; Gebert and Groengroeft, 2006a). Important rates of irrigation of the biofilter bed by rain may cause a decrease in the EC, up to 40%, by preventing the flow of biogas (Berger et al., 2005; Horz et al., 2005). On the other hand, even with a well constructed collection system, leaks always exist in such landfill covers, leading to the development of very important levels of emission in certain zones, up to 9000 g \( \text{CH}_4 \).m\(^{-2}\).d\(^{-1}\) (Maurice et al., 1999; Chanton and Liptay, 2000; Bajic and Zeiss, 2001; Spokas et al., 2006). The covering of the whole landfill with a 0.1-0.6 m layer of mulch or compost helps to avoid uncontrolled \( \text{CH}_4 \) emissions from older landfills, when IL < 90 g.m\(^{-2}\).d\(^{-1}\) (Chanton and Liptay, 2000; Mor et al., 2006).

The performance of the landfill cover in the treatment of \( \text{CH}_4 \) is influenced by two main parameters: the temperature and the available oxygen concentration. During winter, the \( \text{CH}_4 \)
conversion within landfill covers is reduced to around 3-10% (Chanton et al., 1999; Chanton and Liptay, 2000; Giani et al., 2002; Spokas et al., 2006). However, at an ambient temperature of 2°C, Christophersen et al. (2000) have noted that it was still possible to biodegrade all of the CH$_4$ produced in older landfills if IL is inferior to 70 g.m$^{-2}$.d$^{-1}$. Indeed, the microbial activity, combined with the isolation effect of the bed, contributes to keeping the inner bed layer at temperatures 5-8°C higher than the ambient temperature (Berger et al., 2005). In summer, the CH$_4$ conversion can reach 50% or more (Börjesson et al., 1998; Chanton et al., 1999; Chanton and Liptay, 2000; Perera et al., 2002; Spokas et al., 2006). On the other hand, the diffusion of atmospheric O$_2$ is limited and generally, an oxygenated zone of only 0.6-0.8 m is observed (Nozhevnikova et al., 1993; Börjesson and Svensson, 1997; Klusman and Dick, 2000; Christophersen and Kjeldsen, 2001; Chiemchaisri et al., 2001b; Perera et al., 2002; Tagaris et al., 2003; Crossman et al., 2004; Kallistova et al., 2005).

The landfill cover height must be at least 0.7 m for achieving best results (Giani et al., 2002). In order to reduce the influence of temperature, and the problems related to O$_2$ diffusion, on the landfill covers and also for open biofilters, many authors have favored the use of multi-layer beds (Bajic and Zeiss, 2001; Streese and Stegmann, 2003; Berger et al., 2005). For example, at the lowest bed level (0.25-0.9 m above entry point), a material, with the mean porosity such as soils or sand, is provided. This layer is employed for the retention of the filter bed humidity, in order to avoid quick bed drying events. The most important part of the overall CH$_4$ elimination process (typically 60%) will take place in the second layer, made of compost, for example (Bajic and Zeiss, 2001; Berger et al., 2005). On a landfill site, the use of composts of ~0.3 to 0.6 m deep, instead of soils as an oxidation layer, can double the overall CH$_4$ elimination because of the availability of nutrients for the bacteria, while the higher porosity level leads in turn to a more satisfactory diffusion of the O$_2$ uptake (Hilger and Humer, 2003). A third layer may be used at the top of the biofilter as a heat retention blanket, which will provide a particularly important practical feature to the biofilter when the atmospheric temperature falls during the winter season (Straka et al., 1999; Kallistova et al., 2005).
1.7. Conclusion

An important source of greenhouse gas emissions is that related to methane contained in biogas and released from sanitary landfills. In the present paper, a brief review of the composition, the production and valorization of the biogas is described. When this valorization is not possible, an alternative treatment lies in the biofiltration remediation of CH₄ emissions, particularly from older and smaller landfills. The main part of this paper focuses on this biotechnology.

The biofilter can be either an open or a closed system, equipped with either an active or a passive oxygen feed system. The use of open systems, whilst being more financially interesting, can also permit methane conversions of 60 % and even more in specific cases, even if control of the process operational laboratory scale parameters is barely feasible. But, to our knowledge, there is no application in North America for this landfill technology. However, landfill covers play the role of a natural biofilter and eliminate up to 320 g CH₄.m⁻².d⁻¹. On the other hand, closed systems are often more compact and provide for the better management and control of the operational parameters. The bed volume required for CH₄ control in a biofilter is at least 1 m³ bed for a CH₄ gas flow in the range of 0.01 m³.h⁻¹ to 2.5 m³.h⁻¹.

The majority of authors appear to agree on the point that matured compost constitutes a satisfactory filter material for supporting the biofiltration of CH₄. Indeed, both the presence of nutrients in the compost, in addition to its physical properties supports the growth of methanotrophs. The filter bed optimal temperature appears to lie between 29°C and 30°C, and its optimal moisture level is found to lie between 25 % and 50 % wt/wt, on a wet basis. However, interesting results could also be obtained when using an inorganic-based bed biofilter.

Methane biofiltration is, at the same time, both a simple and a complex process. Indeed, even if the overall phenomenon of the reaction seems to be well known, many aspects are still misunderstood and contradictory theories are proposed, especially in relation to reaction optimization like nutrients, for long-term operations.
1.8. Acknowledgements

The authors gratefully acknowledge the Natural Sciences and Engineering Research Council of Canada (NSERC) for their financial contribution to the project and express their gratitude to Dr. P. Lanigan for text review. One of the authors (J. Nikiema) would like to thank the NSERC for providing a scholarship for her doctoral studies (Canada Graduate Scholarships Program).
2.1. Abstract

Nitrogen is known to have an influence on the methane biodegradation. However, the quantities of nitrogen to be provided during the biological treatment of methane are still unclear. In this study, the influence of the concentration of nitrogen, provided in the form of nitrate through a nutrient solution, has been determined. The influence of the methane inlet load on the methane elimination performance was also investigated. The lab-scale study has been conducted with 2 filter materials: one of an organic type and the other of an inorganic type. The inorganic material appeared to give stable elimination capacities, up to 3 times higher than those with the organic material. The maximum elimination capacities were 36 g/m³/h in the inorganic-based bed and 15 g/m³/h in the organic-based bed. For both filter materials, it was confirmed that the increase of the inlet load of methane results in an increase of the elimination capacity, more important in the inorganic-based biofilter, when the nitrogen concentration was above 0.25 g/L, than in the organic-based bed. We also established that the optimum nitrogen concentration required for a proper operation is usually around 0.75 g/L but lower levels of nitrogen, i.e. 0.50 g/L could be applied when the inlet load is below 55 g/m³/h. The knowledge of the nitrogen requirement for a specific inlet load favors a proper operation of the methane biofilter, which leads to high methane removal efficiencies.
Résumé

L’azote est un élément nutritif reconnu pour affecter la biodégradation du méthane. Toutefois, les quantités exactes de cet élément qui doivent être fournies au bioréacteur lors du traitement biologique du méthane demeurent floues. Dans cette étude, l’influence de la concentration de l’azote, fourni sous la forme de nitrate au moyen d’une solution nutritive, a été déterminée. L’influence de la charge initiale de méthane a également été étudiée. En outre, cette étude expérimentale, menée à l’échelle laboratoire, a permis de comparer deux types de lits filtrants: l’un de type organique, et l’autre de type inorganique. Ce dernier s’est révélé le plus efficace puisqu’il a permis d’obtenir des capacités d’élimination jusqu’à 3 fois plus importantes que celle réalisées dans les mêmes conditions par le lit organique. La capacité d’élimination maximale a été de 36 g/m$^3$/h dans le lit inorganique et de 15 g/m$^3$/h dans le lit organique. Pour les 2 matériaux filtrants, il a été confirmé que l’augmentation de la charge initiale de méthane occasionne une augmentation de la capacité d’élimination, certes plus importante dans le biofiltre garni avec le matériau inorganique que dans celui organique, lorsque la concentration d’azote dans la solution nutritive était $> 0.25$ g/L. Il a également été prouvé que la concentration optimale d’azote requise pour le bon fonctionnement du biofiltre se situe autour de $0.75$ g/L. Toutefois, des concentrations plus faibles, i.e. $0.50$ g/L pourraient être appliquées lorsque la charge initiale de méthane est inférieure à $55$ g/m$^3$/h. Cette détermination de la quantité d’azote requise pour une charge initiale donnée de méthane favorise un fonctionnement optimal du biofiltre, ce qui résulte en des conversions de méthane élevées.

2.2. Introduction

Methane (CH$_4$) is among the most abundant hydrocarbons in nature. In Canada, agriculture, landfills, natural gas delivery systems or petroleum exploitation are the main sources of CH$_4$ emissions (Environment Canada, 2008). For the control of this greenhouse gas, several processes are exploited to date. Incineration when applicable, with heat recovery or not, is the most often used. Valorization through chemical reactions, leading to valuable products like methanol, may also be performed (Nikiema et al., 2007). In some particular cases, when such solutions cannot be applied, (like for old or small landfills), biofiltration has proved to be
interesting (Abichou et al., 2006). With this biotechnology, micro-organisms, in particular the methanotrophs, oxidize the methane pollutant to generate less harmful products like water, carbon dioxide (CO₂), biomass and salts (Nikiema et al., 2005).

For an efficient operation of a CH₄ biofilter, several parameters must be controlled, the most important being the physicochemical characteristics of the filtering bed (which include the availability and types of nutrients, average size of the bed particles, etc.), the CH₄ flow rate and concentration, and the operating parameters, like temperature and humidity of the packing material and of the polluted gas.

For biofiltration processes, compost-based beds are usually preferred because they naturally contain nutrients, useful for the growth of bacteria during biofiltration. Various experiments, reported in the literature, were undertaken with composts as a filter material (Nikiema et al., 2007). In the case of CH₄ biofiltration, Streese and Stegmann (2003) reported an elimination capacity (EC) of 63 g/m³/h obtained 3 months after the starting of a bench-scale biofilter for an inlet load (IL) of 130 g/m³/h. But this performance rapidly decreased after the 5th month of operation, probably because of the reduction of nutrients availability in the biofilter, of the accumulation of exopolysaccharides in the packing material and also of the compaction of the packing material. A decrease of the CH₄ elimination performance after 2-3 months of operation only, for a similar filter material has been observed by Hettiaratchi and Stein (2001).

In addition, several experiments of CH₄ biofiltration, carried out with soil-based beds, are reported in literature (Nikiema et al., 2007). In general, landfill cover soils were the most often used since their natural exposure to CH₄ emissions favors the growth of indigenous methanotrophs. Some experiments of CH₄ biofiltration using soils-based beds lead to satisfactory results. For example, an elimination capacity of around 18 g/m²/h, which is equivalent to 60 g/m³/h (80 % of conversion, CH₄ retention time of 1.9 hours) has been reported (Park et al., 2002). The use of soils-based beads led thus to elimination capacities similar to those achieved with compost beads (Park et al., 2002; Streese and Stegmann, 2003). But most experiments confirmed that soil-based beds are less interesting than compost materials, probably because of the limitation of the nutrients availability in soils. This latter is
linked with their organic content, which is variable, from one soil to another (Nikiema et al., 2007).

On the other hand, inorganic filter beds offer many advantages due to the facts that 1) the particles size can be easily controlled; 2) they offer good mechanical properties which allow reducing compactions’ risks. However, such beds contain no nutrient. The work of Nikiema et al. (2005) was the first study on CH₄ biofiltration without percolation using an inert inorganic material having an average particle size of around 5 mm. The EC obtained was 29 g/m²/h for an IL of 75 g/m³/h confirming the usefulness of inorganic beds for CH₄ biofiltration (Nikiema et al., 2005).

Regarding the influence of the CH₄ inlet load, little information exists. As reported in the literature, inlet loads of up to 2000 g/m³/h were tested under various other operating conditions (temperature, retention time, etc.). In general, it was noted with soils and composts that the increase in the CH₄ inlet load results in an increase of the elimination capacity and a reduction of the conversion. With a soil-based bed, the increase of the IL from 4.0 to 14.4 g/m²/h resulted in an increase of the EC from 2.6 to 5.0 g/m²/h according to Hettiaratchi et al. (2000). However, exceptions are reported; for example, after increasing the inlet load from 7.8 to 12.5 g/m²/h in a compost-based bed, a decrease of the CH₄ conversion and of the EC from 100 to 50 % and from 7.8 to 6.3 g/m²/h respectively was noted (Hettiaratchi and Stein, 2001). Therefore, the influence of the inlet load on the CH₄ elimination in biofilters remains unclear and still requires some investigation.

It is known that during CH₄ biofiltration, gaseous compounds like ammonia, when they are available in the biofilter, and some ions like ammonium, nitrites, and nitrates, when they are present in the biofilms, may improve or limit the efficiency of the process (Hanson and Hanson, 1996). However, concerning the required quantity of nitrogen for the biofiltration process, variable and sometimes contradictory results are presented in the literature (Bodelier and Laanbroek, 2004). For example, according to Chiemchaisri et al. (2001), a concentration of 30 mg N per kg soil is high enough to inhibit the CH₄ elimination in a soil-based bed while in other experiments, nitrogen concentrations reaching 200 mg N per kg soil were necessary before any inhibition appeared (Nikiema et al., 2007).
The objectives of the research reported in this paper are:

1. To measure the influence of the inlet load of CH$_4$ on biofiltration performances using either an organic or an inorganic material;
2. To optimize the quantity of nitrogen to be added in the nutrient solution in the form of nitrates. The choice of nitrates as source of nitrogen for this study is due to the fact that it was, at many occasions, preferred to ammonium (Mancinelli, 1995). Indeed, during methane biofiltration in the presence of ammonium, some proportion (typically 12-28%) of methanotrophic activity is diverted towards the nitrification of ammonium, which leads to the reduction of the overall CH$_4$ elimination performance (Novikov and Stepanov, 2002).
3. To compare the performance of two filter bed materials, one of organic type, the other of inorganic type, when used for CH$_4$ biofiltration.

2.3. Material and methods

2.3.1. Filter material

Two filter materials were used during this study. Material 1 is mature compost produced from vegetable residues which was provided by GSI Environnement Inc. (Sherbrooke (Québec), Canada). This compost undergoes a coarse sifting (around 5 mm grid), which allows the elimination of fine particles. Thus, only the refuse (composed of fine matter aggregates) is introduced into the biofilter. Material 2 is inorganic gravel material. The particles are nearly of cylindrical shape, and their average length is of 5-6 mm. Material 2 is very porous and its initial surface area (including pores) is estimated to 8.5 km$^2$/m$^3$. Before use, the material is washed with water to eliminate possible impurities.

2.3.2. Biofilter configuration and equipments

Figure 2-1 presents the flowsheet of the biofiltration system used for this experiment. The CH$_4$ used during the experiments came from a pressurized cylinder of CH$_4$ with a purity of 99 % (Praxair Inc., Sherbrooke, Canada). This pollutant was mixed with ambient air (taken from the
air network of the Université de Sherbrooke) previously humidified to at least 90%. Thus, the obtained gas mixture, used to feed the biofilter, contained some carbon dioxide, at a concentration close to that in the ambient air (that is to say approximately 0.7 g/m³).

![Diagram of Lab-scale biofiltration system](image)

**Figure 2-1: Lab-scale biofiltration system**

The biofilter was an up-flow system, made of 3 identical sections forming 3 stages. It contained 1 m height of filtering bed, which corresponded to an effective volume of about 0.018 m³. During this study, the biofilter was daily humidified with a nutrient solution whose composition varied according to the type of experiment carried out at a constant volume ratio of 0.1 m³ nutrient solution per m³ of filter bed. The performance of the biofilter (i.e. concentrations of CH₄ and CO₂ at the entry and exit of each stage) was followed-up via two analyzers, one of total hydrocarbons from Horiba (Model FIA 510) and the other of CO₂ from
Siemens (Model Ultramat 22P). The average inlet concentrations of CH₄ for this study remained between 0.8 and 6.0 g/m³ (1300 to 10000 ppmv) (± 5%). The total gas flow rate was fixed at 0.25 m³/h. A read-out unit was used for the measurement of the pressure drop (data were collected at the time of measurement of the other parameters and not during irrigation).

2.3.3. Nutrient solution

Three different nutrient solutions were tested during this study.

**Nutrient solution 1:** Nutrient solution 1 (NS1) was composed only of nitrogen in the form of potassium nitrate (KNO₃) dissolved in tap water. The concentration of this compound was varied as needed. The choice of KNO₃ is due to the fact that it has been often used for the preparation of culture media for methanotrophs (Whittenbury et al., 1970). NS1 was tested only on organic filtering bed (Material 1).

**Nutrient solution 2:** The composition of nutrient solution 2 (NS2) is similar to that presented by Fox et al. (1989). It is mainly composed of nitrogen in the form of sodium nitrate (NaNO₃), which concentration varied during the study, phosphorus, potassium, and microelements dissolved in tap water. The quantities used of the various compounds to prepare one liter solution are presented in Table 2-1. As potassium nitrate, sodium nitrate has been frequently used as a nitrogen source for the preparation of culture media for methanotrophs (Sun Choi et al., 2003). NS2 has been tested on both the organic and inorganic materials.

**Nutrient solution 3:** Nutrient solution 3 (NS3) was composed only of nitrogen in the form of NaNO₃ dissolved in water (variable concentration). NS3 has been tested only on inorganic material (Material 2).
TABLE 2-1: COMPOSITION OF THE MULTI-COMPONENT NUTRIENT SOLUTION (NS2)

<table>
<thead>
<tr>
<th>Components</th>
<th>Concentrations (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaNO₃</td>
<td>0.85 to 6.07</td>
</tr>
<tr>
<td>Na₂HPO₄</td>
<td>0.86</td>
</tr>
<tr>
<td>KH₂PO₄</td>
<td>0.53</td>
</tr>
<tr>
<td>K₂SO₄</td>
<td>0.17</td>
</tr>
<tr>
<td>MnSO₄·7H₂O</td>
<td>0.037</td>
</tr>
<tr>
<td>CaCl₂·2H₂O</td>
<td>0.007</td>
</tr>
<tr>
<td>FeSO₄·7H₂O</td>
<td>0.00112</td>
</tr>
<tr>
<td>ZnSO₄·7H₂O</td>
<td>0.000576</td>
</tr>
<tr>
<td>MnSO₄·7H₂O</td>
<td>0.000466</td>
</tr>
<tr>
<td>CuSO₄·5H₂O</td>
<td>0.00025</td>
</tr>
<tr>
<td>KI</td>
<td>0.000166</td>
</tr>
<tr>
<td>H₃BO₃</td>
<td>0.000124</td>
</tr>
<tr>
<td>NaMoO₄·2H₂O</td>
<td>0.000096</td>
</tr>
<tr>
<td>CoCl₂·6H₂O</td>
<td>0.000096</td>
</tr>
</tbody>
</table>

2.4. Results and discussion

Table 2-2 presents the parameters used to describe the results of CH₄ biodegradation, which are: inlet load (IL), conversion (X), elimination capacity (EC) and CO₂ production rate ($P_{CO₂}$).
### TABLE 2-2: PARAMETERS USED TO QUANTIFY THE PERFORMANCE OF A BIOFILTER

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Methods of determination</th>
</tr>
</thead>
<tbody>
<tr>
<td>IL: Volumetric inlet load (g/m$^3$/h)</td>
<td>$IL = \frac{C_{(CH_4)_{in}} \times Q}{V}$</td>
</tr>
<tr>
<td>IL: Surfacic inlet load (g/m$^2$/h)</td>
<td>$IL = \frac{C_{(CH_4)_{in}} \times Q}{S}$</td>
</tr>
<tr>
<td>X: Conversion (%)</td>
<td>$X = \frac{C_{(CH_4)<em>{out}} - C</em>{(CH_4)<em>{in}}}{C</em>{(CH_4)_{in}}} \times 100$</td>
</tr>
<tr>
<td>EC: Elimination capacity (g/m$^3$/h or g/m$^3$/h)</td>
<td>$EC = IL \times \frac{X}{100}$</td>
</tr>
<tr>
<td>$P_{CO_2}$: Carbon dioxide production rate (g/m$^3$/h)</td>
<td>$P_{CO_2} = \left( \frac{C_{(CO_2)<em>{out}} - C</em>{(CO_2)_{in}}}{V} \right) \times Q$</td>
</tr>
</tbody>
</table>

**Note:** $C_{CH_4}$ = Methane concentration in g/m$^3$; $C_{CO_2}$ = Carbon dioxide concentration in g/m$^3$; Q = Volumetric flow rate of air mixture in m$^3$/h; S = Biofilter bed cross-section in m$^2$; V = Biofilter bed volume in m$^3$.

### 2.4.1. Methane elimination in the compost-based bed

Figure 2-2 presents the EC of CH$_4$ in the organic bed (expressed in g/m$^3$/h) as a function of the nitrogen concentration (NS1) for an IL of 75 g/m$^3$/h. The tested nitrogen concentrations were varied between 0.14 and 2.0 g/L. Figure 2-2 reveals that the EC is comprised between 6 and 12 g/m$^3$/h. Indeed, a small nitrogen limitation phase is observed when the nitrogen concentration is around 0.14 g/L, which resulted in a low EC (6 g/m$^3$/h). Then, the increase of the nitrogen concentration from 0.14 to 0.25 g/L allows improving the EC in the biofilter by 100%, from 6 to 12 g/m$^3$/h. Beyond 0.25 g-N/L (from 0.50 to 2.0 g-N/L), one notes that EC is maintained between 10 and 11 g/m$^3$/h.
Figure 2-2: The elimination capacity in the organic-based biofilter as a function of the nitrogen concentration in NS1 for an inlet load of 75 g/m$^3$/h.

On the other hand, Figure 2-3 presents the EC for the organic bed (expressed in g/m$^3$/h) as a function of the nitrogen concentration in NS2 (ILs of 55, 75 and 95 g/m$^3$/h). The tested nitrogen concentrations were varied between 0.14 and 1.0 g/L. By increasing the nitrogen content in the NS2 from 0.14 to 0.75 g/L, the ECs were slightly improved. The optimum nitrogen concentration with NS2 is found to be around 0.75 g/L and is not affected by the IL in the range of 55 to 95 g/m$^3$/h. At the optimum nitrogen level, the ECs are 12, 14.5 and 15 g/m$^3$/h, respectively for ILs of 55, 75 and 95 g/m$^3$/h. But when the nitrogen concentration in the NS2 reached 1.0 g/L, a 25% decrease on average of the CH$_4$ EC in the biofilter was observed, compared to the maximum values mentioned earlier.
The comparison of both compost-based bed biofilters using NS1 and NS2 when IL equals 75 g/m³/h (Figures 2-2 and 2-3) reveals that both nutrient solutions give quite similar results in terms of EC (between 10 and 14 g/m³/h), except for a N-concentration 0.14 g/L, for which the NS2 appears to give better results, more than 100% higher, than those with NS1 (EC = 13 versus 6 g/m³/h). In addition, the performance of the organic-based bed biofilter was not satisfactory in all tested conditions (EC ≤ 15 g/m³/h for IL comprised between 55 and 95 g/m³/h). This indicates doubtless that important factors, not optimized in the present study, influenced negatively the behavior of the organic biofilter. The reasons why the organic material was unsuccessful have not been investigated in detail since this was not the main interest in the present study. However, among possible explanations of this low performance impeded by the organic-based bed biofilters, one can mention its texture, making the media less suitable for methanotrophs growth than other media. Finally, biological reactions other
than CH₄ biodegradation were probably occurring in the compost-based bed biofilter creating a competition between micro-organisms which was damageable for the removal of the targeted pollutant (data not shown).

2.4.2. Methane elimination in the inorganic-based bed

- **Elimination capacities with NS2**

Because of the unsatisfactory results obtained with the organic material, it has been decided to test the use of an inorganic packing material. Figure 2-4 presents the EC of CH₄ in the inorganic filter bed as a function of the IL of CH₄ for various nitrogen concentrations in NS2 (0.14, 0.25, 0.50, 0.75 and 1.0 g/L). The methane ILs were varied between 12 and 95 g/m³/h, in order to determine the influence of the IL on the CH₄ elimination capacity of the biofilter.

![Figure 2-4: The elimination capacity in the inorganic-based biofilter as a function of the inlet load for nitrogen concentrations in NS2 of 0.14; 0.25; 0.50; 0.75 and 1.0 g/l.](image-url)
In the inorganic material, both the nitrogen concentration and the IL influence the EC of the biofilter. In the case of the IL, its influence increases with the nitrogen concentration in the nutrient solution (Figure 2-4). For example, when the nitrogen concentration in NS2 is 0.14 g/L, it is noted that the EC changes barely from 10 to 11 g/m³/h (10% of variation) for methane IL varied between 30 and 55 g/m³/h. Then, up to an IL of 95 g/m³/h, the EC slightly decreases and stabilizes at values between 8 and 9 g/m³/h. This decrease shows that IL of CH₄ can limit the biofilter performance when the nitrogen concentration is not high enough. On the other hand, for a nitrogen concentration in NS2 of 0.25 g/L, a 50% increase of the EC (from 9.5 to 14.5 g/m³/h) is obtained when the IL of CH₄ is varied from 20 to 35 g/m³/h. Then, a stability of the EC at around 14 g/m³/h for ILs comprised between 35 and 95 g/m³/h (similar to the one observed for 0.14 g/L) is noticed. Nevertheless, for nitrogen concentrations of 0.50 to 1.0 g/L, a continuous increase of the EC with the IL is observed for the entire study range. Typically, at 0.75 g-N/L, the EC goes from 7 to 24 g/m³/h when the IL is raised from 12 to 55 g/m³/h and reaches 36 g/m³/h when the IL is 95 g/m³/h. The highest CH₄ conversion is 50% and is obtained for ILs below 55 g/m³/h.

Regarding the nitrogen concentration influence, it can be determined from Figure 2-4 that nitrogen is a key factor that strongly affects the EC of the inorganic-based biofilter. The optimum level of nitrogen in the nutrient solution depends on the IL and is found to be 0.50 g/L for IL of 55 g/m³/h and below. Indeed, for an IL of 55 g/m³/h, the maximum EC (26 g/m³/h), obtained when the nitrogen concentration is 0.50 g/L, is respectively 80% and 135% higher than the EC measured at 0.25 and 0.14 g-N/L. In addition, when the IL is comprised between 12 and 36 g/m³/h, one notes that ECs at 0.50 and 0.75 g-N/L are quite the same, confirming that a nitrogen concentration of 0.50 g/L is enough. On the other hand, for an IL between 75 and 95 g/m³/h, the optimum level of nitrogen in the nutrient solution is 0.75 g/L so that increasing the nitrogen concentration from 0.14 to 0.75 g/L at an IL of 75 g/m³/h triples the EC, which passes from 10 to 33 g/m³/h.

When the nitrogen concentration becomes higher than the optimal values, one notes an inhibition caused by the excess of nitrogen and resulting in a decrease of the EC in the biofilter. Typically, at an IL of 95 g/m³/h, increasing the N-concentration from 0.75 to 1.0 g/L causes a 10% decrease of the EC, from 36 to 33 g/m³/h (Figure 2-4). At an IL of 55 g/m³/h,
the increase of the N-concentration up to 1.0 g/L caused an abrupt decrease of the EC. This behavior is shown in Figure 2-5, which represents the IL and the EC as a function of time.

![Figure 2-5: The inlet load and elimination capacity in the inorganic-based biofilter as a function of time, at nitrogen concentrations in NS2 of 1.0 and 0.50 g/l.](image)

It was noted after one week of quasi-steady state operation (EC = 22 g/m³/h at an IL of 55 g/m³/h), a major and continuous decrease of the EC down to 5 g/m³/h in less than 2 weeks. In order to stop the decrease of the EC, the IL was increased to 95 g/m³/h. Then, the nitrogen concentration in NS2 was reduced of 50 %, from 1.0 g/L to 0.50 g/L, in order to facilitate the restarting of the biofilter. The biofilter then stabilized after 19 days, and the final EC was then the same as the one previously obtained under the same operating conditions. It is to be mentioned that, at an IL of nearly 15 g/m³/h in a biofilter irrigated with a nutrient solution containing 0.50 g-N/L, an inhibition similar to the one observed at IL = 55 g/m³/h and 1.0 g-N/L was noted and the EC decreased of 50 % within one week (Figure 2-4). The behavior
described hereby confirms that the N-concentration can inhibit the biofilter performance and that it requires a proper adjustment, depending on the IL of CH₄. This is a reason that can explain the diversity of optimum nitrogen concentrations proposed in the literature, especially during soil-based experiments (Nikiema et al., 2007).

● Carbon dioxide production

Figure 2-6 presents the production rate of CO₂ in the biofilter packed with an inorganic material as a function of the IL and the nitrogen concentration. One notes that P_{CO₂} follows a trend roughly similar to that of EC (Figure 2-4) when expressed as a function of the same parameters.

![Figure 2-6: The carbon dioxide production rate in the inorganic-based biofilter as a function of the inlet load for nitrogen concentrations in NS2 of 0.14; 0.25; 0.50; 0.75 and 1.0 g/l.](image-url)
The CO₂ production in the biofilter is the result of the biological activity. To assess the contribution of CH₄ elimination to the CO₂ production, one can define a ratio α representing the mass of CO₂ produced per m³ of filter bed per hour divided by the mass of CH₄ eliminated in the biofilter per m³ of filter bed per hour (Nikiema et al., 2005). When considering a chemical process for which no carbon accumulation through biomass growth occurs,

\[ \alpha = 2.75 \text{ g CO}_2/\text{g CH}_4 \]  
(Equation 2-1).

\[ \text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \]  
(Eq. 2-1)

This value of α represents, in theory, the highest possible value that can be obtained during CH₄ elimination through biological and non-biological processes. In addition, during biological processes, part of the carbon content of CH₄ is used for anabolism into biomass, which results in lower values of α (as compared to the maximum value), according to Equation 2-2.

\[ \text{CH}_4 + x\text{O}_2 \rightarrow y\text{CO}_2 + z\text{H}_2\text{O} + \text{Biomass} + \text{Salts} \]  
(Eq. 2-2)

With \( x < 2 \) and \( y < 1 \) and \( z < 2 \); \( x, y \) and \( z \) being stoichiometric coefficients.

Since the carbon ends in the form either of CO₂ or biomass, the lower the CO₂ production in the biofilter (which also means the lower the values of α), the higher the biomass growth. However, high bacterial multiplication rate favors the biomass accumulation in the biofilter and increases the filter bed clogging rate.

The values of α (calculated from Figures 2-4 and 2-6) obtained for the inorganic-packed biofilter usually remained below the theoretical maximum value of 2.75 g CO₂/g CH₄ for IL \( \geq 20 \text{ g/m}^3/\text{h} \). For example, the average value of α is around 2.3 g CO₂/g CH₄ for IL \( \geq 55 \text{ g/m}^3/\text{h} \). On the other hand, for IL \( \leq 20 \text{ g/m}^3/\text{h} \), α remained between 2.7 and 3.4 g CO₂/g CH₄, with an average value of 3.0 g CO₂/g CH₄. Indeed, the decrease of the methane EC, linked to the number of active micro-organisms in the biofilter, observed for low IL values, favors the increase in the density of inactive biomass and, consequently, an increase in the CO₂ production rate, which explains the high values of α (Nikiema et al., 2007).
Figure 2-7 presents the values of $\alpha$ obtained with the inorganic-based bed as a function of the N-concentration at ILs of 30, 75 and 95 g/m$^3$/h. It shows that there is no evident relationship between $\alpha$ and the nitrogen concentration. However, the maximum $\alpha$ values are observed at 0.50 g-N/L for all the studied IL values. This suggested that, at N-concentration of 0.50 g/L, the clogging rates should be the lowest. Such conclusion has not been however confirmed by the present study since, as for organic biofilter, the pressure drop in the inorganic biofilter remained always low, $\leq$ 1 Pa/(m of packing).

![Figure 2-7: The ratio $\alpha$ in the elimination capacity in the inorganic-based biofilter as a function of the nitrogen concentration in NS2 for inlet loads of 30, 75 and 95 g/m$^3$/h.](image)

According to various authors, the values of $\alpha$ should be 1.45 g CO$_2$/g CH$_4$ for type I methanotrophs (using the ribulose mono-phosphate pathway for formaldehyde assimilation)
and 1.63 g CO₂/g CH₄ for type II methanotrophs (using the serine pathway for formaldehyde assimilation) (He et al., 2006; Hilger and Humer, 2003). Our measured values of α are significantly higher (e.g. for IL ≥ 55 g/m³/h, the average value of α is 2.3 g CO₂/g CH₄), which suggests the presence of other types of micro-organisms in the CH₄ biofilter, and implies that mechanisms, other than methane biodegradation, are involved in the CO₂ production in the CH₄ biofilter.

○ Comparison between filter materials

One objective of our study was to compare the biofiltration performance of CH₄ in two beds, one of an organic type and the other of inorganic type. The results obtained during the present study confirmed that the behavior of the inorganic-based biofilter is different from that of the organic-based biofilter. Although the organic-based biofilters were in the past privileged because of their intrinsic content of nutrients and indigenous micro-organisms, it seems that, in the case of CH₄, an inorganic bed is to be preferred (Nikiema et al., 2007). The EC of CH₄ is 2 to 3 times higher for the inorganic material at optimized conditions of nitrogen than for an organic material for an IL comprised between 55 and 95 g/m³/h.

○ Elimination capacities with NS3

Since the use of NS2 resulted in better results in terms of EC and conversion compared to NS1 in the organic bed, the investigation of whether or not the nitrogen content was the only cause of this behavior was performed. For that purpose, NS3, a nutrient solution containing only nitrogen in the form of sodium nitrate (no other element was present), was tested using the inorganic material. The experiment was conducted at an IL of 75 g/m³/h. Figure 2-8 illustrates the EC as a function of the nitrogen concentration in the NS3. Four nitrogen concentrations in NS3 were tested: 0.25, 0.50, 0.75 and 1.0 g/L. Under these operating conditions, one notes that the EC remained between 13 and 15 g/m³/h. The optimum value of the nitrogen concentration in the nutrient solution was around 0.50 g/L (instead of 0.75 g/L when using the NS2 for biofilter irrigation). Moreover, the maximum EC reached by the biofilter irrigated with NS3 (at 0.5 g/L) corresponded to less than 50% of the maximum value recorded with
These remarks brought us to the conclusion that there are other nutrients, in addition to 
nitrogen, which influence the performance in CH₄ elimination in a biofilter.

Figure 2-8: The elimination capacity in the inorganic-based biofilter as a function of the 
nitrogen concentration in NS2 and NS3 for an inlet load of 75 g/m³/h.

2.5. Conclusion

The goals of this study were to determine the influence of the CH₄ inlet load and to optimize 
the concentration of nitrogen (provided in the form of nitrate ions) in the nutrient solution on 
the performance of 2 biofilters, one packed with an organic material, the other with an 
inorganic material. Based on the results of the present study, it can be concluded that an 
inorganic packing is more valuable than a compost-based one, in the case of CH₄ biofiltration. 
In addition, nitrogen has proved to be an important nutrient. But the presence of additional 
nutrients, such as phosphate, potassium and microelements in the multi-component nutrient
solution (NS2) used for biofilter irrigation, resulted in better results when compared to a solution containing only a nitrogen source (NS3).

With the NS2, and within the inorganic packing material, the influences of the IL and the nitrogen concentration are much more obvious than within the compost-based bed biofilter. In general, the increase of the IL has caused an increase of the EC when nitrogen was not limiting, i.e. 0.50 g-N/L or more. On the other hand, when the nitrogen concentration in the NS2 was below 0.25 g-N/L, one noted no change or a slight decrease of the EC with the increase of the IL (> 40 g/m$^3$/h). The optimum nitrogen concentrations were also determined, as a function of the IL. They are 0.50 and 0.75 g-N/L, for IL < 55 g/m$^3$/h and IL > 55 g/m$^3$/h, respectively.

The production rate of CO$_2$ is an indicator of the biological behavior in biofilters. In the methane biofilter, packed with the inorganic material, both the EC and the production rate of CO$_2$ followed similar trends. In addition, it was noted that other phenomena (presumably biomass degradation), in addition to the biodegradation of CH$_4$ by the methanotrophs, result in the formation of CO$_2$ at low inlet loads.

2.6. Acknowledgments

The authors are indebted to the Natural Science and Engineering Research Council of Canada (NSERC) for their financial support to this project. J. Nikiema acknowledges support from Canada Graduate Scholarships Program. The authors are also thankful to GSI Environnement inc. (Sherbrooke, Québec, Canada) for providing the compost.
CHAPITRE 3. THE INFLUENCE OF PHOSPHORUS, POTASSIUM AND COPPER ON METHANE BIOFILTERATION PERFORMANCE

Authors: J. Nikiema, R. Brzezinski and M. Heitz


3.1. Abstract

Bacteria require, in addition to a carbon source, a variety of nutrients such as phosphorus, potassium and several other micronutrients including copper and metals. The study described in this paper has been conducted with the aim of determining the influence of phosphorus, potassium, and certain trace nutrients such as copper on methane elimination in a biofilter. The study revealed that the particular phosphorus concentration leading to the greatest elimination capacity, which was 44.7 g/m$^3$/h at an inlet load of 75 g/m$^3$/h, was 3.1 g/L. The influence of the phosphorus concentration on the methane elimination capacities was also investigated for methane inlet loads of between 8 and 95 g/m$^3$/h. The optimum range of the nitrogen/phosphorus mass ratios, determined during this study ranged from 0.5 to 2.5. It was established that, in comparison with phosphorus concentration, potassium concentration does not seem to be a determining element for the biological removal efficiency and does not significantly affect the micro-organisms' growth rate. However, a concentration of 0.076 g/L of potassium is recommended in the irrigation nutrient solution. The influence of the copper concentration was also studied by varying its concentration between the values of 0 and 0.006 g/L. The results have also shown that copper has a minor impact on the biofiltration of methane. This paper is the first report describing the influence of several nutrients in a biofilter. The knowledge provided by this study is necessary for the achievement of a biofilter indebted to methane control.
Les bactéries requièrent, en plus d’une source de carbone, plusieurs nutriments tels le phosphore, le potassium ainsi que divers micronutriments incluant le cuivre et des métaux. L’étude décrite dans le présent article, a été menée dans le but de déterminer l’influence, sur la bioélimination du méthane, du phosphore, du potassium, et de certains micronutriments tels le cuivre. Cette étude a révélé que la concentration de phosphore permettant la capacité d’élimination la plus importante, soit 44.7 g/m³/h à une charge initiale de méthane de 75 g/m³/h, était de 3.1 g/L. L’influence de la concentration de phosphore a également été étudiée pour des charges initiales de méthane comprises entre 8 et 95 g/m³/h. Les ratios massiques azote/phosphore optimaux, identifiés lors de cette étude, se sont situés entre 0.5 et 2.5. De plus, il a été établi que la concentration du potassium, comparativement à celle du phosphore, ne semble pas très déterminante pour l’efficacité du procédé biologique d’élimination du méthane et affecte peu le fonctionnement des micro-organismes. Néanmoins, une concentration de potassium autour de 0.076 g/L est recommandée dans la solution nutritive utilisée pour l’irrigation du biofiltre. En outre, l’influence de la concentration du cuivre, entre 0 et 0.006 g/L a également été étudiée. Les résultats obtenus démontrent que le cuivre joue un rôle mineur lors de la biofiltration du méthane. Cet article est le premier du genre décrivant l’influence de plusieurs nutriments dans un biofiltre. Les connaissances acquises au travers de cette étude se révèlent nécessaires pour le bon fonctionnement d’un biofiltre destiné au contrôle du méthane.

3.2. Introduction

Methane is a greenhouse gas (GHG) 21 times more detrimental than carbon dioxide. In Canada in 2005, anthropogenic methane emissions were estimated to be 1.1 $10^8$ metric tons, when expressed in CO₂ equivalents. The main anthropogenic emission sources of this pollutant are energy (50 %), agriculture (25 %) and waste storage within landfills (25 %) (Environment Canada, 2008). The methane emitted by landfills is contained in the biogas generated when wastes are biodegraded. When possible, this biogas is collected through venting systems which are sometimes coupled with membranes (collection efficiency usually
between 60 and 90 %) and is burned, with or without energy recovery. Thus, one avoids the
emission of this harmful GHG directly into the atmosphere. However, for the portion which is
not collected, or for landfills not equipped with collection systems, it is important to find an
alternative in order to control the methane emissions (Nikiema et al., 2007a).

The objective of the present study is to develop a low cost, high performance biotechnology,
able to remove the methane efficiently from the biogas and avoid its emission into the
atmosphere. Such technology could replace flares which are generally characterized by
investment and operational costs higher than for biological processes, including biofiltration.
In order to improve the performance of methane bioelimination, it is important to establish the
input quantities of nutrients to be provided to the biofilter in order to ensure that nutrients are
available to sustain the process.

It is now universally accepted that bacteria require several nutrients for their sustained growth.
Generally, the main nutrients are nitrogen (N), phosphorus (P), potassium (K), copper (Cu),
sulphur (S), manganese (Mg), calcium (Ca), iron (Fe), sodium (Na) and chlorine (Cl)
(Nikiema et al., 2007a,b; Metcalf and Eddy, 2003). For achieving in biofiltration, it is thus
important to ensure that these nutrients are available to sustain the growth of the micro­
organisms. Compost materials typically contain, on a weight basis, 1% of the total N (of
which 0.3% of the N is biologically available, i.e. in the form of ammonium and nitrate ions),
1% of the total P (up to 0.6% of the P is biologically available) and less than 0.1% of the
available K (Delhomenie, 2002; Humer and Lechner, 1999). When such organic-based beds
are used for the control of low inlet loads of methane (CH₄) (< 15 g/m³/h) or the volatile
organic compounds (VOCs) that are easily biodegradable (such as the alcohols and related
odorous compounds), the availability of the intrinsic nutrients makes it unnecessary to use the
addition of extra nutrients, as reported by several authors (Delhoménie and Heitz, 2005; Janni
et al., 2001). However, during several experiments, using compost material-based bed
biofilters for the control of the VOC pollutants (including hydrocarbons, alcohols, etc.), the
filter bed is frequently enriched with variable quantities of N, P, K and micro-nutrients. The
mass ratios of the C/N/P to be used, based on the mineral content of bacteria cells, are
generally comprised of between 100/5/1 and 100/15/3 (Jorio and Heitz, 1999).
Enrichment with nutrients can be effected prior to the biofiltration. For lab-scale experiments, a highly concentrated nutrient solution (of mass N/P/K ratios around 7/1/1) was mixed with the organic packing material (e.g. by forming a packing material with ~ 0.4% g fertilizer/g of packing) (Chan and Lin, 2005; Otten et al., 2004; Cherry and Thompson, 1997). This pretreatment of the packing material then enables the biofilter to operate for several weeks (typically 15 weeks) at maximum removal efficiencies. In such cases however, a continuous decrease in the nutrient availability in the biofilter occurred with time (Moe and Irvine, 2001). To maintain the biofilter efficiency, periodic irrigation, with some 1.5 to 3 mL water per m³ of gas, is necessary (typically, every 2 days of operation) which aids in the control of the filter bed drying (Chan and Lin, 2006). Another approach consists of daily irrigation of the biofilter with a nutrient solution. This method is to be applied when the above mentioned one cannot be used. The challenge therefore is to lower, to a certain extent, the irrigation frequency of the packing. Table 3-1 presents the values for different nutrient ratios tested for the biological control of various pollutants (such as methane and VOCs), as reported in the literature, including the N/P, P/K, Mg/K, Ca/K, Mn/Cu, B/Cu, Zn/Mn ratios. As can be noted in the Table 3-1, several types of nutrient solutions with variable composition are reported to have been tested in the literature.

The objective of this study was the determination of the influence of the macronutrients (P, K) and micronutrient (Cu) used in the nutrient solution. As observed in the case of nitrogen, one supposed that the optimisation of the P, K and Cu concentrations could improve the methane elimination performance.

In the following sections, the influences (according to the literature) of those nutrients that may play important roles during the methane biofiltration are presented.
### TABLE 3-1: TYPICAL COMPOSITIONS FOR THE NUTRIENTS PROPOSED BY THE AUTHORS

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>N/P</th>
<th>P/K</th>
<th>Mg/K</th>
<th>Ca/K</th>
<th>Mn/Cu</th>
<th>B/Cu</th>
<th>Zn/Mn</th>
</tr>
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<tbody>
<tr>
<td>Benzene 1</td>
<td>0.08</td>
<td>0.92</td>
<td>0.02</td>
<td>0.01</td>
<td>-</td>
<td>-</td>
<td>28.15</td>
</tr>
<tr>
<td>Ethanol 2</td>
<td>0.93</td>
<td>0.79</td>
<td>0.07</td>
<td>0.02</td>
<td>1.75</td>
<td>0.41</td>
<td>5.12</td>
</tr>
<tr>
<td>Methane 3</td>
<td>&gt; 0.5</td>
<td>20</td>
<td>0.05</td>
<td>0.03</td>
<td>1.45</td>
<td>0.27</td>
<td>1.42</td>
</tr>
<tr>
<td>Methanotrophic growth medium 4</td>
<td>0.35</td>
<td>0.04</td>
<td>0.25</td>
<td>0.18</td>
<td>10.91</td>
<td>0.69</td>
<td>0.17</td>
</tr>
<tr>
<td>Methanol 5</td>
<td>0.22</td>
<td>2.82</td>
<td>0.05</td>
<td>0.08</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>n-Butyric acid (odor) 6</td>
<td>0.91</td>
<td>2.31</td>
<td>0.29</td>
<td>0.14</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
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<td>VOC</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Odor 7</td>
<td>0.57</td>
<td>0.64</td>
<td>0.02</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Odor 8</td>
<td>0.20</td>
<td>0.58</td>
<td>0.01</td>
<td>0.01</td>
<td>-</td>
<td>-</td>
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<tr>
<td>Toluene 9</td>
<td>0.47</td>
<td>0.73</td>
<td>0.01</td>
<td>-</td>
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<td>-</td>
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</tr>
<tr>
<td>Trichloroethylene 10</td>
<td>1.02</td>
<td>0.20</td>
<td>-</td>
<td>-</td>
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<td>0.53</td>
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<td>0.01</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>VOC mixture 12</td>
<td>1.92</td>
<td>0.79</td>
<td>0.17</td>
<td>0.02</td>
<td>5.18</td>
<td>-</td>
<td>0.40</td>
</tr>
<tr>
<td>Xylene 13</td>
<td>2.16</td>
<td>0.79</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>


#### 3.2.1. The role of phosphorus according to the literature

The requirement for the availability of P varies from one micro-organism to another. The molar ratios, C/P, characterizing heterotrophic bacteria as collected from lakes, coastal waters, etc. vary from 5 to 500. This difference in the P requirement can sometimes be linked to the RNA content of the micro-organism (containing nearly 10% of P), the RNA and DNA of bacteria representing around 20% and 3% respectively, of the dry mass of the bacteria cells (Metcalf and Eddy, 2003). In general, RNA content increases and DNA content decreases, with increased growth rates (as shown in enterobacteria) (Smith and Prairie, 2004).
Phosphorus is the main element known to control bacterial growth in several common environments. In natural environments, such as lakes, it has been demonstrated that the growth rate of some micro-organisms is exponentially increased with increasing P concentrations and that the high values of growth rate are more likely to be linked with P availability than with carbon availability (e.g. 1.4 d\(^{-1}\) for P concentrations > 35 µg/L, versus 0.1 d\(^{-1}\) for P concentrations < 5 µg/L) (Estrada et al., 2008). Furthermore, in the presence of high P concentrations, bacterial predators do not have their growth rates increased to levels similar to those of the bacteria, what results in an accumulation of bacteria within the system.

A similar phenomenon, with both phytoplankton and phytoplankton consumers was also observed in natural systems in the presence of high concentrations of P (Smith and Prairie, 2004; Makino et al., 2003). On the other hand, in addition to the increase in the growth rates of bacteria, induced by the increased P availability, a decrease in their specific respiration rate (defined as the quantity of CO\(_2\) released per cell per hour) was observed (Estrada et al., 2008). In some cases, P limitation negatively affected both the growth and the reproduction of several types of micro-organisms (Hanson and Hanson, 1996).

In air biofilters, P has been of secondary interest for the majority of authors. It is nearly always utilised in the forms of sodium phosphate, potassium phosphate or phosphoric acid. The mass N/P ratios applied in biofilters range usually from 0.08 to 2.16, depending on the type of nutrient solution selected for the study (Table 3-1). This wide range of concentrations translates to the uncertainty in the real needs, in terms of nutrients, supplied during the air biofiltration process.

### 3.2.2. The role of potassium according to the literature

According to Metcalf and Eddy, the dry mass fraction of potassium is 1%, i.e. a theoretical mass ratio for N/P/K of 12/2/1 (Metcalf and Eddy, 2003). Even if most authors admit to the importance of K presence, to our best knowledge, no study has been dedicated so far to K influence on biofiltration efficiency. P/K ratios usually range between 0.04 and 2.2, depending on the type of nutrient solution selected for study (Table 3-1).
3.2.3. The role of copper according to the literature

The enzyme permitting methanotrophs to biodegrade methane is called methane monoxygenase (MMO). It exists in 2 forms: the particulate form (pMMO) and the soluble form (sMMO). The pMMO is expressed by almost all methanotrophs when in the presence of sufficient quantities of Cu, but not at levels greater than 0.27 g/L. The pMMO enzyme has high affinity for CH₄ and insures high growth yields (Crossman et al., 2004). The bacteria are therefore able to respond rapidly, as compared to those which methanotrophy is based on sMMO (type II and type X bacteria), when exposed to CH₄ concentrations < 1000 ppmv (Xin et al., 2002).

Xin et al. (2002) have determined the impact of Cu supply in a culture medium on the growth of the pMMO-based methanotroph Methylosinus trichosporium (Takeguchi et al., 1999). The increase in the Cu concentration, from 0.0001 to 0.0005 g/L resulted in a 12 times increase in the final bacterial density in the culture medium. For the same species, other authors have reported a similar behavior mentioning that the highest allowable concentration of Cu was 0.020 g/L (Mohanty et al., 2000). At higher concentrations, Cu began to inhibit the activity of the pMMO. During experiments dedicated to CH₄ oxidation in rice soils, some authors have observed an improvement in the methane removal efficiency in the presence of 9.5 mg-Cu/(kg of soil) (Nikiema, 2008).

3.3. Material and methods

3.3.1. Description of the laboratory-scale system

Four identical biofilters were operated for these experiments. The CH₄ used during the experiments originated from a pressurized cylinder of CH₄ (99 % V/V purity) (Praxair Inc., Sherbrooke, Canada). The dilution of the CH₄ was performed by mixing the pure CH₄ with the pre-humidified (relative humidity > 90 %) ambient air. The performance of the biofilter (concentrations of CH₄ and CO₂ at the entry and exit of each biofilter stage) was followed using two analyzers, one providing the total hydrocarbons concentration (Horiba, Model FIA
510) and the other, the CO₂ concentration (Siemens, Model Ultramat 22P). The total gas flow rate, within each biofilter, was 0.25 m³/h.

The simplified flowsheet for the lab-scale biofiltration system is presented in Figure 3-1. The up-flow biofilter (135 cm in height, 15 cm of internal diameter and 0.65 cm in wall thickness) is built in Plexiglas and divided into 3 identical superimposed stages. The total height of the packing material in the biofilter is 1 m. Each biofilter therefore has a total reactive bed volume of ~17.5 L. A tank, located at the base of the biofilter, collects the excess irrigation solution. The packing material used during this study is an inorganic stone material, having particles some 5 mm in average diameter. The average specific gravity of the packing is around 1.3 and its initial surface area is around 7 m²/g. Before being introduced into the biofilter, the packing
is washed with water in order to eliminate impurities on its surfaces. The humidification of each biofilter’s packing material was performed daily throughout the study. The quantity of nutrient solution used was approximately 0.1 L nutrient solution per L of filter bed.

3.3.2. Experimental procedure

The nutrient solution was obtained by mixing adequate volumes of five stock solutions and water (Table 3-2). For instance, 10 mL of each solution A, B and D, 2 mL of solution C and 1 mL of solution E were mixed to obtain 1 L of nutrient solution containing 0.75 g-N/L, 0.3 g-P/L and 0.00006 g-Cu/L. These concentrations correspond to the starting points of all of the series of experiments.

In order to find the optimum level of the main macronutrients (P, K) and micronutrient (Cu), the quantities of the solutions A, B and C, as used in the preparation of the nutrient solution, have been varied one at a time. Because each of these main solutions can contain several nutrients, it was not possible to measure the impact of one element alone, except for the P content (when varying the quantities of solutions A, B or C, to be added to the nutrient solution, in fact, the concentration of all elements present in the same solution are varied). As a consequence, the impact of the concentrations of the nutrients belonging to the same main solution was determined simultaneously.

Starting from the previously mentioned levels, the P, K and Cu concentrations were first increased in the nutrient solution, one at the time, up to the highest level tested. Then, the biofilter was gently washed with tap water and the target nutrient was removed from the nutrient solution in order to investigate the influence of its absence. It is to be noted that, for the same methane biofilter, the N concentration had been previously optimized and the recommended level (used in this study) was 0.75 g/L (Nikiema, 2008).

For the initial start-up, all the biofilters involved in the present study were inoculated with the leachate from another biofilter, treating methane, operated at an IL of 75 g/m³/h for approximately one year.
TABLE 3-2: COMPOSITION OF THE 5 MAIN SOLUTIONS USED IN ORDER TO FORM THE EXPERIMENTAL NUTRIENT SOLUTIONS; NS1, NS2 AND NS3.

<table>
<thead>
<tr>
<th>Solutions</th>
<th>Components</th>
<th>Concentrations (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solution A</td>
<td>Na₂HPO₄</td>
<td>86</td>
</tr>
<tr>
<td></td>
<td>KH₂PO₄</td>
<td>53</td>
</tr>
<tr>
<td>Solution B</td>
<td>K₂SO₄</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td>MgSO₄·7H₂O</td>
<td>3.7</td>
</tr>
<tr>
<td></td>
<td>CaCl₂·2H₂O</td>
<td>0.7</td>
</tr>
<tr>
<td>Solution C</td>
<td>ZnSO₄·7H₂O</td>
<td>0.288</td>
</tr>
<tr>
<td></td>
<td>MnSO₄·7H₂O</td>
<td>0.233</td>
</tr>
<tr>
<td></td>
<td>CuSO₄·5H₂O</td>
<td>0.125</td>
</tr>
<tr>
<td></td>
<td>KI</td>
<td>0.083</td>
</tr>
<tr>
<td></td>
<td>H₃BO₃</td>
<td>0.062</td>
</tr>
<tr>
<td></td>
<td>CoCl₂·6H₂O</td>
<td>0.048</td>
</tr>
<tr>
<td></td>
<td>NaMoO₄·2H₂O</td>
<td>0.048</td>
</tr>
<tr>
<td>Solution D</td>
<td>NaN₃</td>
<td>456</td>
</tr>
<tr>
<td>Solution E</td>
<td>FeSO₄·7H₂O</td>
<td>11.2</td>
</tr>
</tbody>
</table>

3.3.3. Assessment parameters

The assessment parameters used in this paper are: the inlet load (IL), the conversion (X), the elimination capacity (EC), and the carbon dioxide production (P\(_{CO₂}\)). They have been determined using the equations presented in Table 3-3.
TABLE 3-3: PARAMETERS USED TO QUANTIFY THE PERFORMANCE OF A BIOFILTER

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Methods of determination</th>
</tr>
</thead>
<tbody>
<tr>
<td>IL: Volumetric inlet load (g/m⁴/h)</td>
<td>[ IL = \frac{C_{(CH_4)_{in}} \times Q}{V} ]</td>
</tr>
<tr>
<td>X: Conversion (%)</td>
<td>[ X = \frac{C_{(CH_4)<em>{in}} - C</em>{(CH_4)<em>{out}}}{C</em>{(CH_4)_{in}}} \times 100 ]</td>
</tr>
<tr>
<td>EC: Elimination capacity (g/m²/hr or g/m⁴/h)</td>
<td>[ EC = IL \times \frac{X}{100} ]</td>
</tr>
<tr>
<td>( P_{\text{CO}_2} ): Carbon dioxide production rate (g/m³/h)</td>
<td>[ P_{\text{CO}<em>2} = \frac{\left( C</em>{\text{CO}<em>2}^{\text{out}} - C</em>{\text{CO}_2}^{\text{in}} \right) \times Q}{V} ]</td>
</tr>
</tbody>
</table>

\( C_{\text{CH}_4} \) = Methane concentration in g/m³; \( C_{\text{CO}_2} \) = Carbon dioxide concentration in g/m³; \( Q \) = Flow rate of polluted gas in m³/h; \( V \) = Biofilter bed volume in m³; \( \text{in} \) = inlet; \( \text{out} \) = outlet.

3.4. Results

3.4.1. Influence of phosphorus

The composition of the nutrient solution NS1, as used during this set of experiments, is presented in Table 3-4. To measure the influence of the P content during CH₄ biofiltration, the quantity of solution A (in which 60 % of the P originates from the dibasic sodium phosphate component and the remainder from the monobasic potassium phosphate), used for the preparation of 1 L of nutrient solution, has been varied between 0 and 200 mL.
TABLE 3-4: PREPARATION OF NUTRIENT SOLUTIONS; NS1, NS2 AND NS3, USING SOLUTIONS A, B, C, D AND E.

<table>
<thead>
<tr>
<th></th>
<th>Quantity of solution A (mL/L)</th>
<th>Quantity of solution B (mL/L)</th>
<th>Quantity of solution C (mL/L)</th>
<th>Quantity of solution D (mL/L)</th>
<th>Quantity of solution E (mL/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NS1</td>
<td>0 to 200</td>
<td>10</td>
<td>2</td>
<td>10</td>
<td>1</td>
</tr>
<tr>
<td>NS2</td>
<td>10</td>
<td>0 to 500</td>
<td>2</td>
<td>10</td>
<td>1</td>
</tr>
<tr>
<td>NS3</td>
<td>10</td>
<td>10</td>
<td>0 to 200</td>
<td>10</td>
<td>1</td>
</tr>
</tbody>
</table>

3.4.2. Elimination capacity at an inlet load of 75 g/m³/h

Figure 3-2 presents the elimination capacity and the carbon dioxide production rate measured for P concentrations comprised of between 0.0 and 6.2 g/L. When the P concentration is increased, an increase of the EC can be noted. The optimum level of P in the nutrient solution appears to be around 3.1 g/L, corresponding to a maximal EC of 44.7 g/m³/h. This value is 35% higher than the EC at 0.3 g-P/L (33.9 g/m³/h) and 175% higher than the EC at 6.2 g-P/L (16.2 g/m³/h). Therefore, the N/P mass ratio, leading to the greatest CH₄ bioelimination performance, is 0.24 when both types of nutrients are provided via the nutrient solution used for the daily irrigation of the biofilter. This mass ratio is lower than the theoretical one for the bacteria, suggested by Metcalf and Eddy, which is 6 (Nikiema, 2008; Metcalf and Eddy, 2003). It means that an excess of P has to be applied to the biofilter for maximum efficiency.

A test without P addition was also conducted (Figure 3-2). The results obtained confirmed that EC values as high as 31.8 g/m³/h can be obtained. This value is only some 7% lower than the EC at 0.3 g-P/L and is 40% lower than the highest EC, at 3.1 g-P/L. This result is quite surprising; however, it probably arises from the fact that, before testing the operating mode without the P addition, the biofilter was already colonized by methanotrophs. Indeed, while the biofilter had been washed prior to this test to remove residual P present in the packing, the biomass was still present, to some extent, in the packing. It can be supposed that both biomass...
decay and decomposition, phenomena that release nutrients into the packing (as previously reported during volatile organic compounds biofiltration), helped to ensure the maintenance of the biomass and the quite high removal efficiencies (Nikiema et al., 2007b). This supports the view that if, for any reason, a biofilter in operation is left without regular P provision for some weeks (4 weeks in this study), this would not have a severe detrimental effect on the EC (i.e. around 40 % reduction). However, such an operating mode, i.e. without P addition, is certainly not recommended during the start-up phase of a new biofilter because the low growth rates, caused by the absence of P, will result in lag phase extension.

![Figure 3-2: The elimination capacity (g/m³/h) and the carbon dioxide production rate (g/m³/h) as a function of the phosphorus concentration (g/L); Inlet load = 75 g/m³/h.](image)

The increase in the EC with increase of the P concentration was also translated into an increase in the bacterial growth rate, within the methane biofilter. This observation is
comparable to the behavior previously reported from natural environments, especially those concerned with the increase in the biomass growth rates with increasing P concentration. However, decrease of EC at high P concentrations (> 3.1 g-P/L) was not so often reported for biofilters, probably because most studies were conducted under P limitation. In addition, it has been found, from the present study that high P levels in the nutrient solution are not necessarily recommended because of the increased biomass growth rates, which, in turn, cause a decrease in the EC because of clogging. For example, the value of the EC of 44.7 g/m$^3$/h, obtained at 3.1 g-P/L, can be maintained only for a short time period, e.g. nearly 30 days. After this period, the biofilter clogs-up and its EC decreases. It is to be recalled that the decrease in the performance observed when the biofilter is clogged results from an excessive accumulation of biomass which then disturbs the gas flow and favors the appearance of anaerobic zones (Delhoménie et al., 2003). The biofilter operation must then be terminated and the excess biomass removed.

To illustrate this behavior, Figure 3-3 presents the pressure drop increase measured in the biofilter, for a P concentration of 3.1 g/L and as a function of time (IL of 75 g/m$^3$/h). The EC is also presented in the same Figure. At day 0, the packed bed was hand-washed and the pressure drop within the biofilter was nil. A continuous and regular increase in the pressure drop with time was observed because of biomass accumulation. The increase in the P concentration also had an influence on the start-up time period. Start-up was achieved in 7 - 10 days for a P concentration of 3.1 g-P/L (Figure 3-3), what is faster than the period of 2 weeks observed at a P concentration of 0.3 g/L (data not shown).

This observation reveals that, for a rapid start-up of a biofilter, P concentrations between 1.5 and 3.1 g/L are preferable to lower P concentrations. However, to avoid frequent interruptions of the biological reactor, somewhat lower P concentrations are preferable for long-term operation. Mass N/P ratios, ranging from 0.5 to 2.5, are therefore recommended during for methane biofiltration (CH$_4$ concentrations < 10000 ppmv, at a gas flow rate of 0.25 m$^3$/h). The lower the N/P mass ratio, the higher the clogging rate developed within the biofilter. Previous results, obtained at N/P mass ratio of 2.5 ([N] = 0.75 g/L and [P] = 0.3 g/L in the nutrient solution) confirm that the biofilter performance (EC = 33.9 g/m$^3$/h) can be readily maintained...
unchanged (for up to 1 year) without the appearance of clogging related problems in the biofilter (Nikiema and Heitz, 2007).

Figure 3-3: The variations of the pressure drop (Pa/m) and the elimination capacity (g/m³/h) with time (days); phosphorus concentration = 3.1 g/L and an inlet load = 75 g/m³/h.

3.4.3. Production of carbon dioxide at an inlet load of 75 g/m³/h

The production of carbon dioxide was also investigated during this study. Thus, in Figure 3-2, it is noted that the $\text{P}_{\text{CO}_2}$ follows a tendency somewhat different from that of the EC. Three ranges can be distinguished; i.e. a range of increased values of $\text{P}_{\text{CO}_2}$, for P concentrations from 0 to 1.5 g/L (range I), a range of stability, for P concentrations between 1.5 and 4.5 g/L (range II) and a range of decreased values, where the P concentration is greater than 4.5 g/L (range III). In order to visualise this uncommon behavior of \( \text{P}_{\text{CO}_2} \), a plot representing the ratio $\text{P}_{\text{CO}_2}/\text{EC}$ (i.e. $\alpha$) as a function of the P concentration is shown on Figure 3-4. The EC is also
displayed for comparison purposes, as it can be noted that $\alpha$ and EC have inverse tendencies. During several previous methane biofiltration experiments where the N concentrations in the nutrient solutions were varied between 0.14 and 1.0 g/L, it was demonstrated that both the EC and the $P_{CO_2}$ followed similar tendencies (Nikiema, 2008). In such an ideal situation, $\alpha$ remains nearly constant. A very different behavior is actually observed in Figure 3-4, when $P$ concentration varies between 0 and 6.2 g/L.

![Figure 3-4: The ratio (carbon dioxide production)/(elimination capacity) (i.e. $\alpha$) and the elimination capacity (g/m$^3$/h) as a function of the phosphorus concentration (g/L); Inlet load = 75 g/m$^3$/h.](image)

The main conclusion that can be drawn from Figure 3-4 is such that, while EC increases due to the increase of the $P$ concentration, $P_{CO_2}$ does not exceed a threshold value of 85 g/m$^3$/h, which thus results in a decrease of $\alpha$. This response is probably linked to the decrease in the respiration rate of the micro-organisms when placed in the presence of high $P$ concentrations.
(Smith and Prairie, 2004). This phenomenon is linked to the increase in the biomass growth rate, caused by the increase in the P concentration. However, at values above 3.1 g-P/L, even if the growth rate remains high at such P levels, the high P concentrations may have caused an increase in the mortality occurring in the biofilter as suggested by the lower EC value. The availability of this additional carbon source, that is subsequently biodegraded, causes an increase in the $P_{\text{co}_2}$.

3.4.4. Influence of the P concentration on biofilter efficiency with variable inlet loads

- **Influence on the elimination capacity**

Figure 3-5 presents the EC as a function of the IL (over the range between 8 and 95 g/m$^3$/h) for two concentrations of P in the nutrient solution, i.e. 0.3 and 1.5 g/L (the 0.3 g/L level corresponds to a low P concentration case while the 1.5 g/L level is the optimized concentration, i.e. the one allowing the biofilter to perform at its best with minimum maintenance). It is obvious that the increase in the P concentration produces an increase in the EC value. This increase is however low for IL values < 50 g/m$^3$/h (< 25 %), but it appears to become more and more important as the IL values continue to increase. Indeed, an increase of IL from nearly 50 to nearly 90 g/m$^3$/h results in an increase of the EC values of more than 100 % (from around 29 to around 59 g/m$^3$/h) and of 50 % (from around 24 to around 36 g/m$^3$/h), for P concentrations of 1.5 and 0.3 g/L, respectively. On the other hand, at nearly 50 and 90 g/m$^3$/h, the increase in the P concentration, from 0.3 to 1.5 g/L, causes an increase in the EC values of 23 % and 64 %, respectively. It can therefore be concluded that, in the ranges of IL and P concentrations presently considered, the increase in the EC, resulting from that of the IL (50-100 %), is more noticeable than the one resulting from the P concentration increase (23-64 %).
Influence on the carbon dioxide production

During the same experiment, the $P_{\text{CO}_2}$ was also studied. The results obtained are presented in Figure 3.6 which displays the $P_{\text{CO}_2}$ as a function of the IL for the two P concentrations in the test nutrient solution, i.e. 0.3 and 1.5 g/L. As can be noted, at a specific IL, the $P_{\text{CO}_2}$ almost always increases with increases in the P concentration (from 0.3 to 1.5 g-P/L) but these increases (< 25%) are lower than those of EC (up to 65%, as previously discussed), observed at the same time (in fact, the increase in the $P_{\text{CO}_2}$ is some 2 to 4 times lower than that one measured with the EC parameter). The reason for this behavior of the $P_{\text{CO}_2}$ is that there is here a combination of 3 specific phenomena: i.e. a decrease in the respiration rate (decreasing the values of $P_{\text{CO}_2}$) and an increase in the biomass accumulation (increasing the values of $P_{\text{CO}_2}$),
both being caused by the increase in the P concentration, and finally an increase of the $P_{CO_2}$, resulting from the increase of the IL. Over the present study range, the increase of $P_{CO_2}$ resulting from the increase of the IL is slightly more noticeable than the one resulting from the increase in the P concentration.

![Figure 3-6: The carbon dioxide production (g/m$^3$/h) as a function of the inlet load (g/m$^3$/h) for the two phosphorus concentrations, i.e. 0.3 and 1.5 g/L.](image)

**3.4.5. Influence of potassium, magnesium and calcium**

The composition of the nutrient solution NS2, used during the following experiment, is presented in Table 3-4. The K, Mg and Ca concentrations (through solution B) were varied simultaneously in the biofilter; however, the same mass ratios were maintained: Mg/K = 0.048 and Ca/K = 0.025. The values for these mass ratios have been previously proposed and applied for growth of methanotrophs in liquid media (Nikiema, 2008).
Elimination capacity at an inlet load of 75 g/m³/h

Figure 3-7 presents both EC and the ratio, $P_{CO_2}/EC$, for K concentrations varying from 0 to 3.8 g/L. In order to maintain the mass ratios, Mg/K and Ca/K, at constant values, the Mg concentrations and the Ca concentrations were varied simultaneously, from 0 to 0.18 g/L and from 0 to 0.1 g/L, respectively. As it can be noted, these three parameters do not seem to be determinant in the biological removal efficiency. Almost 3 distinct ranges can be identified in the Figure 3-7. The first range corresponds to the slight improvement of the EC value (around 15%, from 26.4 to 31.3 g/m³/h), caused by the increase in the concentration of K, from 0 to 0.076 g/L. Then, the EC remains constant, between 26 and 28 g/m³/h over the range II, i.e. for K concentrations between 0.152 and 1.525 g/L. Over the last range, a decrease in the EC values (down to 20.9 g/m³/h) for K concentrations > 1.525 g/L can be noted.

Figure 3-7: The elimination capacity (g/m³/h) and the ratio $\alpha$ (i.e. (carbon dioxide production) / (elimination capacity)) as a function of the potassium concentrations (g/L); Inlet load = 75 g/m³/h.
A conclusion derived from this study is that the K is not major nutrients for the methanotrophs involved in methane bioelimination, as compared to N and P. However, the presence of small concentrations of K (0.076 g/L) favors the satisfactory behavior of the methane biofilter. Excessive concentrations of K, Mg and Ca lead to performance reduction.

○ **Production of carbon dioxide at an inlet load of 75 g/m³/h**

The ratio \( P_{CO_2} / EC \) in the methane biofilter, measured in the presence of various concentrations of K, Mg and Ca remained quite constant, i.e. between 2.40 and 2.56, which confirms that the \( P_{CO_2} \) follows the same tendency as the EC (Figure 3-7). This means that K, Mg and Ca do not significantly affect the growth rate of the micro-organisms but simply aids them in their performance, which can slightly improve the EC of the biofilter. As a consequence, no detectable effect of the increased minerals on the biofilter clogging rate could be noted.

3.4.6. **Influence of copper, zinc, manganese, boron, molybdenum, cobalt and iodine**

The composition of the nutrient solution NS3, used during these experiments, is presented in Table 3-4. Among the micro-nutrients provided through the use of solution C are: Cu, Zn, Mn, B, Mo, Co and I, Cu being known to be among the most important of the trace elements (Nikiema et al., 2007a). As in the previous experiments, the Cu concentrations were varied while maintaining the same mass ratios (as proposed from previous studies) with the other trace elements (Table 3-5).
**TABLE 3-5: MAXIMUM CONCENTRATIONS AND MASS RATIOS OF TRACE MINERALS PRESENT IN SOLUTION C.**

<table>
<thead>
<tr>
<th>Mineral: X</th>
<th>Source</th>
<th>Maximum concentrations (g/L)</th>
<th>Mass ratio: X/Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>ZnSO₄·7H₂O</td>
<td>0.0131</td>
<td>2.06</td>
</tr>
<tr>
<td>Mn</td>
<td>MnSO₄·7H₂O</td>
<td>0.0092</td>
<td>1.45</td>
</tr>
<tr>
<td>B</td>
<td>H₃BO₃</td>
<td>0.0017</td>
<td>0.27</td>
</tr>
<tr>
<td>Mo</td>
<td>NaMoO₄·2H₂O</td>
<td>0.0042</td>
<td>0.66</td>
</tr>
<tr>
<td>Co</td>
<td>CoCl₂·6H₂O</td>
<td>0.0024</td>
<td>0.37</td>
</tr>
<tr>
<td>I</td>
<td>KI</td>
<td>0.0127</td>
<td>1.99</td>
</tr>
<tr>
<td>Cu</td>
<td>CuSO₄·5H₂O</td>
<td>0.0064</td>
<td>1.00</td>
</tr>
</tbody>
</table>

0 Elimination capacity at an inlet load of 75 g/m³/h

Figure 3-8 presents the EC and \( P_{\text{CO}_2} \) for several Cu concentrations, varying between 0 to 0.006 g/L. During this study, the EC remained constant, at values between 32.0 and 34.6 g/m³/h. The highest values were obtained at Cu concentrations of around 0 and 0.003 g/L. From our study, we conclude that Cu, Zn, Mn, B, Mo, Co and I have only a minor impact on methane biofiltration. Their addition to the nutrient solution is almost unnecessary. To explain this circumstance, one can mention that the tap water, used for irrigation, already contains most of those trace minerals in concentrations that seem to be sufficient to sustain the biological process (average Cu concentration: 0.000053 g/L and average B concentration: < 0.0001 g/L).

During this experiment, copper was found not to be of real importance. This can be correlated with the observation that a type II methanotroph, *Methylocystis parvus* was identified as the main constituent of the bacterial population of our biofilter (Nikiema et al., 2005). Type II bacteria are known for their ability to grow in the presence of low Cu concentrations (Nikiema et al., 2007a). The results obtained in this study are therefore in accordance with the previously published results.
Figure 3-8: The elimination capacity (g/m³/h) and the carbon dioxide production rate (g/m³/h) as a function of the copper concentration (g/L); Inlet load = 75 g/m³/h.

○ Production of carbon dioxide at an inlet load of 75 g/m³/h

Figure 3-8 shows that P_{CO₂} changed noticeably during the experiment. A continuous increase, from 70.5 to 81.5 g/m³/h, was observed over the range of the study. It can therefore be concluded that the lower levels of trace minerals are preferable, since they lead to lower P_{CO₂} values. During this study, none of these minerals had any substantial effect on the rate of biofilter clogging.

3.5. Conclusion

So far, the biofiltration of methane has been relatively difficult to achieve. Indeed, EC values obtained for CH₄ biofiltration are relatively low, as compared to more easily biodegradable
components for which EC can be superior to $300 \text{ g/m}^3/\text{h}$. In the case of methane, the main difficulty lies in the choice of a suitable packing material. Organic packing materials contain nutrients, but can also contain inhibitory components, detrimental to methane biofiltration. Durability problems may also be encountered. In previous experiments, we have shown that the use of inorganic packing materials can be advantageous. However, inorganic packing materials do not provide any nutrients for microbial metabolism which must be added separately. The influence of nutrients supply on methanotrophs has been studied in the past years. However, most studies have been performed on pure cultures, while numerous cell-cell interactions exist in a biofilm developing inside a biofilter. For example, a nitrogen concentration of $0.14 \text{ g/L}$ has been recommended for use in bacterial culture media, but a higher concentration of $0.75 \text{ g/L}$ has been determined as optimal for biofiltration. Such an increase of N concentration contributed to increasing the EC from 9 to $33 \text{ g/m}^3/\text{h}$.

The main objective of this study aimed to determine the influence of nutrients such as phosphorus, potassium and various trace metals including copper on biofiltration parameters. It revealed that P concentration has an important influence on elimination capacity values measured in the biofilter and needs to be optimized for a particular process. Indeed, the P concentration increase, up $3.1 \text{ g-P/L}$, caused an increase in the elimination capacity value of up to $40 \%$. It also resulted in an increase in the bacterial growth rate within the methane biofilter, which thereby reduced the start-up time. However, P concentrations of around $1.5 \text{ g-P/L}$ are preferable for long-term operations. The K does not seem to be determinant for the biological removal efficiency (the variations in the K concentrations result in low increases or decreases of the EC), in comparison to P, but the addition of a small concentration of K ($0.076 \text{ g/L}$) favors the satisfactory behavior of the methane biofilter. A similar behavior was observed for additions of Mg and Ca while it was also found that the K addition did not significantly affect the growth rate of the micro-organisms. The influence of the Cu presence was studied in the biofilter by varying its concentration between 0 and $0.006 \text{ g/L}$. The results have shown that the Cu played a limited role within the present experiments, during the methane biofiltration. When considering the $P_{\text{CO}_2}$ values, it was found that the lower Cu concentrations are to be preferred.
3.6. Acknowledgments

The authors are indebted to the Natural Science and Engineering Research Council of Canada (NSERC) for their financial support to this project. In particular, co-author, J. Nikiema, would also like to thank NSERC for providing the supporting scholarship for her doctoral studies (Canada Graduate Scholarships Program). The authors are also indebted to A. Martin-Dubreuil for his participation in performing some laboratory tests and to both, Professor J. Peter Jones and Dr. P. Lanigan, for text revision.
CHAPITRE 4. THE INFLUENCE OF THE GAS FLOW RATE DURING METHANE BIOFILTRATION ON AN INORGANIC PACKING MATERIAL

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4.1. Abstract

The influence of the gas flow rate, when varied between 1 and 5.5 L/min, on the conversion, the elimination capacity and the carbon dioxide production, during the biofiltration of methane using a biofilter charged with an inorganic packing material, has been investigated. The methane concentrations considered for this purpose were selected from the operating range of 1300 to 12000 ppmv. The experiments involved were conducted, using a nitrogen minimal salt nutrient solution, for the biofilter periodic irrigation, in which the nitrogen concentration was maintained at 0.75 g/L, and the phosphorus concentration was of 0.3 or 1.5 g/L. The results obtained from this study have confirmed the view that the gas flow rate is a very important parameter, the optimum values found, leading to methane conversions of ≥ 90 %, being ≤ 2 L/min for inlet loads ≤ 55 g/m³/h. Based on this result, it was then established that the maximum volumetric load of methane in the biofilter must be estimated at around 0.075 m³ (methane)/m³ (biofilter)/h, i.e. 6.8 m³ (polluted gas)/m³ (biofilter)/h. In addition, when the gas flow rate is selected between 1 and 4.2 L/min, it has an influence on the elimination capacity. However, the gas flow rate does not affect the carbon dioxide production within the biofilter. It has also been established that the high phosphorus level (i.e. 1.5 g/L), present in the nutrient solution, is to be preferred in the biofilter.
Résumé

L’influence du débit de la phase gazeuse, lorsque varié entre 1 et 5.5 L/min, sur la conversion, la capacité d’élimination ainsi que la production de dioxyde de carbone, lors de la biofiltration du méthane utilisant un biofiltre garni avec un matériau inorganique, a été étudiée. Les concentrations de méthane considérées à cet effet appartaient à un intervalle compris entre 1300 et 12000 ppmv. Lors de ces expériences, une solution nutritive de type «nitrogen minimal salt», dans laquelle la concentration d’azote était maintenue à 0.75 g/L et celle de phosphore à 0.3 ou 1.5 g/L, a été utilisée pour l’irrigation périodique du biofiltre. Les résultats obtenus de cette étude confirment sans nul doute que le débit du gaz pollué est un paramètre de grande importance. Les valeurs de débit gazeux ≤ 2 L/min sont celles optimales, c’est-à-dire permettant des conversions de méthane ≥ 90 % pour des charges de méthane à l’entrée du biofiltre ≤ 55 g/m³/h. S’appuyant sur ce résultat, il a été déduit que la charge volumétrique maximale de méthane dans le biofiltre se situe autour de 0.075 m³ (méthane)/m³ (biofiltre)/h, soit 6.8 m³ (gaz pollué)/m³ (biofiltre)/h. De plus, lorsque le débit gazeux est compris entre 1 et 4.2 L/min, il a une influence sur la capacité d’élimination. Néanmoins, le débit des gaz pollués n’influence pas la production de dioxyde de carbone dans le biofiltre. Il a également été prouvé qu’une concentration de phosphore autour de 1.5 g/L dans la solution nutritive est préférable à une autre de 0.3 g/L, pour un bon fonctionnement du biofiltre.

4.2. Introduction

Methane (CH₄) is a greenhouse gas (GHG), having a global warming potential some 21 times greater than that of carbon dioxide (CO₂) (US EPA, 2008). It is also, after CO₂, the most important GHG, when considering its contribution to the greenhouse effect (15 % for CH₄, versus 78 % for CO₂ and 6 % for nitrous oxide (N₂O)) (Environment Canada, 2008a). Among the now major anthropogenic CH₄ emission sources are the sanitary landfills, contributing, in 2005, some 25 % of the total atmospheric CH₄ emissions in Canada (Environment Canada, 2008b). Indeed, CH₄ is one major constituent of the biogas (up to 70 %) that is today generated in landfills (Nikiema et al., 2005). On the other hand, in Canada, the average non-dangerous waste production per inhabitant during year 2004 was estimated to be around 1040
kg per inhabitant, while the number of landfills was estimated at around 10000. The reason why this last quoted number seems high is because, nationwide, a large amount of such wastes is discarded (without much treatment) through landfilling (some 75 % in 2005), in contrast to what is generally observed in European countries where, in 2004, only some 47 % of the overall wastes produced was landfilled (Nikiema et al., 2007; Roussel, 2008).

To control these CH₄ emissions from landfills, several solutions are now being developed. Combustion, for example, requires a minimal biogas flow rate of 30 m³/h, and a CH₄ concentration preferably of ≥ 30 % V/V, which makes it unsuitable for the smaller and older landfills. Indeed, in Canada, many landfills (including those maintained by cities of less than 35000 inhabitants, having capacities of less than 200000 m³) can be considered to be of small size. On the other hand, old landfills are those of more than 25 years of age (the biogas volume production decreases over time, the same change applies to its CH₄ content). In 2000, some 35 % of Canadian landfills were, more that 20 years old, even if they received some 44 % of the total wastes that were landfilled in the same year (Cameron et al., 2005). Flaring may also be utilized, to avoid the emission of CH₄ into the atmosphere, and when in the presence of a) biogas flow rates of at least 10-15 m³/h and b) CH₄ concentration of ≥ 20 % V/V (Haubrichs and Widmann, 2006). However, this elimination technique is considered by several authors to be a non-environmentally-friendly process because the process generally results in some emissions, mainly into the atmosphere, of dangerous pollutants, such as the dioxins.

In Canada, in 2005, some 52 landfills were equipped with gas collection systems (this represents approximately 25 % more than in 2001) (Environment Canada, 2006). Some 8 of these valorized their collected biogas by combustion and, within some 31 landfills, flares were used; the 13 other landfills remaining were equipped for operating both processes. The total amount of CH₄ collected was approximately 314000 metric tons (of which some 51 % is valorized through combustion and some 49 % is flared), corresponding to 22 % of the overall CH₄ generated by landfills (Environment Canada, 2008a).

For the control of typical biogas effluents, characterized by their low flow rates and low methane concentrations, i.e. < 15 m³/h and < 20 % V/V, respectively, the use of biological
processes is an interesting alternative. Indeed, some aerobic bacteria, such as the methanotrophs, are able to biodegrade CH₄, which results in the formation of water, CO₂ (both at ratios below those obtained from regular chemical oxidation), salts and new biomass. Most recent experimental work has focussed mainly on biofiltration, a bioprocess known for its low operational costs, but a few other biological processes are also mentioned in the literature (Nikiema et al., 2007).

Several processing parameters affect the efficiency of the methane biofilter. One can mention here the nutrients availability, and the gas flow rate (GFR). Indeed, sufficient nutrients concentrations are necessary to support the growth of the micro-organisms within the biofilter. On the other hand, the GFR affects the transfer of the CH₄ from the gas phase to the biofilm (Perry and Green, 1997). When the GFR is high, the empty bed residence time (EBRT) is correspondingly short. Therefore, the pollutant and the other gaseous elements have less time to be transferred to the biofilm and vice versa, and these aspects have a detrimental effect on the biofilter performance. On the other hand, when the GFR is low, the EBRT is high, resulting in either less or almost no limitation, in terms of mass transfer at the gas-liquid interface, but increases the requirement in terms of the biofilter volume (Kim and Deshusses, 2008a, b). A compromise, between the EBRT and the biofilter performance, must therefore be found.

During the control of CH₄ emissions through the landfill biogas, GFR can appear to be an important parameter, especially when the biogas collection is not actively performed (i.e. using only passively vented gas wells). Indeed, in this case, it is to be noted that the biogas emissions depend on the atmospheric air pressure and they vary throughout the day (Nikiema, 2006).

The aim of this study has therefore been the measurement of the influence of the GFR on the CH₄ elimination, through biofiltration, and to estimate the maximum level of GFR allowing conversions within the biofilter above 90 %. On the other hand, because the biodegradation of CH₄ in the biofilter is the consequence of the microbial activity (which consumes the pollutant), the efficiency of this bioprocess is affected by the number and type of the micro-organisms developed in the biofilter, which in turn, is determined by various parameters such
as the nutritional conditions (i.e. the macronutrients (e.g. nitrogen, phosphorus) and micronutrients (e.g. copper) concentrations). It is to be noted that the nitrogen concentration has been previously optimized, and the optimum value found to be located at around 0.75 g-N/L (Nikiema, 2008). Therefore, during this study, the performance of the biofilter under different gas flow regimes, at 2 different phosphorus concentrations, are compared: one being lower than the optimal value (P-concentration = 0.3 g/L), the other being at the level optimized for a proper biofilter operation at an inlet load (IL) of 75 g/m³/h (P-concentration = 1.5 g/L) (Nikiema et al., 2008). The goal has therefore been to determine if the phosphorus concentration can modify the influence of the GFR on the biofilter.

4.3. Material and methods

The packing material is an inorganic gravel material, stone cylindrical pieces. It has been proved elsewhere that inorganic materials give better elimination capacities than a compost based-bed biofilter (Nikiema et al., 2005). This column packing had been tested several times and had proven to be efficient for the CH₄ control task. The density of this packing material is around 1200 kg/m³. In addition, the void fraction within the biofilter is 0.40 and its initial surface area (i.e. including pores) is around 7 m²/g. As a pre-treatment, this material was rinsed with water in order to eliminate the possible impurities present at its surface.

The flowsheet of the up-flow biofiltration system is presented in Figure 4-1. Three identical biofilters were used for these experiments. Each biofilter is an assembled cylindrical tube, built in Plexiglas and composed of 3 identical stages, with a total effective packing material height of around 1 m. The internal diameter of the biofilter is 15 cm, which leads to a total reactive bed volume of around 0.0175 m³/biofilter. The CH₄ provision is ensured through a cylinder filled with pure methane (99 % V/V) and purchased from Praxair Inc. (Sherbrooke, Canada). To generate the polluted gas to be introduced into a biofilter, the pure CH₄ effluent was mixed with a pre-humidified (relative humidity > 90 %) ambient air effluent. Thus, the obtained inlet gas mixture contains approximately 0.7 g/m³ of carbon dioxide (the same concentration as in the ambient air). The room temperature was generally maintained at around 23°C (± 3°C).
In order to maintain sufficient humidity in the biofilter, and to provide nutrients to the microorganisms, filter irrigation was performed daily throughout the study. The quantity of nutrient solution used is approximately 0.1 L of nutrient solution per L of biofilter, the excess irrigation liquid being collected at the base of the biofilter. Two nutrient solutions, of nitrate minimal salt (NMS) type, were tested during this study. The composition of the nutrient solution, NS1, is based on that used by Nikiema (2008). In NS1, the P-concentration is 0.3 g/L. On the other hand, the nutrient solution NS2 has a phosphorus concentration some 5 times that of NS1 (i.e. P-concentration = 1.5 g/L). The specific quantities (g) of the different elements to be dissolved in water, in order to form 1 L of NS1 or NS2, are given in Table 4.1. Biofilter 1 was operated at the lower phosphorus concentration (0.3 g-P/L); Biofilter 2 at the highest phosphorus concentration (1.5 g-P/L); Biofilter 3 was used to complete the previous experiences and to ensure the reproducibility of the runs.
TABLE 4-1: COMPOSITION OF THE NUTRIENT SOLUTIONS: NS1 AND NS2

<table>
<thead>
<tr>
<th>Components</th>
<th>NS1[^1,^2] (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaNO₃</td>
<td>4.56</td>
</tr>
<tr>
<td>Na₂HPO₄</td>
<td>0.86</td>
</tr>
<tr>
<td>KH₂PO₄</td>
<td>0.53</td>
</tr>
<tr>
<td>K₂SO₄</td>
<td>0.17</td>
</tr>
<tr>
<td>MnSO₄·7H₂O</td>
<td>0.037</td>
</tr>
<tr>
<td>CaCl₂·2H₂O</td>
<td>0.007</td>
</tr>
<tr>
<td>FeSO₄·7H₂O</td>
<td>0.00112</td>
</tr>
<tr>
<td>ZnSO₄·7H₂O</td>
<td>0.000576</td>
</tr>
<tr>
<td>MnSO₄·7H₂O</td>
<td>0.000466</td>
</tr>
<tr>
<td>CuSO₄·5H₂O</td>
<td>0.00025</td>
</tr>
<tr>
<td>KI</td>
<td>0.000166</td>
</tr>
<tr>
<td>H₃BO₃</td>
<td>0.000124</td>
</tr>
<tr>
<td>NaMoO₄·2H₂O</td>
<td>0.000096</td>
</tr>
<tr>
<td>CoCl₂·6H₂O</td>
<td>0.000096</td>
</tr>
</tbody>
</table>

[^1]: The composition of NS2 is similar to the one of NS1 except for Na₂HPO₄ (4.3 g/L) and KH₂PO₄ (2.65 g/L).
[^2]: The pH of the nutrient solutions is nearly 7. It can be adjusted, if necessary, by using sodium hydroxide or sulfuric acid liquid solutions.

To start-up each experiment, an inoculation was performed by pouring, on the top of the bioreactor, 1 L of the leachate of a biofilter which has been employed treating CH₄ for at least 6 months. It is to be noted that all biofilters, used in this study, were inoculated with the leachate of the same biofilter and the start-up was generally completed after some 3 to 4 weeks (the start-up is considered completed when the elimination capacity stops increasing with time). In addition, one experiment took nearly one month: around 3 weeks to attain the quasi-steady state and around 1 week to confirm the EC value.

The parameters used for the description of the results are defined in Table 4-2 and are: inlet load (IL), conversion (X), elimination capacity (EC), volumetric load (VL) and CO₂ production rate ($P_{CO₂}$). The results presented in this paper correspond to quasi-steady state operation (to determine that the quasi-steady state is actually reached, the EC must remain...
nearly constant (i.e. variation < 5%), for at least one week, at each operating condition). On the other hand, the follow-up of the biofilter performance, i.e. concentrations of CH₄ and CO₂, at the entry and exit of each stage, was achieved using two analyzers, one for the total hydrocarbons from Horiba (Model FIA 510), and the other for the CO₂ from Siemens (Model Ultramat 22P).

**TABLE 4-2: DESCRIPTION OF THE ASSESSMENT PARAMETERS**

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Methods of determination</th>
</tr>
</thead>
<tbody>
<tr>
<td>IL: Inlet load (g/m³/h)</td>
<td>[ IL = \frac{C(CH_4)<em>n \cdot Q</em>{\text{Total}}}{V} ]</td>
</tr>
<tr>
<td>VL: Volumetric load of methane (m³/m³/h)</td>
<td>[ VL = \frac{Q_{CH_4}}{V} ]</td>
</tr>
<tr>
<td>X: Conversion (%)</td>
<td>[ X = 100 \cdot \frac{(C(CH_4)<em>n - C(CH_4)</em>\text{out})}{C(CH_4)_n} ]</td>
</tr>
<tr>
<td>EC: Elimination capacity (g/m³/h)</td>
<td>[ EC = IL \times \frac{X}{100} ]</td>
</tr>
<tr>
<td>( P_{CO_2} ): Carbon dioxide production rate (g/m³/h)</td>
<td>[ P_{CO_2} = \frac{(C(CO_2)_\text{tot} - C(CO_2)<em>n) \cdot Q</em>{\text{Total}}}{V} ]</td>
</tr>
</tbody>
</table>

\( C_{CH_4} \) = Methane concentration in g/m³; \( C_{CO_2} \) = Carbon dioxide concentration in g/m³; \( Q_{\text{Total}} \) = Volumetric flow rate of air mixture in m³/h; \( Q_{CH_4} \) = Volumetric flow rate of methane in m³/h; \( V \) = Biofilter volume in m³.

On the other hand, in order to determine the influence of the GFR in a biofilter, the GFR has been varied between 1 and 5.5 L/min. The first GFR tested was 4.2 L/min and corresponded to the starting point. Thence, the GFR was increased to 5.5 L/min and decreased continuously until reaching 1 L/min. At each GFR, the different CH₄ concentrations were tested randomly. For lab-security reasons, it was not possible to work at CH₄ concentrations superior to 12000 ppmv.
4.4. Results

4.4.1. Influence of the flow rate on the conversion

- Low phosphorus concentration

Figure 4-2 presents the conversion as a function of the inlet CH$_4$ concentration, varied between 1300 and 10000 ppmv, for 4 different GFRs at the biofilter entrance (i.e. 1, 2, 3 and 5.5 L/min; EBRT of 17.5, 8.7, 5.8 and 3.2 min, respectively) when in the presence of NS1 (low P concentration). The analysis of the Figure 4-2 reveals that the GFR, in the range of 1 to 5.5 L/min, plays an important role on the biofilter performance. Indeed, it is clearly observed that as the GFR increases, the conversion decreases. For example, for a CH$_4$ concentration of around 7500 ppmv, X is 95 % when the GFR is 1 L/min and decreases to around 35 % when it is 5.5 L/min. This variation in the conversion, following the change of the GFR at 7500 ppmv, is similar to that observed at all the other CH$_4$ concentrations tested, i.e. lying between 1500 and 10000 ppmv (X decreases of around 20-25 % after the GFR has been raised, from 1 to 2 L/min, and of around 18 % when the GFR is increased, from 2 to 3 L/min or from 3 to 5.5 L/min). Therefore, from Figure 4-2, it appears that the lower the GFR, the higher were the chances of effecting a total removal of the CH$_4$ within the biofilter.

On the other hand, one also observed a decrease in the value of X as the CH$_4$ concentration increased at a defined GFR. For example, when the GFR is nearly 1 L/min, the conversion remains at around 100 % for CH$_4$ concentrations inferior to 5000 ppmv. The increase in the CH$_4$ concentration above this limit then contributes to the decrease in the conversion (e.g. at around 10000 ppmv, X is nearly 93 %). The conversion decrease (of 7 %), observed with the increase in the CH$_4$ concentration up to 10000 ppmv at 1 L/min, is similar (in terms of proportions) to that observed at the other GFRs (e.g. as X passes from 60 to 52 % (which corresponds to a 8 % decrease) when the CH$_4$ concentration is increased, from around 2000 to around 10000 ppmv, at a GFR of 3 L/min).
Figure 4-2: Conversion as a function of inlet methane concentration for gas flow rates of 1, 2, 3 and 5.5 L/min; nutrient solution: 0.3 g-P/L.

It is to be noted that the tripling of the GFR, from 1 to 3 L/min at 2500 ppmv, causes a decrease in the value of X of some 40 %, while the tripling of the CH$_4$ concentration, from 2500 to 7500 ppmv, results in a less than 7 % decrease in the conversion at GFR values of 1 or 3 L/min (Figure 4-2). Therefore, it can be established that the variation of the conversion, when induced by the increase in the CH$_4$ concentration in the range from 1300 to 10000 ppmv, is less important than the one resulting from an increase in the GFR in the range from 1 to 5.5 L/min. This leads to the conclusion that the GFR is a more critical factor, for the CH$_4$ conversion, than the CH$_4$ concentration, over the present study range. As a consequence, in a biofilter installed at a real landfill site, important fluctuations in the GFR will probably appear to be more detrimental for the biofilter conversion than the variations related to the CH$_4$ concentrations.
High phosphorus concentration

Figure 4-3 represents the conversion, obtained at GFRs of 2, 3 and 5.5 L/min and using the biofilter irrigated with NS2 (high P concentration), as a function of the CH₄ concentration (1300 to 12000 ppmv). Results presented in Figure 4-3 confirm that the GFR, when it is comprised of between 3 and 5.5 L/min, does not affect the level of variation in the value of X (which is of < 10 %) resulting from the increase in the CH₄ concentration up to 10000 ppmv (this has also been noted previously with Figure 4-2, for low P concentration and for GFRs of between 2 and 5.5 L/min). In addition, all curves in Figures 4-2 and 4-3 have nearly identical slopes, of -0.0011, on average, when the GFR is comprised of between 3 and 5.5 L/min. This means that, at these GFR values, the increase in the P-concentration of the nutrient solution (1.5 g/L instead of 0.3 g/L) has no effect on the level of variation of X resulting from the increase in the CH₄ concentration.

Figure 4-3: Conversion as a function of inlet methane concentration for gas flow rates of 2, 3 and 5.5 L/min; nutrient solution: 1.5 g-P/L.
However, when the GFR is 2 L/min, at high value of the P-concentration (1.5 g/L), the variation in the value of X is different from that with the low P-concentration (0.3 g/L). At this GFR value, the slopes of X, when presented as a function of the CH$_4$ concentration, are -0.0012 for NS1 i.e. some 4 times that with NS2 which is -0.0003. This means that, at a GFR of 2 L/min, the high P-concentration in the NS2 has the effect of limiting the decrease in X when the CH$_4$ concentration increases up to 10000 ppmv, as compared to that observed when a low P-concentration is utilized. Therefore, it can be concluded that, for low GFR and in the presence of 1.5 g-P/L in the nutrient solution, the biofilter performs well and stands up well with CH$_4$ concentration variations.

On the other hand, the difference between the performance of the CH$_4$ biofiltration, with NS1 or NS2 (i.e. the performance observed within NS2, minus the one within NS1, at similar GFR), represents the reaction limitation that could exist if the P-nutrient is not provided in sufficient quantities. From Figures 4-2 and 4-3, it is to be noted that this difference, in terms of the value of X, is around 30 % on average for a GFR of 3 L/min, while it is only 15 % on average at a GFR of 5.5 L/min (for CH$_4$ concentrations ≤ 1 % V/V). This behavior confirms that, when in the presence of GFRs of around 3 L/min, the P nutrient availability is a more critical factor for the biofilter operation than when in the presence of a GFR of 5.5 L/min. The reason is that, at a GFR of 3 L/min, the mass transfer of the CH$_4$ at the interface gas-biofilm is easier than that at a GFR of 5.5 L/min and the reaction could become the limiting step. So, the use of higher concentration of P (1.5 g/L) favors the conversion values. But, when the GFR is of 5.5 L/min, the mass transfer, at the interface gas-biofilm, becomes the limiting step. Therefore, even after irrigation with NS2 (high P-concentration), the biofilter conversion is only 15 % greater than with NS1 (low P-concentration). This confirms the point that, even in a biofilter in which nutrients are sufficiently provided, the GFR remains a very critical factor for ensuring the biological process efficiency.

### 4.4.2. Operational ranges and optimal volumetric loads

In considering the results as presented in Figure 4-3, one can define at least 2 separate operational ranges of the GFR. When the GFR ≤ 2 L/min (range I), this corresponds to the best operational region, i.e. the one supporting CH$_4$ removal efficiencies, rising to between 90
and 100% for an initial inlet concentration ≤ 1.1 % V/V. In range I, the mass transfer at the interface gas-biofilm does not seem to be problematic for the biofilter performance, but a reaction limitation can exist when the P concentration in the nutrient solution is not previously optimized (Figure 4-2). Therefore, while operating the biofilter within range I, it is important to provide it with sufficient quantities of nutrients, such as P, in order to enhance the bioreaction. On the other hand, when the GFR ≥ 3 L/min (range II), the CH₄ removal efficiencies are spread out between values of 35 and 90 %, depending on the inlet CH₄ concentration value. In range II, the mass transfer at the interface gas-biofilm becomes an increasingly critical parameter, as the GFR value increases while the reaction limitation becomes of minor importance at the same time.

In general, biofiltration is suitable for the control of high GFR (up to 500000 m³/h) of these effluents characterized by their low concentrations (3-5 g/m³) of both volatile organic compounds (VOCs) and volatile inorganic compounds (VICs). In the case of CH₄ biofiltration, the results presented in this study show that the gas flow rate must be controlled because it dramatically affects the performance of the biofilter. This study has so established that the GFR must preferably be ≤ 2 L/min for good removal efficiencies (i.e. ≥ 90 %), corresponding to EBRT ≥ 8.7 min, for a CH₄ concentration ≤ 1.1 % V/V, and in the presence of sufficient quantities of nutrients for the bacterial growth (e.g. [N] = 0.75 g/L and [P] = 1.5 g/L). In comparison to values relative to other pollutant (VOCs or VICs) biofiltration technologies (usually comprised of between 0.5 and 2 min), the present EBRT values are high (Jorio and Heitz, 1999). The reason why the high EBRT values are necessary is because of the low solubility of CH₄ pollutant in water, as compared to other pollutants, controlled by biofiltration. As an example, the unitless Henry’s law constant is 2.2 10⁻⁴ for methanol (i.e. nearly total solubility) and 30.2 for CH₄ at 25°C (the lower this unitless Henry’s law constant, the higher the solubility for similar concentrations in the gas phase) (Metcalf and Eddy, 2003; Gupta et al., 2000). However, it is to be noted that the Henry coefficient in biofilm can be very different from that of water (Pagans et al., 2007). The EBRT value proposed in the present paper is lower than others that have been applied to the CH₄ biofilters. For example, du Plessis et al. tested in biofilters EBRTs comprised of between 7 and 140 min, at CH₄ concentrations of ≤ 2.5 % V/V. They found that it was possible to obtain 70 % removal
efficiency in the biofilter when the EBRT is 10.6 min, and the CH$_4$ concentrations < 0.5 % (V/V). On the other hand, an EBRT of 20 min was necessary during the biotrickling experiment, conducted by Sly et al., 1993, in order to obtain a CH$_4$ conversion of 90 % when the input CH$_4$ concentration is around 1 % V/V.

The optimum volumetric gas load, as proposed by the results of this study, is 6.8 m$^3$ (gas)/m$^3$ (biofilter)/h, for a CH$_4$ inlet concentration of 1.1 % V/V (higher concentrations have not to date been tested), which corresponds to a volumetric load of CH$_4$ of 0.075 m$^3$/m$^3$/h. These values are higher than those proposed by Streese and Stegmann (2003), i.e. 0.5 to 1 m$^3$ (gas)/m$^3$/h for a CH$_4$ inlet concentration of 2.5 % V/V (volumetric load of CH$_4$ ranging from 0.012 to 0.025 m$^3$/m$^3$/h). However, it is to be noted that the optimum volumetric gas load, proposed by this study for the control of the CH$_4$, remains lower than those applied for VOCs or VICs’ control (i.e. 50 to 100 m$^3$ (gas)/m$^3$ (biofilter)/h) (Jorio and Heitz, 1999). This observation is in accordance with the paper of du Plessis et al. (2003), in which the authors affirm that the bed volume of the CH$_4$ biofilter must be at least some 100 times larger than the one required for odorous pollutants control, when in the presence of similar total gas volumes waiting to be treated (e.g. 1 m$^3$ of biogas, versus 1 m$^3$ of air containing odorous compounds). Nevertheless, it is important to mention that the total gas volumes to be treated in CH$_4$ biofiltration (< 15 m$^3$/h) are not as high as those in other gas biotreatment plants (up to 500000 m$^3$/h).

4.4.3. Influence of the gas flow rate on the elimination capacity and the production of carbon dioxide

Elimination capacity

Figure 4-4 presents the EC in the biofilter, irrigated with NS2, as a function of the CH$_4$ inlet concentration and the GFR applied to the biofilter, the latter rate being of 2, 4.2 or 5.5 L/min. The EC obtained in the biofilter, irrigated with NS1 at the same GFRs, are presented, for comparison purposes.
During this study, when using both nutrient solutions (NS1 and NS2), it has been observed that, as the GFR increases up to 4.2 L/min, the elimination capacity also increases. However, it is important to note that the increase in the EC is not proportional to the one in the GFR. For example, with NS1, for a CH$_4$ concentration of around 9000 ppmv, the EC is nearly 30 g/m$^3$/h when the gas flow rate is 2 L/min and increases to around 38 g/m$^3$/h (27 % increase) when the total GFR becomes 4.2 L/min (110 % increase). On the other hand, the increase in the CH$_4$ concentration also causes an increase in the EC at a constant GFR for all of the P-concentrations considered in this study. For example, at 2 L/min within the biofilter irrigated with NS2, the EC increases almost linearly with the CH$_4$ concentration increase (EC = 0.0041 C$_{CH_4}$).
However, it is to be noted that when the GFR is 5.5 L/min, the EC remains at nearly the same value as the one at 4.2 L/min (at a defined CH₄ concentration, and with NS1 or NS2). For example, with NS2, it is around 60 g/m³/h at 9800 ppmv for GFRs of 4.2 or 5.5 L/min. Also, it can be noted that, in the presence of high P-concentrations in the nutrient solution (NS2), the maximum values of the EC appear higher than for the lower P-concentration (NS1). For example, at around 5500 ppmv, the maximum EC value with NS2 exceeds by 35 % that with NS1 (35 versus 26 g/m³/h), while at around 10000 ppmv, it exceeds by 45 % (60 versus 41 g/m³/h).

The existence of maximal EC values (that the CH₄ biofilter is unable to exceed, no matter the GFR value, i.e. 4.2 and 5.5 L/min), as revealed by this study, has not been reported, according to our present knowledge. However, additional experiments, performed with a CH₄ biofilter packed with another inorganic packing material (2 mm of average particle diameter), have revealed that, on the contrary, the EC even tends to decrease when the GFR is increased from 4.2 to 5.5 L/min (data not shown).

〇 Production of carbon dioxide

Figure 4-5 presents the CO₂ production as a function of the EC, for the 2 test biofilters, one irrigated with NS1 and the other irrigated with NS2, when GFR values of 2, 3, 4.2 or 5.5 L/min are applied at the entry point of the biofilter. It is to be noted that the P_{CO₂} is generally considered as an indicator of the biological activity in the bioreactor (Delhoménie et al., 2008; Dastous et al., 2007).
Figure 4-5: Carbon dioxide production as a function of methane elimination capacity for gas flow rates of 2, 3, 4.2 and 5.5 L/min; nutrient solutions: NS1 (0.3 g-P/L) and NS2 (1.5 g-P/L).

In Figure 4-5, it can be readily noted that $P_{\text{CO}_2}$ depends on the concentration of P present in the nutrient solution and not on the GFR. Indeed, the values of $P_{\text{CO}_2}$, as a function of the EC, are similar at GFRs of 2, 3, 4.2 or 5.5 L/min, but the curves representing $P_{\text{CO}_2}$, as a function of the EC, follow different trends for each of the 2 test nutrient solutions (NS1 or NS2). For example, when the EC = 25 g/m$^3$/h, the CO$_2$ production is nearly 60 g/m$^3$/h in the biofilter irrigated with NS1 (0.3 g-P/L), for all GFR, i.e. 2, 3, 4.2 and 5.5 L/min. In addition, to obtain a CO$_2$ production rate of around 85 g/m$^3$/h, the EC needs to be around 38 g/m$^3$/h, when using NS1, instead of around 58 g/m$^3$/h in the case of NS2 (1.5 g-P/L). Therefore, the results set out in Figure 4-5 tend to show that the behavior of the micro-organisms does not change when only the GFR is varied in the biofilter. However, after switching the nutrient solution, from that of a low P-concentration (NS1) to a high P-concentration (NS2), it is to be noted that the
slope of the $P_{\text{CO}_2}$, presented as a function of the EC, decreased somewhat, from 1.90 to 1.35 (30 % decrease), suggesting an increase of the biomass production.

The decrease of the $P_{\text{CO}_2}$, after use of a higher P-concentration in the nutrient solution, is principally caused by the increase in the biomass growth rates, observed in biofilters irrigated with high P-concentration solutions (Nikiema et al., 2008). Because the carbon becomes used in the form of released CO$_2$ or is used to generate the biomass, the increase in the biomass growth rates leads to the decrease of the $P_{\text{CO}_2}$.

### 4.5. Conclusion

The main objective of this study was the determination of the influence of the gas flow rate on methane biofiltration. The experiment was conducted, using 2 different nutrient solutions: NS1 in which P-concentration was at a low level, i.e. 0.3 g/L; and NS2 in which the P-concentration was at the optimum level: 1.5 g/L. The results obtained following this study indicate that the GFR is a very important parameter which affects the biofilter performance. In addition, the effect of the GFR on the biofilter performance revealed more sensitive than the one of the CH$_4$ concentration.

The best biofilter performance was obtained when the GFR of the biofilter was ≤ 2 L/min. In such conditions, one noted that the biofilter conversion is ≥ 90 % for CH$_4$ concentrations of up to 1.1 % V/V. When the GFR was increased, a decrease in the conversion of CH$_4$ in the biofilter was noted. Indeed, the GFR affected the transfer rate of CH$_4$ at the gas-biofilm interface and a limitation was noticeable for GFR ≥ 3 L/min. However, the GFR did not affected the $P_{\text{CO}_2}$ under all conditions (NS1 or NS2).

Regarding the influence of P for the CH$_4$ biofilter, this study has confirmed that with NS2 (high P-concentration), the biofilter was able to perform with EC levels of up to 45 % higher than when the biofilter was in the presence of low P-concentrations. At both P-concentrations, it was noted that the EC reached a maximum value that the biofilter was unable to exceed, when the GFR was 4.2 or 5.5 L/min, for CH$_4$ concentrations in the study range. During this
study, the P-concentration showed an influence on the bioreaction performance and affected the $P_{CO_2}$ in such a way that the slope of the curve representing the $P_{CO_2}$ as a function of the EC decreased, from 1.90 to 1.35, after the nutrient solution had been changed, from NS1 to NS2.

4.6. Acknowledgments

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5.1. Abstract

The aim of this present paper is to describe the determination of the main microbial kinetic parameters, using a new and simplified technique. The procedure involved was applied as a test case to methane, being both a hydrocarbon and a greenhouse gas. For this purpose, an up-flow biofilter treating methane was operated, with an inlet load of 1800 g.m$^{-3}$.d$^{-1}$. Bed samples from this biofilter were extracted during the period of steady state operations and subsequently employed for the determination of the biofilter kinetic parameters. This study allowed highlighting two methane concentrations' ranges: from 1000 to 14500 ppmv and from 14500 to 27000 ppmv. For the first range, the Monod model proves to be suitable with the kinetic parameters: $\mu_{max} = 0.43 \text{ day}^{-1}$ and $K_m = 5.37 \text{ g.m}^{-3}$. For the second range, neither the Monod nor the Haldane's formulation could directly be used. However, a mathematical adjustment of the Monod model allows to find kinetic parameters $\mu'_{max} = 1.09 \text{ day}^{-1}$ and $K'_m = 7.59 \text{ g.m}^{-3}$. The biomass yields for the tested methane concentrations have also been determined and showed 2 different tendencies, depending on the same 2 ranges. For the first range of methane concentrations, the biomass yield was quite constant with an average value around 0.36 g biomass.(g methane)$^{-1}$ while for the second range, it could be approached by a polynomial second-order regression. The maximum value of the biomass yield obtained on the second range was 0.8 g biomass.(g methane)$^{-1}$ at a methane initial concentration of 20000 ppmv.
Résumé

L’objectif de cet article est de décrire la détermination des principaux paramètres cinétiques à partir d’une méthode simplifiée récemment développée. Cette dernière a ainsi été appliquée, pour des fins de validation, au méthane qui est à la fois un hydrocarbure et un gaz à effet de serre. À cet effet, un biofiltre à écoulement ascendant a été alimenté avec une charge initiale de méthane de 1800 g.m\(^{-3}\). Des échantillons de lit filtrant ont ensuite été prélevés dans le biofiltre, lorsque le régime permanent a été atteint, et utilisés pour la détermination des paramètres cinétiques. Cette étude a permis d’identifier 2 gammes de concentrations de méthane, soit de 1000 à 14500 ppmv et de 14500 à 27000 ppmv. Pour la première gamme, le modèle de Monod s’est révélé approprié, les paramètres étant \(\mu_{\text{max}} = 0.43\) j\(^{-1}\) et \(K_m = 5.37\) g.m\(^{-3}\). Pour la seconde gamme de concentrations de méthane, aucun des modèles de Monod ou de Haldane ne pouvait être directement utilisé. Néanmoins, un ajustement mathématique du modèle de Monod a donné les paramètres suivants: \(\mu'_{\text{max}} = 1.09\) j\(^{-1}\) et \(K'_m = 7.59\) g.m\(^{-3}\). Par ailleurs, les rendements de biomasse ont été déterminés et ont suivi des tendances différentes, en fonction de la gamme de concentrations de méthane considérée. Ainsi, pour la première gamme de concentrations de méthane, les rendements de biomasse sont demeurés quasi-constants, avec une valeur moyenne de 0.36 g biomasse.(g méthane\(^{-1}\)) tandis que pour la deuxième gamme, ils pouvaient être approchés à l’aide d’une régression polynomiale de second ordre. Le rendement de biomasse maximum, qui a été mesuré dans la seconde gamme, était de 0.8 g biomasse.(g méthane\(^{-1}\)) à une concentration de méthane initiale de 20000 ppmv.

5.2. Introduction

Since the 1960s, biofiltration has been very often used to control emissions of contaminated gaseous effluents (Kim and Sorial, 2007; Civilini, 2006; Janni et al., 2001). The advantages of biofilters used in this role are: 1) they are usually operated at both room temperature and pressure; and 2) the microbial activity (metabolic energy) converts pollutants, such as methane (CH\(_4\)), into mineral products (water, carbon dioxide (CO\(_2\)), etc.), salts and biomass. Methane is a low molecular weight hydrocarbon gas, well known for its impact on the global greenhouse effect. Emissions to atmosphere of this compound in Canada have thus been
estimated to be at the level of around 92 million metric tons (CO₂ equivalent), for the year 2003 only (Environment Canada, 2005).

The rate of CH₄ biodegradation, as achieved by the relevant bacteria (methanotrophs) contained in filter beds, is one of the main factors controlling the CH₄ biofiltration process. Therefore, some knowledge of the kinetics of the CH₄ biodegradation process is the starting point for the modeling of its biofiltration process. Very few experimental studies of this type have been conducted in the case of CH₄. Most published studies have been performed with either biofilms or with liquid culture media, using the simultaneous treatment of CH₄ and chlorinated compounds, such as trichloroethylene (Broholm et al., 1992; Smith and McCarty, 1997; Arcangeli and Arvin, 1999). On the other hand, the results obtained in these cases have not always been representative of the real natural phenomenon, the mass transfers not always being similar between those conditions achieved in the tests and those experienced in the real biofilter.

Thus, the protocol, as applied in this study for the determination of the involved microkinetic parameters, utilizes biomass samples taken directly from the biofilter. It therefore considers both the Monod and the Haldane kinetic models, in order to characterize more fully the obtained experimental data.

5.3. Equipment and procedures

In order to conduct the particular experiments leading to the determination of the needed kinetic parameters, it is necessary to operate a continuous laboratory-scale biofilter from which bed samples are extracted, according to a schedule. The samples are then either directly utilized for the kinetic tests, or are otherwise pretreated for the extraction of the contained micro-organisms.

5.3.1. Continuous biofiltration setup

The continuous, upflow biofiltration system for methane has been presented elsewhere (Nikiema et al., 2005). In the methane biofilter, the filter bed consisted of an inorganic
material, having an average particle size of 5 mm and a density of near 1200 kg.m⁻³ (additional details on the inorganic material employed are not currently available, due to the existence of a confidential agreement with the particular company providing the filter material). During the operations, the packing bed was irrigated at a rate of 1 L of nutrient solution per day. The composition of the nutrient solution employed is that presented by Nikiema et al. (2005). The total gas flow rate was maintained at 6 m³.day⁻¹, the initial pollutant concentration being fixed at 4.8 g.m⁻³. Kinetic tests were thereafter undertaken once steady-state conditions were reached in the biofilter.

5.3.2. Kinetic protocol

For each batch reactor, some 20 g of bed pellets, previously extracted from the continuous, steady-state biofilter, were necessary (the amount of pellets was previously optimized to reduce the time required for the completion of each test). After the sampling, and in order to favor the volatilization of the substrate contained in the sample, pellets were left exposed for a few minutes in the laboratory atmosphere.

To perform a kinetic test, it is necessary to follow the evolution of the methane and carbon dioxide mass changes versus time, processes that occur in the batch thermostated (20°C) reactors (i.e. duplicate reactors for the reproducibility, and a blank reactor in which there is no added substrate. The use of the blank reactor allows the verification that there is no residual CH₄ available in the solid extracts). The batch reactor is made of pyrex and has a volume of 0.5 L. The biomass is attached to the solid filter bed particles, these are subsequently extracted from the biofilter and thereafter introduced into the batch reactor. It is to be noted that each test run begins only after the substrate is been introduced into the reactor. The headspace gases are regularly sampled by means of a gastight syringe (100 μL, Hamilton), through a septum, so that the reactors remain leak-proof during the program of tests. Measurements of the CH₄ and CO₂ concentrations in the product gases were performed with a gas chromatograph, coupled to a mass spectrometer (GC/MS, Hewlett Packard, 5890 Series II and CP-PoraBOND, (Varian, Quebec)). The collected data (methane and carbon dioxide concentrations) were related to the biomass concentrations’ change. For each pollutant
concentration, experiments were conducted at least twice and differences between the specific growth rate values obtained were less than 5% on average for all experiments.

5.3.3. Analysis tools

To represent the microbial growth kinetics, the Monod (Equation 5-1) and the Haldane (Equation 5-2) models have been considered:

\[ \mu = \frac{\mu_{\text{max}} S}{K_m + S} \]  
(Eq. 5-1)

\[ \mu = \frac{\mu' S}{K_h + S + \frac{S^2}{K_i}} \]  
(Eq. 5-2)

where \( \mu \) is the specific growth rate (d\(^{-1}\)), \( \mu_{\text{max}} \) (d\(^{-1}\)) and \( K_m \) (g.m\(^{-3}\)) are the Monod model parameters, \( \mu' \) (d\(^{-1}\)), \( K_h \) (g.m\(^{-3}\)) and \( K_i \) (g.m\(^{-3}\)), the Haldane model parameters, and \( S \) the substrate concentration present in the biofilm (g.m\(^{-3}\)).

The first order (or exponential) microbial growth kinetics is now described as follows:

\[ \frac{dB(t)}{dt} = \mu B(t) \]  
(Eq. 5-3)

where \( t \) is the elapsed time, and \( B(t) \) is the mass of biomass (g) at time \( t \). Now, by considering the exponential phase of the microbial growth, where \( \mu \) is maximal and constant, and by integrating Equation 5-3, it becomes:

\[ \ln(B(t)) = \ln(B_0) + \mu t \]  
(Eq. 5-4)

where \( B_0 \) is the initial mass (at \( t = 0 \)) of the biomass contained in the batch reactor (g).

Then, according to the biomass yield coefficient, \( Y(t) \), the biomass production can be correlated to the substrate consumption as follows:
\[ Y(t) = \frac{B(t) - B_0}{m_0 - m(t)} \]  
(Eq. 5-5)

where \( m_0 \) is the initial mass of substrate (g), and \( m(t) \) (g) is the mass of substrate at time \( t \).

On the other hand, \( Y(t) \) is able to slightly vary during the experiment. To simplify the calculations, an average value noted \( Y \) is determined, according to Equation 5-6:

\[ Y = \text{Average} [Y(t)] \]  
(Eq. 5-6)

The determination of the initial mass of biomass was effected by means of a method based on the Bradford method, a colorimetric method used for the determination of the concentration of proteins in a solution (Kamizake et al., 2003). Considering an average ratio of 50% wt/wt (concentration of proteins)/(concentration of biomass), the initial concentration of biomass per unit mass of filter material was then determined. The initial biomass concentrations for each pollutant were measured several times during the experiments. The average value obtained was around 1700 g biomass.m\(^3\).

For these experiments, the diffusion limitation between the reactor headspace and the biolayer that contains the micro-organisms is neglected. So, the substrate concentration in the biofilm at time \( t \) (\( S(t) \)) equals the headspace concentration of the substrate (\( C(t) \)), and thus Equation 5-5 becomes:

\[ B(t) = B_0 + Y(m_0 - V_{gas}S) \]  
(Eq. 5-7)

By solving the following stoechiometric analysis of the biodegradation reaction balances:

\[ a\text{CH}_4 + b\text{O}_2 + \text{Nutrients} \rightarrow c\text{CH}_{1.8}\text{N}_{0.2}\text{O}_{0.5} + d\text{H}_2\text{O} + e\text{CO}_2 + \text{Salts} \]  
(Eq. 5-8)

where \( \text{CH}_{1.8}\text{N}_{0.2}\text{O}_{0.5} \) is the biomass formula (Jorio et al., 2005; Bailey and Ollis, 1986), the expression for \( Y(t) \) becomes:
\[ Y_{\text{Methane}}(t) = 1.54 \left( 1 - \frac{16}{44} \frac{m_{\text{CO}_2}(t) - m_{0,\text{CO}_2}}{m_{0,\text{CH}_4} - m_{\text{CH}_4}(t)} \right) \]  
(Eq. 5-9)

where \( m_x(t) \) (in g) stands for the mass of \( X \) at an elapsed time \( t \) and \( m_{0,x} \) stands for the initial mass of \( X \) in the reactor (g), \( X \) being either the \( \text{CH}_4 \) or the \( \text{CO}_2 \).

5.4. Results and discussion

5.4.1. Determination of the specific growth rates

By measuring the headspace concentrations of the substrate and carbon dioxide in the batch reactor, the mass of biomass (\( B \)) can be theoretically quantified at various elapsed times by using Equation 5-7, once the biomass yields, given by Equation 5-9, is determined. Experimental data for solid extracts, as reported in Figure 5.1, illustrate typical evolutions of the mass of biomass and methane concentration versus time during kinetic tests when \( C_{0,\text{CH}_4} = 9.6 \text{ g.m}^3 \).

When the initial methane concentration is below 7 g.m\(^3\), 3 reaction domains can be easily identified: i.e. 1) a lag phase, with nearly no change in the mass of biomass or methane concentrations; 2) an exponential growth phase, with maximum growth or degradation rates; and 3) a growth deceleration phase (decreasing slopes) (those data are not shown). However, for initial methane concentrations of 9.6 g.m\(^3\), there is no evident lag phase, as it can be noticed in Figure 5-1. For initial methane concentrations higher than 9.6 g.m\(^3\), a trend similar to the one in Figure 5.1 is observed (those data are not shown). It confirms that, by increasing the initial methane concentration, it is possible to reduce the lag phase during the start-up of a methane treating biofilter (Nikiema et al., 2007).

The determination of \( \mu \), corresponding to each initial concentration of methane, is effected by plotting \( \ln(B) \) versus time, with the data in the exponential phase. The slopes of the least-
squares linear regressions provide the values of μ for each initial concentration of pollutants, as suggested by Equation 5-4.

Figure 5-1: Typical experimental evolutions of the mass of biomass and methane concentration versus time (20 g solid extracts, \( C_{0,CH_4} = 9.6 \text{ g.m}^{-3} \)).

5.4.2. Determination of the kinetic parameters

The determination of the kinetic parameters was done only using bed samples taken from the biofilter upper stage. It is to be noted that the present method, with solid extracts, and without an addition of extra nutrient solution, allows approaching the behavior of a real biofilter.

The values of the specific growth rates were determined for \( \text{CH}_4 \) concentrations varying from 1000 to 27000 ppmv, that to say 0.65 to 17.70 g.m\(^{-3}\). For security reasons, higher \( \text{CH}_4 \)
concentrations values could not be tested. Then, $\frac{C_{0,CH_4}}{\mu}$ was plotted as a function of $C_{0,CH_4}$ and linear and 2nd-order polynomial regression used to estimate the kinetic parameters of CH$_4$ biodegradation, for the Monod and the Haldane models respectively.

After applying this method, one found that neither the Monod model nor the Haldane model could be used to approach the experimental specific growth rates, as it can be observed in Figure 5.2. Based on this fact, 2 ranges of CH$_4$ concentrations have been defined: the first (range I) from 0.65 to 9.6 g.m$^3$ (1000 to 14500 ppmv) and the second (range II) from 9.6 to 17.70 g.m$^3$ (14500 to 27000 ppmv). For each specific range, the kinetic parameters have been determined.

![Figure 5.2: Evolution of the specific growth rate versus the initial methane concentration: Representation of the Monod and Haldane models considering all experimental data.](image)
Figure 5-3 presents the ratio $\frac{C_{0,\text{CH}_4}}{\mu}$ as a function of $C_{0,\text{CH}_4}$ using data belonging to range I. The linear and 2nd-order polynomial regressions for Monod and Haldane models, respectively, were then used to estimate the kinetic parameters which turned to be:

$$\mu_{\text{max}} = 0.43 \text{ day}^{-1}; K_m = 5.37 \text{ g.m}^{-3} \quad \text{(Monod model)} \quad \text{(Eq. 5-10)}$$

$$\mu^* = 0.19 \text{ day}^{-1}; K_h = 1.35 \text{ g.m}^{-3}; K_i = -17.88 \text{ g.m}^{-3} \quad \text{(Haldane model)} \quad \text{(Eq. 5-11)}$$

Figure 5-3: Evolution of $\frac{C_{0,\text{CH}_4}}{\mu}$ versus the initial methane concentration for range I.

It can be noticed here the negative value of the inhibition parameter of the Haldane model which shows that there is no methane inhibition in this range. On the contrary, it proves that
the methane growth rates are stimulated by the increase of the initial methane concentration. This result is conclusive because it is shown that the performance in CH\(_4\) elimination by methanotrophs increases with CH\(_4\) concentration up to 130 g.m\(^{-3}\) (200 000 ppmv) (Bender and Conrad, 1995).

For range II, it was not possible to determine directly the kinetic parameters with both models. Therefore, a mathematical transformation was made by writing \(C'_{0,CH_4} = C_{0,CH_4} - 9.6\) and \(\mu' = \mu - 0.29\) where: \(C'_{0,CH_4}\) represents the adjusted initial methane concentration; \(\mu'\) represents the adjusted specific growth rate; 9.6 corresponds to the concentration in g.m\(^{-3}\) of 14500 ppmv of CH\(_4\) (the limit of range I); and 0.29 day\(^{-1}\) corresponds to the specific growth rate at an initial methane concentration of 9.6 g.m\(^{-3}\). Therefore, \(\frac{C'_{0,CH_4}}{\mu'}\) was represented as a function of \(C'_{0,CH_4}\) and linear and 2nd-order polynomial regression have been used to estimate the kinetic parameters (Figure 5.4).

\[
\mu_{max}' = 1.09 \text{ day}^{-1}; K'_m = 7.59 \text{ g.m}^{-3} \quad \text{(Monod model)} \quad \text{(Eq. 5-12)}
\]

\[
\mu'^* = 1.62 \text{ day}^{-1}; K'_h = 12.00 \text{ g.m}^{-3}; K'_i = 18.38 \text{ g.m}^{-3} \quad \text{(Haldane model)} \quad \text{(Eq. 5-13)}
\]

Figure 5.5 presents the specific growth rates as a function of the initial methane concentration along with Monod and Haldane models representations. As it can be seen, both models can be used to approximate the \(\mu\) values. However, the Monod model is simpler and therefore to be preferred. In range I, the specific growth rate doubles, from 0.14 to 0.29 day\(^{-1}\), when the initial methane concentration goes from 2.9 to 9.6 g.m\(^{-3}\) (more than 3 times) while in range II, increasing the initial methane concentration from 9.6 to 17.70 g.m\(^{-3}\) (nearly double) almost triples the growth rate: from 0.29 to 0.84 day\(^{-1}\). Nevertheless, the overall growth rates are low, compared, for example, to those obtained with toluene, which is also conclusive (Lavoie, 2005). Also, there is still no apparent inhibition for range II.
The existence of two ranges, with specific methane degradation characteristics, is supported by previous experiments which have shown that methanotrophs are spread over 2 main types. Indeed, type I methanotrophs are usually able to grow on methane concentrations below 1000 ppmv while for type II methanotrophs, the preferred range is 10000 ppmv and higher. However, there are exceptions and some type I bacteria appear to grow better in the presence of methane concentrations above 10000 ppmv and vice-versa (Nikiema et al., 2007). The continuous biofilter, from which solid extracts were taken, was operated with methane concentration of about 7200 ppmv (4.8 g.m\(^{-3}\)), and at that concentration, it is argued that both types of methanotrophs may grow in the media (Henckel et al., 2000). Nevertheless, the bacteria previously found to dominate (at 75%) in the methane biofilter is *Methylocystis parvus*, a type II methanotroph (Nikiema et al., 2005).
In general, type I bacteria are characterized by a higher affinity (selectivity) for methane, as compared to type II bacteria. However, type II methanotrophs usually have higher rates of biodegradation of methane. Therefore, one explanation of the special behavior noticed during our experiments can be that, below 14500 ppmv, only type I micro-organisms are favored and type II bacteria are not especially active even if they are dominant in the biofilter. As the methane concentration increases (above 14500 ppmv), an increase in the bacterial activity of the type II methanotrophs is noted. This increase of the growth rate causes thereafter an increase of the biomass yield, as shown below.

Figure 5.6 presents the average values of the biomass yield expressed in g biomass.(g methane)$^{-1}$ when the methane concentration varies from 0.65 to 17.70 g.m$^{-3}$. The analysis of this graph also confirms the presence of the two ranges of methane concentrations previously
mentioned. For range I, Y varies little with a slight and continuous increase, from 0.34 to 0.39 g biomass per g methane. Above 9.6 g.m⁻³ (14500 ppmv), the increase is more noticeable and the value at 13.1 g.m⁻³ (20000 ppmv) is double that at 9.6 g.m⁻³ (0.80 versus 0.39 g biomass per g methane). Then, a decrease to 0.66 g biomass per g methane is observed at 17.70 g.m⁻³ (27000 ppmv). It is to be noted that the theoretical maximum yield, obtained by considering that all methane is used to generate biomass (no carbon dioxide production), is 1.54 g biomass per g methane. Also, the values of the biomass yields reported in the literature, which are usually between 0.02 and 0.8 g biomass per g methane, are similar to our results (Arcangeli and Arvin, 1999).

In the continuous inorganic biofilter from which the samples were taken, it has been previously demonstrated that the percentage of assimilation of the methane in the biomass during the biofiltration process was around 25 % (Nikiema et al., 2005). Therefore, the experimental biomass yield for the laboratory-scale biofilter, obtained by following the amount of carbon dioxide produced (g) per g of methane oxidized, is 0.39 g biomass per g methane. This latter value should, in principle, be slightly over-evaluated because of the presence of a small proportion of methane non-degrading micro-organisms (which can also generate carbon dioxide) in the biofilter. This experimental biomass yield (0.39 g biomass per g methane at an inlet methane concentration of 4.8 g.m⁻³) is close to the theoretical value of 0.35 g biomass per g methane suggested by Figure 5.6 for the same initial methane concentration (4.8 g.m⁻³).

After this study, it can be concluded that the methane concentration favoring the growth of the micro-organisms (high Y: 0.8 g biomass per g methane and high μ: 0.7 day⁻¹) is located around 20000 ppmv. This concentration is interesting especially during the start-up of a biofilter. However, for a continuous operation, the methane concentration should remain below 14500 ppmv in order to avoid rapid clogging of the biofilter caused by an important rate of bacterial multiplication.
5.5. Conclusion

This paper reports an experimental determination of the microkinetic parameters characterizing a continuous, steady-state biofilter, treating methane. The method, as described in the present paper, consisted of studying the growth of the microbial extracts immobilized on bed pellets that were directly sampled from an operating biofilter. In the case of the methane biodegradation kinetics, 2 ranges of CH₄ concentrations were identified. The first range (range I) was from 0.65 to 9.6 g.m⁻³, while the second (range II) from 9.6 to 17.70 g.m⁻³. For each of these ranges, the kinetic parameters were determined, after mathematical transformation when necessary. The Monod model was found to be accurate, with \( \mu_{\text{max}} = 0.43 \) d⁻¹ and \( K_m = 5.37 \) g.m⁻³, for range I and \( \mu'_{\text{max}} = 1.09 \) d⁻¹ and \( K'_m = 7.59 \) g.m⁻³ for range II. The biomass yields were also determined and were comprised between 0.34 and 0.80 g biomass. (g
methane)\(^1\). According our knowledge, this is the first study of determination of microkinetic parameters issued from a methane biofilter. However, experiments with higher methane concentrations will have to be done to confirm the present tendencies.

5.6. Acknowledgements

The authors are indebted to the Natural Science and Engineering Research Council of Canada (NSERC) for their financial support to this project. One co-author, J. Nikiema, also thanks the NSERC (Canada Graduate Scholarships Program) for providing a scholarship for her doctoral studies. The authors also wish to thank: Professor Ryszard Brzezinski (Department of Biology, Faculty of Science, Université de Sherbrooke), for allowing them to perform microbiological tests in his laboratory, and Corinne Gagnon-Poirier, an undergraduate student, for her participation in performing the tests with the solid extracts. They also express their gratitude to Dr. P. Lanigan for text revision.
5.7. Notations

\begin{align*}
a, b, c, d, e & \quad \text{Stoichiometric coefficients of the methane biodegradation balance} \\
B & \quad \text{Mass of biomass} \quad g \\
B_0 & \quad \text{Initial mass of biomass} \quad g \\
C & \quad \text{Concentration of substrate in the reactor headspace} \quad g.m^{-3} \\
C_{0,x} & \quad \text{Initial substrate concentration of } X \text{ in the biofilm} \quad g.m^{-3} \\
K_h & \quad \text{Haldane constant} \quad g.m^{-3} \\
K_i & \quad \text{Haldane inhibition constant} \quad g.m^{-3} \\
K_m & \quad \text{Monod constant} \quad g.m^{-3} \\
K'_h & \quad \text{Adjusted Haldane constant} \quad g.m^{-3} \\
K'_i & \quad \text{Adjusted Haldane inhibition constant} \quad g.m^{-3} \\
K'_m & \quad \text{Adjusted Monod constant} \quad g.m^{-3} \\
m_{0,x} & \quad \text{Initial mass of } X \quad g \\
m_{f,x} & \quad \text{Final mass of } X \quad g \\
S & \quad \text{Concentration of substrate in the liquid phase} \quad g.m^{-3} \\
t & \quad \text{Time} \quad d \\
X & \quad \text{Methane or carbon dioxide} \quad (-) \\
Y & \quad \text{Biomass yield coefficient} \quad g \text{ biomass.}(g \text{ substrate})^{-1} \\
\mu & \quad \text{Specific microbial growth rate} \quad d^{-1} \\
\mu' & \quad \text{Adjusted specific microbial growth rate} \quad d^{-1} \\
\mu_{\text{max}} & \quad \text{Maximum specific growth rate in the Monod model} \quad d^{-1} \\
\mu'_{\text{max}} & \quad \text{Maximum specific growth rate in the adjusted Monod model} \quad d^{-1} \\
\mu^* & \quad \text{Maximum specific growth rate in the Haldane model} \quad d^{-1} \\
\mu'^* & \quad \text{Maximum specific growth rate in the adjusted Haldane model} \quad d^{-1} \\
\end{align*}
6.1. Abstract

Methane is a greenhouse gas, emitted from various sources such as landfills, and effectively removed by biofiltration process. This paper presents a steady state model of methane biofiltration taking into consideration the impact of various parameters, such as the inlet methane concentration, the overall gas flow rate and the packing bed average temperature, on the methane biofilter efficiency. More specifically, the model developed here considers that the average bed temperature is influenced by the elimination capacity of the methane in the biofilter, and subsequently, it has some influence on the bacterial growth rates and also on the Henry coefficients. When using this model, it is possible to estimate the biofilter performance in terms of some parameters, such as the conversion, elimination capacity and carbon dioxide production. Comparison of the model predicted performance values with the experimental data (in the range of concentrations ranging between 1500 to 9500 ppmv) yields satisfactory results (< 2-10 % error, depending on the inlet methane concentration and on the performance parameter).

Résumé

Le méthane est un gaz à effet de serre issu de diverses sources, notamment des sites d’enfouissement sanitaire, qui peut être éliminé de façon efficace grâce à la biofiltration. Cet article présente une modélisation de la biofiltration du méthane en régime permanent. Le modèle développé prend en considération l’impact de différents paramètres tels la
concentration initiale de méthane, le débit total du gaz pollué et la température moyenne du biofiltre, sur les performances du biofiltre. Plus précisément, le modèle développé considère que la température moyenne du biofiltre est déterminée par la capacité d'élimination du méthane dans le biofiltre, et qu'elle influence la croissance microbienne de même que les coefficients de Henry. À partir de ce modèle, il est possible d'estimer la performance du biofiltre chargé de l'élimination du méthane en termes de conversion, de capacité d'élimination et de production de dioxyde de carbone. La comparaison des résultats expérimentaux avec ceux prédits par le modèle (dans la gamme de concentrations de méthane comprises entre 1500 et 9500 ppmv) s'est révélée satisfaisante (l'erreur n'excédant pas 2 à 10 %, en fonction des concentrations initiales de méthane et du paramètre de performance considéré).

6.2. Introduction

Methane (CH₄) is a greenhouse gas that is 21 times more detrimental to atmospheric stability than carbon dioxide (CO₂). The emissions of this pollutant to atmosphere are mainly related to energy generation, agriculture and waste disposal landfills. Several earlier studies have demonstrated that the CH₄ emitted from these sources can be efficiently controlled by means of biofiltration (Nikiema, 2008). Methane biodegradation is realized by the methanotrophs, i.e. those bacteria that use the released CH₄ as their sole and unique carbon source, in order to satisfy their metabolic needs. In addition to the methanotrophic population, the availability of nutrients (mainly as nitrogen and phosphorus elements) and supportive operating conditions, such as the moisture of the packing material, the packing bed temperature, the gas flow rate and the inlet CH₄ concentration, are all to be accounted for among the factors needing to be closely controlled for operating a successful bioprocess.

To date, the optimization of most of the main operating parameters for the biological elimination of CH₄ in biofilters is being continued, the way they affect the bioprocess efficiency being understood. It is therefore now easier to operate the closed biofilter and to obtain high elimination capacities (> 60 g/m³/h) and conversions (80 to 100 %) within the biofilter (Nikiema, 2008). The next step is therefore to apply the practical conclusions
resulting from the lab-scale study to either a pilot-scale or an industrial closed biofilter set-up. To date, there is no such industrial biofilter known to be installed in a landfill facility. Some pilot-scale experiments only have either been conducted or are presently being conducted all over the world (e.g. in Germany, in Australia and in China). These tests are being conducted with open biofiltration systems only and are therefore exposed to various climatic conditions (e.g. the temperatures and the humidities) which affect both their individual performance and also the load of CH$_4$ pollutant to be treated.

The objective of this present study is that of developing a steady state model that takes into account the important operating parameters, such as the inlet CH$_4$ concentration, the gas flow rate and the packed bed average temperature, affecting the CH$_4$ biofilter efficiency. Such a model could then be used to estimate the overall biofilter efficiency, i.e. in terms of the conversion, elimination capacity and carbon dioxide production ($P_{CO_2}$).

### 6.3. Model development

#### 6.3.1. Hypothesis

To generate the mathematical model of the methane biofilter presented in this paper, some assumptions have been made and are described in the following.

1. In the CH$_4$ biofilter, there is no oxygen (O$_2$) supply limitation because O$_2$ is abundantly present (around 20 % V/V for O$_2$ versus < 1.2 % V/V for CH$_4$) and is more readily transferred than the CH$_4$. The diffusion coefficients are $2.5 \times 10^{-5}$ and $1.49 \times 10^{-5}$ cm$^2$/s for O$_2$ and CH$_4$, respectively, at a temperature of 298 K (Jorio et al., 2003; King and Adamsen, 1992).

2. In the typical biofilter, the gas flow follows a plug-flow regime. Indeed, when clogging is present in a biofilter, the existence of dead zones (i.e. preferential pathways) leads to deviation from the plug-flow model behavior. In such cases, a dispersion coefficient could be introduced into the model. It was not necessary to take such parameter into consideration (i.e. to consider a deviation from the plug flow regime) within the present CH$_4$ biofilter, because there was generally, almost no filter bed clogging observed.
3. In general, models consider a planar geography, which means that the biofilm covers the packing material particle entirely. This present model will adopt a similar assumption. It will be noted that, in some particular cases, the existence of uncovered filter material particles are considered and generally, it is supposed that the uncovered surface intervenes in the process, through adsorption, if the packing material permits it. However, in our present case, the pollutant CH$_4$ cannot be readily adsorbed under the present operating conditions (e.g. gas humidity > 80 %) (Crosdale et al., 2008) and the present inorganic packing material is not generally used as an adsorbent.

4. The biofilm is uniform in the biofilter, having constant and uniform density and other characteristics, including its thickness (estimated at an average value of 85 $\mu$m).

5. The density of the biomass is nearly constant over the entire biofilter. This assumption is believed to be acceptable for the steady state operation (i.e. after the start-up period is completed) since almost no clogging was seen to occur within the biofilter over a year (Nikiema and Heitz, 2007).

6. The biodegradation occurs only on the external surface of each particle of filter bed material. This means that the biodegradation occurring inside the pores is neglected.

7. The process by-products (e.g. CO$_2$) do not affect the CH$_4$ removal micro-kinetics in the biofilter. Indeed, no acidic or alkaline intermediates are generated during the CH$_4$ biodegradation. In addition, the possible co-metabolism of the CH$_4$ with the CO$_2$ in some methanotrophic populations, such as reported by Acha et al. (2002), will be neglected.

8. The effects of the irrigation will be neglected. It will be supposed that the moisture control within the biofilter does not disturb its behavior. Indeed, excessive moisture is detrimental for the elimination of hydrophobic compounds such as CH$_4$ in biofilters (Bagherpour et al., 2005).

9. The packing material’s temperature will be considered to be uniform over all of the inorganic biofilter length, as revealed in previous experiments (Nikiema et al., 2005).

10. It will be considered that the elimination capacity (EC) is doubled after the operating temperature has been increased by 7°C (for temperatures < 30°C). According to the literature, a temperature increase of some 5 to 10°C is necessary to double the EC (an average value of 7°C has been adopted in this study) (Dammann et al., 1999; Streese et al., 2001).

11. It will be supposed that the average temperature of the packing material only affects the values of the growth rates and the Henry coefficients.
12. The diffusion coefficients are independent of the temperature and of the biomass density. This was assumed because it is difficult to estimate the impact of the temperature variation on these parameters. In general, the equations used to assess diffusion coefficients in water solutions are not very precise (they usually allow 6 to 20% error). Therefore, experimental values determined at 25°C, have been preferred (Perry and Green, 1997). On the other hand, some authors consider that the diffusion coefficient within the biofilm of a pollutant (e.g. phenol and toluene) varies, depending on the density of the biomass (Fan et al., 1990; Jorio et al., 2003). However, the present knowledge concerning CH₄ does not permit to assess the influence of the biomass density on the CH₄ mass transfer nor does it prove that the equation, as proposed by Fan et al. (1990), can be efficiently applied to the CH₄ case.

13. Diffusion of CH₄ and CO₂ molecules in the air itself will be neglected. In addition, it is also accepted that the different concentrations of CH₄ and CO₂ in the gas phase and in the liquid phase obey the Henry's law.

14. The mass transfer at the gas-biofilm interface (which depends on several parameters, including the hydrodynamics of the gas flow and the packing characteristics, i.e. the surface area and bed porosity (Maldonado et al., 2008)) is described using Fick's law.

The synthesis of the general phenomena, as considered in this model, is presented in Figure 6-1. On the other hand, the values of the model parameters are indicated in Table 6-1.

6.3.2. Mathematical model

- In the gas phase

Two components are of particular interest in the gas phase: i.e. the CH₄ and the CO₂. The general mass balances within the gas phase involve essentially three terms: the accumulation term, a convection term, and a mass exchange term through the interface of the gas phase with the biofilm. These three phenomena are described by the following equation:
Figure 6-1: Phenomena occurring within the biofilter and considered in the present model.

### TABLE 6-1: VALUES OF THE MODEL PARAMETERS

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Values</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>2750 m²/m³</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>0.015 m</td>
<td></td>
</tr>
<tr>
<td>D₁₂₅₆</td>
<td>1.49 × 10⁹ m²/s</td>
<td>King and Adamsen, 1992</td>
</tr>
<tr>
<td>D₁₂₅₇</td>
<td>1.96 × 10⁹ m²/s</td>
<td>Jorio et al., 2003</td>
</tr>
<tr>
<td>Kₘ</td>
<td>5.37 g/m³</td>
<td>Delhoménie et al., 2008</td>
</tr>
<tr>
<td>V</td>
<td>0.0177 m³</td>
<td></td>
</tr>
<tr>
<td>X</td>
<td>100 000 g/m³</td>
<td></td>
</tr>
<tr>
<td>Y</td>
<td>0.34 g biomass/g CH₄</td>
<td>Delhoménie et al., 2008</td>
</tr>
<tr>
<td>H</td>
<td>1 m</td>
<td></td>
</tr>
<tr>
<td>ε</td>
<td>0.40</td>
<td></td>
</tr>
<tr>
<td>δ</td>
<td>85 × 10⁻⁶ m</td>
<td></td>
</tr>
<tr>
<td>μₘ</td>
<td>4.98 × 10⁶ m/s</td>
<td>Delhoménie et al., 2008</td>
</tr>
</tbody>
</table>
\[-u_g \cdot \frac{\partial C_p}{\partial z} + D_p \cdot A \cdot \left( \frac{\partial S_p}{\partial x} \right)_{x=0} = \varepsilon \frac{\partial C_p}{\partial t} \]  

(Eq. 6-1)

where:

- \( C_p(x,z,t) \): the concentration, at time \( t \), of \( P \) (g/m\(^3\)) within the gas phase \( (0 \leq z \leq H) \)
- \( S_p(x,z,t) \): the concentration, at time \( t \), of \( P \) (g/m\(^3\)) within the biofilm \( (0 \leq x \leq \delta) \);
- \( x, z \): the axis coordinates (Figure 6-1);
- \( \delta \): the thickness of the biofilm;
- \( P \): CO\(_2\) or CH\(_4\);
- \( H \): the total height of the biofilter;
- \( \varepsilon \): the porosity of the biofilter packing material (dimensionless);
- \( u_g \): the gas velocity (m/s) within the biofilter;
- \( A \): the specific surface of the packing material (m\(^2\)/m\(^3\));
- \( D_p \): Diffusion coefficient of \( P \) in the biofilm (m\(^2\)/s).

During steady state operations, there is no accumulation of the pollutant, of the by-products or indeed, of the products within the biofilter. Equation 6-1 therefore becomes:

\[-u_g \cdot \frac{\partial C_p}{\partial z} + D_p \cdot A \cdot \left( \frac{\partial S_p}{\partial x} \right)_{x=0} = 0 \]  

(Eq. 6-2)

The steady state initial condition can then be written as follows:

- At \( z = 0 \): \( C_p(z) = C_{p, \text{in}} \)  

(Eq. 6-3)

with \( C_{p, \text{in}} \) representing the concentration of \( P \) at the inlet flow of the biofilter.

\section*{In the biofilm}

Within the biofilm, CH\(_4\) becomes biodegraded, forming CO\(_2\), among others. The mass balances within the biofilm are then dominated by 3 mains phenomena: i.e. diffusion, accumulation and biodegradation. Therefore, the mass balances can be written as follows:
Methane: \( D_{CH_4} \cdot \frac{\partial^2 S_{CH_4}}{\partial x^2} - r = \frac{\partial S_{CH_4}}{\partial t} \)  
(Eq. 6-4)

Carbon dioxide: \( D_{CO_2} \cdot \frac{\partial^2 S_{CO_2}}{\partial x^2} + \alpha_{CO_2/CH_4} \cdot r = \frac{\partial S_{CO_2}}{\partial t} \)  
(Eq. 6-5)

with:

- \( r \) being the CH\(_4\) consumption rate (g/m\(^3\) (filter bed)/s);
- \( \alpha_{CO_2/CH_4} \) the apparent yield of CO\(_2\) (g CO\(_2\) dissolved in the biofilm / g CH\(_4\) consumed)

For a steady state operation, there is no accumulation and Equations 6-4 and 6-5 become, respectively;

Methane: \( D_{CH_4} \cdot \frac{\partial^2 S_{CH_4}}{\partial x^2} - r = 0 \)  
(Eq. 6-6)

Carbon dioxide: \( D_{CO_2} \cdot \frac{\partial^2 S_{CO_2}}{\partial x^2} + \alpha_{CO_2/CH_4} \cdot r = 0 \)  
(Eq. 6-7)

The steady state boundary conditions inside the biofilm can be written as follows:

- At \( x = 0 \) and for \( 0 \leq z \leq H \): \( S_p(0,z) = \frac{C_p(z)}{H_p(T)} \)  
(Eq. 6-8)

- At \( x = \delta \) and for \( 0 \leq z \leq H \): \( \frac{\partial S_p(\delta,z)}{\partial x} = 0 \)  
(Eq. 6-9)

where:

- \( H_p(T) \) is the Henry coefficient of \( P \), depending on the temperature \( T \) (in °C) and derived from the following equations (Metcalf and Eddy, 2003):

\[
\frac{1}{H_{CH_4}} = 4.559 \cdot (T + 273.15) \times 10^{\left(\frac{673.74}{T+273.15} - 6.880\right)}
\]  
(Eq. 6-10)
Biodegradation

Previous experiments have shown that the Monod model can be used to describe the kinetics of the biodegradation occurring within the biofilm when the CH$_4$ concentration is not greater than 14500 ppmv (Delhoménie et al., 2008). Therefore, one may set:

\[
\mu = \frac{\mu_m \cdot S_{CH_4}}{K_m + S_{CH_4}} \tag{Eq. 6-12}
\]

with:

- \(\mu\): specific growth rate of the micro-organisms within the biofilm (1/s);
- \(\mu_m\): maximum specific growth rate of micro-organisms within the biofilm (1/s);
- \(K_m\): Monod constant (g/m$^3$).

As a consequence, the CH$_4$ consumption rate can be written as follows:

\[
r = \frac{X_b \cdot \mu}{Y} \tag{Eq. 6-13}
\]

with:

- \(X_b\): density of biomass (g/m$^3$);
- \(Y\): biomass yield coefficient (g biomass/g CH$_4$).

One can define: \(k(T) = \frac{\mu_m}{Y}\) where \(k(T)\) is the temperature dependant maximum substrate utilisation rate (1/s). Considering that this dependence can be modeled using the van’t Hoff-Arrhenius equation (Metcalf and Eddy, 2003), the following equation can be written:
\[
\frac{\mu_m}{Y} = k(T) = k_{20^\circ C} \cdot \theta^{T-20} \quad \text{(Eq. 6-14)}
\]

with:

- \(\theta\): temperature coefficient;
- \(k_{20^\circ C}\) (1/s) being the maximum substrate utilisation rate at 20\(^\circ\)C:
  \[
  k_{20^\circ C} = 1.464 \times 10^{-5} \text{ [l/s]} \quad \text{(after experimental determination of } \mu_m \text{ and } Y, \text{ at } 20 \text{ °C)} \]
  (Delhomenie et al., 2008).

Knowing that the elimination capacity is doubled following an increase in the temperature of 7\(^\circ\)C (from 20 to 27\(^\circ\)C), one can determine that \(\theta = 1.104\).

As a result, Equation 6-14 becomes:

\[
k(T) = 1.464 \times 10^{-5} \cdot 1.104^{T-20} \quad \text{(Eq. 6-15)}
\]

The biodegradation term in Equation 6-7 is now written as:

\[
r = \sigma(S_{CH_4}, T) = \frac{X_b \cdot k(T) \cdot S_{CH_4}}{K_m + S_{CH_4}} \quad \text{(Eq. 6-16)}
\]

The steady state operating temperature, \(T\), is related to the pollutant elimination capacity of the overall process: \(T = g(EC)\). This EC is directly computed from the gas pollutant concentration at the biofilter outlet, \(C_{CH_4}(H)\), and thus a relation of the form \(T = f(C_{CH_4}(H))\) must hold for a stationary state to be reached.

In summarizing this section, the equations describing the biofilter mathematical model may be outlined as follows: find the temperature \(T\), the concentrations \(C_{CH_4}(z)\) and \(C_{CO_2}(z)\) contained in the gas phase and the concentrations \(S_{CH_4}(x,z)\) and \(S_{CO_2}(x,z)\) inside the biofilm, which are the solutions of the system of coupled, algebraic-differential equations:

\[
T = f(C_{CH_4}(H)) \quad \text{(Eq. 6-17)}
\]
\[-u_g \cdot \frac{dC_{CH_4}}{dz} + D_{CH_4} \cdot A \left( \frac{\partial S_{CH_4}}{\partial x} \right)_{x=0} = 0 \quad 0 < z \leq H \quad C_{CH_4}(0) = C_{CH_4, in} \quad \text{(Eq. 6-18)}\]

\[-u_g \cdot \frac{dC_{CO_2}}{dz} + D_{CO_2} \cdot A \left( \frac{\partial S_{CO_2}}{\partial x} \right)_{x=0} = 0 \quad 0 < z \leq H \quad C_{CO_2}(0) = C_{CO_2, in} \quad \text{(Eq. 6-19)}\]

\[D_{CH_4} \cdot \frac{\partial^2 S_{CH_4}}{\partial x^2} - \sigma(S_{CH_4}, T) = 0 \quad 0 < x < \delta \quad 0 < z \leq H \quad \text{(Eq. 6-20)}\]

\[S_{CH_4}(0,z) = \frac{C_{CH_4}(z)}{H_{CH_4}(T)} \quad \frac{\partial S_{CH_4}(\delta,z)}{\partial x} = 0 \quad \text{(Eq. 6-21)}\]

\[D_{CO_2} \cdot \frac{\partial^2 S_{CO_2}}{\partial x^2} + \alpha_{CO_2/CH_4} \cdot \sigma(S_{CH_4}, T) = 0 \quad 0 < x < \delta \quad 0 < z \leq H \quad \text{(Eq. 6-22)}\]

\[S_{CO_2}(0,z) = \frac{C_{CO_2}(z)}{H_{CO_2}(T)} \quad \frac{\partial S_{CO_2}(\delta,z)}{\partial x} = 0 \quad \text{(Eq. 6-23)}\]

\[\sigma(S_{CH_4}, T) = \frac{X_b \cdot k(T) \cdot S_{CH_4}}{K_m + S_{CH_4}} \quad \text{(Eq. 6-24)}\]

**Numerical model**

A finite difference numerical approach has been followed to obtain approximate solutions of the biofilter model. The biofilter is thus discretized into \(n_z\) slices, located at heights \(j h_z\), with \(h_z = H/(n_z - 1)\), \(0 \leq j \leq n_z\). Gas phase concentration values at height \(j h_z\) are denoted respectively as \(C_{CH_4,j}\) and \(C_{CO_2,j}\), and the concentrations in the biofilm at same heights are denoted \(S_{CH_4,j}(x)\) and \(S_{CO_2,j}(x)\). Input values for \(C_{CH_4,j}\) and \(C_{CO_2,j}\) are given at \(j = 0\). Next, an order two Runge-Kutta scheme is used to compute the gas concentrations evolving up in the biofilter. The pollutant concentration at the next slice \(j+1\) will be computed as follows:
\[
C_{\text{CH}_4,j+1/2} = C_{\text{CH}_4,j} + \frac{h_z}{2} \cdot \frac{D_{\text{CH}_4} \cdot A}{u_g} \left( \frac{\partial S_{\text{CH}_4,j}}{\partial x} \right)_{x=0} \tag{Eq. 6-25}
\]

\[
C_{\text{CH}_4,j+1} = C_{\text{CH}_4,j} + h_z \cdot \frac{D_{\text{CH}_4} \cdot A}{u_g} \left( \frac{\partial S_{\text{CH}_4,j+1/2}}{\partial x} \right)_{x=0} \tag{Eq. 6-26}
\]

where the expression \( S_{\text{CH}_4,j+1/2}(x) \) stands for the concentration in the biofilm at height \( z = (j + 1/2) h_z \). It is to be noted that same relations may be written for the carbon dioxide concentration \( C_{\text{CO}_2}(z) \).

Equations governing the concentrations within the biofilm are of the elliptic type, the first one is nonlinear. Moreover, these concentration values are essentially driven by the diffusion process occurring in the boundary layer at the gas/biofilm interface. Consequently, a finer density of grid nodes is needed in this layer, near the \( x = 0 \), to capture adequately the essential characteristics of pollutant elimination inside the biofilm. Grid nodes are located at \( x_i \) for \( 0 < i \leq n_x \), with \( x_0 = 0 \) and \( x_{n_x} = \delta \). Converting Equation 6-20 into a finite difference scheme, one obtains, on an interior node \( (2 \leq i \leq n_x -1) \), an algebraic equation which can be outlined under the form:

\[
a_i S_{\text{CH}_4,i-1,j} + b_i S_{\text{CH}_4,i,j} + c_i S_{\text{CH}_4,i+1,j} - \sigma[S_{\text{CH}_4,i,j},T] = 0 \tag{Eq. 6-27}
\]

In the matter of the boundary nodes, \( i = 1 \) and \( i = n_x \), the conditions given by Equation 6-21 are similarly converted to the relations (when the value of \( C_{\text{CH}_4,j} \) is known):

\[
a_i \frac{C_{\text{CH}_4,j}}{H_{\text{CH}_4}(T)} + b_i S_{\text{CH}_4,i,j} + c_i S_{\text{CH}_4,i+1,j} - \sigma[S_{\text{CH}_4,i,j},T] = 0 \tag{Eq. 6-28}
\]

\[
(a_{n_x} + c_{n_x}) S_{\text{CH}_4,n_x+1,j} + b_{n_x} S_{\text{CH}_4,n_x,j} + c_{n_x} S_{\text{CH}_4,n_x+1,j} - \sigma[S_{\text{CH}_4,n_x,j},T] = 0 \tag{Eq. 6-29}
\]

This nonlinear system of algebraic equations is now solved by the Newton-Raphson algorithm. Values of \( S_{\text{CO}_2,i,j} \) are obtained afterwards by computing the solution of the linear
system, resulting from the discretization of Equation 6-22, in which the known values, \( \sigma(S_{\text{CH}_4,j,j}, T) \), now act as source terms. Next, the interface derivatives of the biofilm concentrations are computed by means of a second order, downwind difference which gives, for the pollutant, a relation that can be written as:

\[
\left( \frac{\partial S_{\text{CH}_4,j,j}}{\partial x} \right)_{x=0} = a S_{\text{CH}_4,0,j} + b S_{\text{CH}_4,1,j} + c S_{\text{CH}_4,2,j} \quad \text{(Eq. 6-30)}
\]

The temperature equation (6-17) is taken into account by use of a fixed point method. Let us assume initially an estimated guessed temperature, \( T_i \). The numerical values of the temperature dependent coefficients are computed using \( T_i \), and the differential system is solved. The gas pollutant concentration at the biofilter outlet, \( C_{\text{CH}_4}(H) \), is used to compute the elimination capacity, \( EC(T_i) \), which yields in turn a new temperature value, \( T_2 = g(EC(T_i)) \). This process is repeated until the difference \( |T_{k+1} - T_k| \) becomes lower than a given small value (0.01 °C).

6.4. Materials and methods

6.4.1. Design of the biofiltration system

The biofilter, as modeled in this paper, is a cylindrical tube (15 cm in internal diameter), divided into 3 sections of equal size. Each section of the biofilter is packed with 33 cm height of packing material, leading to a total bed volume of nearly 18 L. The packing material used in this biofilter is of an inorganic nature (rocks), and, is constituted in the majority of nearly cylindrical particles. According to our previous considered assumptions, only the external surface of the packing material is involved in the biodegradation process occurring within our biofilter, the surface area used for the modeling has been estimated to be nearly 2750 m²/m³.

The polluted gas, introduced at the base of the biofilter, was a mixture of humidified air and pure methane gas. The gas flow rates applied into the biofilter were always comprised of
between 1 and 7.5 L/min, while the CH₄ concentrations ranged between 1500 and 9500 ppmv. On the other hand, the irrigation of the packing material within the biofilter was performed once a day, using a 1.5 L of nutrient solution. This latter contained almost all of the necessary nutrients (nitrogen: 0.75 g/L, phosphorus: 0.3 g/L, potassium: 0.076 g/L) and micronutrients (e.g. metallic species in traces) needed to sustain the bacterial growth. Its composition is presented elsewhere (Nikiema, 2008).

6.4.2. Description of the assessment parameters

In order to quantify the amount of the CH₄ pollutant introduced into the biofilter, the inlet load (IL) parameter will be used. This parameter is expressed in g/m³/h and is determined as the following:

\[
IL = \frac{Q}{V} \cdot C_{(CH₄)_{in}}
\]

(Eq. 6-31)

with:

- Q: gas flow rate (m³/h);
- V: biofilter bed volume (m³).

For the assessment of the biofilter performance, the conversion (X), expressed in %, and the elimination capacity (EC), in g/m³/h, have both been used, according to Equations 6-32 and 6-33, respectively:

\[
X = \frac{C_{(CH₄)_{in}} - C_{(CH₄)_{out}}}{C_{(CH₄)_{in}}} \cdot 100
\]

(Eq. 6-32)

\[
EC = \frac{IL \cdot X}{100}
\]

(Eq. 6-33)

In order to obtain the predicted carbon dioxide production (P_{CO₂}), the present equation has been used:
\[ P_{CO_2} = \frac{Q}{V} \cdot \left( C_{CO_2} (H) - C_{CO_2, in} \right) + P_{\text{endo}} \]  \hspace{1cm} (Eq. 6-34a)

with \( P_{\text{endo}} \) representing the endogenous production of CO2, when there is absence of the CH4 pollutant.

It is also to be noted that the predicted \( C_{CO_2} (H) \) is determined by considering only the variation in the CO2 concentration resulting from the biodegradation of the CH4. \( C_{CO_2} (H) \) does not include the endogenous respiration.

For determination of the experimental carbon dioxide production, Equation 6-34b has been employed:

\[ P_{CO_2} = \frac{Q}{V} \cdot \left( C_{CO_2, out} - C_{CO_2, in} \right) \]  \hspace{1cm} (Eq. 34b)

6.5. Results

6.5.1. Parameters' estimation

\( \circ \) Temperature

In the present model, the variation in the microbial kinetic parameters with temperature change within the packing material is considered for the steady state operations (Equation 6-15). Increasing the packing material’s temperature to between 25 and 35°C is generally favorable to the biological process because of the improvement in the kinetic parameters. It is to be noted that the temperature of the packing material not only affects the microkinetics of the bioreaction, but also has an influence on the solubility of the pollutants within the biofilm since the Henry coefficients are temperature-dependant (Equations 6-10 and 6-11). As a consequence, there is a relationship between the biofilter bed temperature and the elimination capacity of the same biofilter. Figure 6-2 represents the average temperature within the biofilter, as a function of the elimination capacity. Figure 6-2 reveals that, as the EC increases
in the biofilter, the average temperature of the biofilter packing material also increases, by following a linear equation (Equation 6-35):

\[ T = 0.0632 \cdot EC + 25.40 \]  
(Eq. 6-35)

This behavior can be explained by the fact that the bioelimination of the CH₄ is an exothermic process. Therefore the higher the elimination capacity, the higher the amount of the energy transferred to the packing material, which consequently increases its temperature.

Figure 6-2: Average biofilter temperature (°C) expressed as a function of the elimination capacity (g/m³/h) for gas flow rates of 4.2 and 5.5 L/min.
Carbon dioxide production

The CH₄ pollutant is utilized by the micro-organisms to satisfy their needs in terms of both energy and carbon. One part of the pollutant will be devoted to the sustaining of the multiplication of the micro-organisms, and the remaining part will be converted into the form of CO₂. In order to solve Equation 6-7, it is necessary to have the value of \( \alpha_{CO₂/CH₄} \), i.e. the apparent yield of CO₂ (g CO₂ dissolved in the biofilm / g CH₄ consumed). In practice, \( \alpha_{CO₂/CH₄} \) is related to the yield of CO₂ (i.e. \( \beta_{CO₂/CH₄} \), g CO₂ produced / g CH₄ consumed) and also to the equilibriums existing between the different carbonate ions present in the biofilm (i.e. HCO⁻ and CO₃²⁻) and the dissolved CO₂, which depend on the pH. It should also be mentioned that the concentrations of the CO₂, HCO₃⁻ and CO₃²⁻ are linked according to the following equation:

\[
[CO₂]_{Produced} = [CO₂]_{Dissolved} + [HCO⁻] + [CO₃²⁻]
\]  
(Eq. 6-36)

However, there is no information available that can facilitate the determination of the value of \( \beta_{CO₂/CH₄} \), so that a direct determination of \( \alpha_{CO₂/CH₄} \) from Equation 6-36 was difficult to realize. Nevertheless, for steady state operation (i.e. when there is no accumulation of any molecule in the biofilter), \( \alpha_{CO₂/CH₄} \) equals the gaseous yield \( \gamma_{CO₂/CH₄} \) (g CO₂ transferred to the gas phase / g CH₄ consumed). This last parameter (\( \gamma_{CO₂/CH₄} \)) can be readily determined, by considering the experimental data (the first step consist of measuring the CH₄ and CO₂ concentrations at the inlet and outlet parts of the biofilter during its steady state operation in order to calculate the CO₂ production corresponding to each methane elimination capacity; the slope of the curve representing production of CO₂ as a function of the elimination capacity corresponds to the value of \( \gamma_{CO₂/CH₄} \)).

Figure 6-3 presents the production of CO₂, in the gas phase, as a function of the elimination capacity of the biofilter, during its steady state operation, at 4.2 L/min and at CH₄ concentrations ranging between 1500 and 9500 ppmv. The slope of the curve corresponds to
the values of $\gamma_{\text{CO}_2/\text{CH}_4}$ and also $\alpha_{\text{CO}_2/\text{CH}_4}$, and turns out to be 2.01. This means that, for 1 g of the CH$_4$ biodegraded, some 2.01 g of CO$_2$ will exit from the biofilter, through the gas phase. The Figure 6-3 also provides with the value of $P_{\text{endo}}$ (intercept of the linear regression line), which turns to be 7 g/m$^3$/h.

![Graph showing production of CO$_2$ as a function of elimination capacity.](image)

Figure 6-3: Production of CO$_2$ (g/m$^3$/h), in the gas phase, as a function of the elimination capacity (g/m$^3$/h) of the biofilter, during steady state operation (gas flow rate = 4.2 L/min; CH$_4$ concentration: $\leq$ 9500 ppmv).

6.5.2. Modeling of the biofilter conversion and elimination capacity

Figures 6-4 and 6-5 present the CH$_4$ conversion (predicted and experimental values) expressed as a function of the gas flow rate, for 2 different inlet CH$_4$ concentrations, i.e. 7500 ppmv and 2500 ppmv. It is to be noted that these 2 values of CH$_4$ concentrations have been selected with the aim of representing each range of CH$_4$ concentration: i.e. from 1500 to 4500 ppmv (i.e.
2500 ppmv) and from 4500 to 1000 ppmv (7500 ppmv). From these figures, it is observed that, as the GFR increases at a constant CH$_4$ concentration, the conversion decreases correspondingly.

At 7500 ppmv, it can be noted that the present model offers a good estimation of the experimental data. For example, at a GFR of 1 and at 5.5 L/min, the model predicts conversions of some 90.9 % (92.7 % for the experimental result) and 36.7 % (36.0 % for the experimental result). More generally, in Figure 6-4, the differences between the experimental conversions and the predicted values never exceed 2 %. Also, in accordance with the model, the highest GFR, allowing CH$_4$ conversions $\geq$ 85 %, is 1.3 L/min, while for a CH$_4$ conversion $\geq$ 95 %, the GFR must be $\leq$ 0.8 L/min (recalling that the 85 % and the 95 % levels are the minimum conversions usually aimed at industry for the control of pollutants difficult to biodegrade and for the volatile organic compounds, respectively). On the other hand, at low CH$_4$ concentrations, i.e. 2500 ppmv (Figure 6-5), based on the experimental data, GFRs of 1.7 and 1.2 L/min are necessary, in order to obtain conversions $\geq$ 85 % and $\geq$ 95 %, respectively. The latter values are higher than those found at 7500 ppmv and confirm the point that it is easier to obtain higher conversions in the biofilter operating at lower CH$_4$ concentrations than in the case of biofiltration at higher CH$_4$ concentrations.

In addition, at 2500 ppmv, it can be noted that both the experimental and the predicted CH$_4$ conversions decrease with the CH$_4$ concentration increase (at a given GFR comprised of between 1 and 5.5 L/min), but the difference between the experimental and the predicted conversion values reaches up to 10 %. For example, at GFR values of 1 and 5.5 L/min, the model predicts conversions of 90 % (nearly 100 % for the experimental result) and 35 % (41 % for the experimental result). To explain this behavior, it can be recalled that the determination of the kinetic parameters has been effected using solid extracts from a biofilter operating at around 7500 ppmv, and which were thereafter exposed to CH$_4$ concentrations of 2500 ppmv, without any additional acclimatization provided in the biofilter (Delhoménie et al., 2008). This lack of acclimatization could lead to a minor deviation of the model from the experimental data. Other causes, like the mass transfer phenomena at low CH$_4$ concentrations, could also be responsible for this behaviour.
Figure 6-4: CH$_4$ conversion (predicted and experimental values) (%) expressed as a function of the gas flow rate (L/min), for an inlet CH$_4$ concentrations of 7500 ppmv.

Figure 6-5: CH$_4$ conversion (predicted and experimental values) (%) expressed as a function of the gas flow rate (L/min), for an inlet CH$_4$ concentrations of 2500 ppmv.
By way of an overall conclusion, it is to be noted that the model developed in this study appears to be very appropriate for the CH$_4$ concentrations ranging from 4500 to 9500 ppmv, the difference between the experimental and estimated conversions, being $\leq 5\%$ for these CH$_4$ concentrations (data not shown). However, the model becomes less and less appropriate as the CH$_4$ concentration decreases, between 4500 and 1500 ppmv. Indeed, as the biofilter inlet CH$_4$ concentration decreases, the difference between the estimated and the experimental values also increases by up to 10%.

Figure 6-6 presents the EC obtained in the CH$_4$ biofilter as a function of the inlet CH$_4$ concentration (at around 1500 to 9500 ppmv). The error range noted when considering the conversion parameter for low CH$_4$ concentrations (e.g. 2500 ppmv), seems high in comparison to the EC parameter: for example, at 1 and 3 L/min and 2500 ppmv of CH$_4$ concentration, the experimental EC values are 5.6 and 9.9 g/m$^3$/h (being conversions of 100 and 60 %, respectively), while the predicted ones are 5.0 and 9.0 g/m$^3$/h (being conversions of 90 and 54 %, respectively). This is caused by the fact that, for the lower CH$_4$ concentrations applied to the biofilter, the EC and IL values are low. In this case, differences between the predicted and the experimental EC that are normally minor (e.g. when the CH$_4$ concentration is 2500 ppmv, $\Delta$EC = 0.6 and 0.9 g/m$^3$/h at 1 and 3 L/min, respectively), corresponds, to a high percentage difference (10 % and 6 %, respectively).

On the other hand, it can be observed that the EC increases with the increases in the inlet CH$_4$ concentration (at 2 L/min, the EC is increased from around 5 to around 29 g/m$^3$/h (and from around 5 to around 30 g/m$^3$/h, according to the model) after increasing the CH$_4$ concentration, from 1500 to 9500 ppmv). The continuous and linear increase of the EC with the inlet CH$_4$ concentration (Figure 6-6) proves that the operating regime is diffusion-limited in the CH$_4$ concentrations' range studied. Also, according to the model, the maximum EC that can be reached in the biofilter, i.e. at a CH$_4$ concentration of 9500 ppmv and a GFR of 5.5 L/min, is 43 g/m$^3$/h, i.e. nearly 5 % higher than the experimental EC value (around 41 g/m$^3$/h).
6.5.3. Modeling of the production of carbon dioxide

Figure 6-7 presents the CO₂ production (g/m³/h) as a function of the GFR (L/min) for an inlet CH₄ concentration of 9500 ppmv. When considering the P₇₅ parameter, it can be concluded that the model provides a good estimation of the experimental data and the differences between the experimental values and the predicted values is always < 7 %. For example, at 4.2 L/min (Figure 6-7), the model predicts a P₇₅ value of 89 g/m³/h, while the experimental data yields a value of 84 g/m³/h (6 % difference).
Figure 6-7: CO₂ production (g/m³/h) as a function of the gas flow rate (L/min) for an inlet CH₄ concentration of 9500 ppmv.

Figure 6-8 presents the P<sub>CO₂</sub>, expressed as a function of the inlet CH₄ concentration (ppmv). Three GFRs have been considered in this Figure, i.e. 1, 3 and 5.5 L/min. It can be observed that the increase in the P<sub>CO₂</sub>, caused by the increase in the CH₄ concentration, is well predicted by the model. For example, at 3 L/min of GFR, the model predicts an increase in the P<sub>CO₂</sub>, from 25 to 80 g/m³/h, when the CH₄ concentration is increased, from 2300 ppmv to 9500 ppmv. Simultaneously, the experimental data are 26 and 79 g/m³/h at 2300 and 9500 ppmv, respectively.
Figure 6-8: CO$_2$ production (g/m$^3$/h) as a function of the inlet CH$_4$ concentration (≤ 9500 ppmv) for different gas flow rates (1 to 5.5 L/min).

According to the present model, P$_{CO_2}$ follows a linear trend with the inlet CH$_4$ concentration, for each GFR. Also, one notes that even at low CH$_4$ concentrations (1500-4500 ppmv), P$_{CO_2}$ are well correlated by the model. This can be explained by the fact that the model takes into consideration the endogenous respiration parameter, P$_{endo}$. Indeed, the quantity of CO$_2$ related to the endogenous respiration represents a significant proportion of the total CO$_2$ generation occurring within the biofilter, when the EC is low.
6.5.4. Modeling of the biofilter temperature

Figure 6-9 presents the average temperature (°C) of the 3 stages of the biofilter as a function of the gas flow rate. It shows that the model is generally well validated by the experimental data. For example, at 9500 ppmv value of the inlet CH₄ concentration, the experimental temperatures are 27.7 and 28.1 °C at 4.2 and 5.5 L/min, respectively. At the same time, the model predicted values are 28.0 and 28.1 °C at 4.2 and 5.5 L/min, respectively. In considering the model, it is to be noted that the GFR variation (over the present study range) does not really affect the average biofilter temperature.

![Graph showing biofilter average temperature as a function of gas flow rate](image)

**Figure 6-9:** Biofilter average temperature (°C) (experimental and predicted values) as a function of the gas flow rate (≤ 5.5 L/min).

However, when the CH₄ concentration varies, it can affect the biofilter temperature. In the present range of CH₄ concentrations, the temperature variation never exceeded 3°C. This
result is in accordance with previous experiments (Nikiema et al., 2007). On the other hand, even if the level of variation of the temperature is not a very important parameter, at the first consideration, it must eventually be taken into consideration because the temperature increase favors the drying of the packing material. This later circumstance will thereafter negatively affect the biofilter performance. To control this phenomenon and to avoid filter bed drying, the biofilter will require more frequent irrigation.

6.6. Profiles of concentrations in the biofilter

Figure 6-10 presents the height of the filter bed within the biofilter as a function of the profiles of the predicted CH₄ and CO₂ concentrations in the gas phase (C(CH₄)(H) and C(CO₂)(H), respectively), at an inlet CH₄ concentration of 9500 ppmv and a GFR in the biofilter of 2 L/min (the C(CO₂)(H) is linked only to the CH₄ biodegradation, and does not include endogenous CO₂). The profiles observed are similar to those generally observed in biofilters (Bhat at al., 2006; Ikemoto et al., 2006). Indeed, the profiles are not linear, which confirms that the pollutant is not uniformly removed within the biofilter. For example, at the biofilter entrance, the CH₄ and CO₂ concentrations are of 6.3 and of 0.7 g/m³, respectively. Thereafter, at the levels z of 0.3, 0.6 and 0.9 m within the biofilter and according to the model, the values of C(CH₄)(z) become 4.3, 3.0 and 2.1 g/m³, while the values of C(CO₂)(z) are 4.5, 7.2 and 9.1 g/m³, respectively. Therefore, it can be noted that the areas near the biofilter entrance are more active than the one near the biofilter exit.
Figure 6-10: Typical height of the filter bed (m) presented as a function of the predicted concentrations of CH₄ and CO₂, within the gas phase (inlet CH₄ concentration = 6.3 g/m³ (or 9500 ppmv); gas flow rate = 2 L/min).

On the other hand, Figure 6-11 presents the profiles of the predicted CH₄ and CO₂ concentrations in the biofilm phase, as a function of the depth in the biofilm (m) at a level z of 0.1 m, within the biofilter. It is noted that between biofilter depths of 0 and 20 × 10⁻⁶ m, the predicted CH₄ concentration decreases rapidly, i.e. from 0.18 to 0.12 g/m³ (33 % decrease). On the other hand, between the depths of 60 × 10⁻⁶ and 85 × 10⁻⁶ m, there is almost no CH₄ biodegradation (only 7 % of the CH₄ elimination is effected in this part of the biofilm). This observation confirms the point that the part of the biofilm nearest the interface gas-biofilm is the most active one, and that the one attached to the packing material is the least active. The analysis of the predicted CO₂ concentration’s profile in the biofilm also confirms the previous finding.
6.7. Discussion – Model’s limits

In order to generate the model, the kinetic parameters that have been chosen are valid, for CH$_4$ concentrations $\leq$ 14500 ppmv. Above this CH$_4$ concentration value, other kinetic parameters must be used (Delhoménie et al., 2008). Therefore, this model will probably not be so well adapted to CH$_4$ concentrations of around or superior to 14500 ppmv. In addition, this model did not integrate the influence of the concentrations of nutrients, mainly nitrogen and phosphorus, in either the biofilter or in the nutrient solution. Previous experiments have demonstrated that these nutrients have a great influence on biofilter performance (Nikiema, 2008). In order to apply this particular model to another biofilter, in which the nutrient
concentrations are different from those in the present study, it is important to determine the kinetic parameters applicable to the new experimental nutrients' concentrations.

Also, this model considers that the biomass density, present in the biofilter, is nearly constant. However, it has been observed that, in CH₄ biofilters, the number living cells and their biomass density could vary, depending on the operating conditions, such as the CH₄ concentration and the biofilter history (e.g. the age of the biofilm) (Nikiema et al., 2007). The density of the biomass can affect the biofilter performance directly, i.e. through the activity of the micro-organisms, and indirectly, i.e. through the mass transfer. On the other hand, the influence of the biomass on the diffusion coefficient (gas in the biofilm) has been neglected and the biofilm has been downgraded to a water based phase. However, on some occasions (e.g. at low CH₄ concentrations, of around 1500 ppmv), the mass transfer could have been slightly favored by the presence of micro-organisms in the biofilm since CH₄ is a hydrophobic compound.

Because this model did not take into consideration the moisture of the packing material and only considers an average packing bed temperature, it will probably not be suitable for the estimation of the performance of an open biofilter treating the CH₄.

### 6.8. Conclusion

The goal of this study has been to develop a model able to predict the conversion, elimination capacity, production of carbon dioxide and the packing material temperature of a closed biofilter, used to treat methane effluents. In addition to the inlet CH₄ concentration, the biofilter temperature has been considered for the model development because of its influence on the bioreaction microkinetics and on the mass transfer coefficients. The results obtained with this model have shown that it is appropriate for the modeling of the CH₄ conversion (i.e. with < 5 % difference) in biofilters used for the treatment of gas effluent with a CH₄ concentration comprised of between 4500 and 9500 ppmv. For lower CH₄ concentrations (< 4500 ppmv), the model tends to predict conversion values lower than the experimental results (5-10 % difference). On the other hand, the elimination capacity, the CO₂ production and the
biofilter average temperature are well correlated over the entire range of CH₄ concentrations of interest, i.e. from 1500 to 9500 ppmv.

### 6.9. Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Specific surface of the packing material (m²/m³)</td>
</tr>
<tr>
<td>Cₚ</td>
<td>Concentration of P within the gas phase (g/m³)</td>
</tr>
<tr>
<td>D</td>
<td>Biofilter inlet diameter (m)</td>
</tr>
<tr>
<td>Dᵔ</td>
<td>Diffusion coefficient of P in the biofilm (m²/s)</td>
</tr>
<tr>
<td>EC</td>
<td>Elimination capacity (g/m³/h)</td>
</tr>
<tr>
<td>H</td>
<td>Height of the packing material within the biofilter (m)</td>
</tr>
<tr>
<td>Hₚ</td>
<td>Henry coefficient of P (dimensionless)</td>
</tr>
<tr>
<td>IL</td>
<td>Inlet load (g/m³/h)</td>
</tr>
<tr>
<td>in</td>
<td>inlet flow</td>
</tr>
<tr>
<td>k(T)</td>
<td>Maximum substrate utilisation rate at a T temperature (1/s)</td>
</tr>
<tr>
<td>Kₘₐₙ</td>
<td>Monod constant (g/m³)</td>
</tr>
<tr>
<td>out</td>
<td>outlet flow</td>
</tr>
<tr>
<td>P</td>
<td>CH₄ or CO₂</td>
</tr>
<tr>
<td>Pₐₜₐₜ</td>
<td>Endogenous production of CO₂ (g/m³/h)</td>
</tr>
<tr>
<td>Pₗᵩᵩ</td>
<td>Carbon dioxide production (g/m³/h)</td>
</tr>
<tr>
<td>Q</td>
<td>Gas flow rate (m³/h)</td>
</tr>
<tr>
<td>r</td>
<td>CH₄ consumption rate (g/m³ (filter bed)/s)</td>
</tr>
<tr>
<td>Sₚ</td>
<td>Concentration of P within the biofilm (g/m³)</td>
</tr>
<tr>
<td>t</td>
<td>Time (s)</td>
</tr>
</tbody>
</table>
Temperature (°C)

Gas velocity within the biofilter (m/s)

Biofilter bed volume (m$^3$)

Depth coordinate in the biofilm (m)

Density of biomass (g/m$^3$)

Conversion (%)

Biomass yield coefficient (g biomass/g CH$_4$)

Biofilter height coordinate (m)

Apparent yield of CO$_2$ (g CO$_2$ dissolved in the biofilm / g CH$_4$ consumed)

Yield (g CO$_2$ produced / g CH$_4$ consumed)

Biofilm thickness (m)

Filter bed-porosity (dimensionless)

Gaseous yield (g CO$_2$ transferred to the gas phase / g CH$_4$ consumed)

Specific growth rate of the micro-organisms within the biofilm (1/s)

Maximum specific growth rate of micro-organisms within the biofilm (1/s)

Methane consumption rate (g/m$^3$ (filter bed)/s)

Temperature coefficient (dimensionless)

6.10. Acknowledgements

The authors are indebted to the Natural Science and Engineering Research Council of Canada (NSERC) for their financial support to this project. In particular, co-author, J. Nikiema, would also like to thank NSERC for providing the supporting scholarship for her doctoral studies.
(Canada Graduate Scholarships Program). The authors are also indebted to Dr. P. Lanigan for text revision.
GENERAL CONCLUSION

The goal of this present doctoral research has been the optimization of the operating parameters of a methane biofilter, with the aim of maximizing its performance with respect to methane removal. The main intended application of the system is to control methane emissions contained in biogas, the latter being generated during the decomposition of organic wastes placed in both the older and smaller landfills.

After analysis of the methane elimination techniques (based on the available literature), it appeared that biofiltration was an interesting approach because of the low operation and implementation costs it generally required. It may be mentioned here that methane bioelimination is observed to be occurring naturally in landfill covers and contributes to the elimination of some 10 to 100 % (depending on the prevailing climatic conditions, which affect the filter bed temperature and moisture) of the fugitive methane emissions, i.e. those emissions that are occurring throughout the landfill cover, and which cannot otherwise be controlled.

The biofilter, chosen for this work, is a fully closed up-flow system, being irrigated daily with a nutrient solution (0.1 m$^3$ of nutrient solution per m$^3$ of filter packing material, the bed irrigation being performed once per day). The overall filter bed configuration adopted is comprised of 3 identical sections, packed with the chosen filter material. It is also equipped with several sampling ports, which allow for monitoring the overall biofilter performance (e.g. the methane concentration) throughout the entire height of the biofilter. Several parameters have initially been identified to have some level of influence on the biofilter performance. They are: the column packing material, the input nutrients, the biofilter operating conditions which include the bed temperature, pH and bed moisture content (that have an influence on the type of micro-organisms that will develop in the biofilter), the methane inlet load and inlet concentration and, finally, the total gas flow rate. Many of these parameters have been the subject of detailed attention during the period of this work.
Two types of packing materials: one composed of compost (an organic material), the other of gravel (an inorganic material), have been compared. It may be recalled that, at the beginning of this study, most researchers were of the view that matured compost constitutes a good filter material for use in the biofiltration of CH₄, mainly because of the presence of various nutrients, within the compost material, able to support the growth of the methanotrophs. However, very few studies on the methane bioelimination process had been conducted with the use of inorganic packing material. Comparison of the 2 packing materials has led to the conclusion that the inorganic packing material is the preferred material, the level of biofilter removal performance being some 2 to 3 times greater than that obtained with the organic packing material. By way of example, at an inlet load of 55 g/m³/h, the elimination capacity observed was at 11 g/m³/h in the organic-based bed biofilter, and 26 g/m³/h in the inorganic based-bed biofilter, when the nitrogen concentration was maintained at 0.5 g/L and the phosphorus concentration at 0.3 g/L.

Among those common nutrients, known to have an influence on the microbial growth rates, are the nitrogen, phosphorus, potassium and various micronutrients, such as copper, which is particularly necessary for the synthesis of the particulate methane monooxygenase enzyme. The influence of the nitrogen concentration in the nutrient solution has been investigated, with respect to the two previously mentioned packing materials: i.e. the compost (organic material) and the gravel (inorganic material). It has been found that, especially in the case of the inorganic packing material, nitrogen has a great influence on the biofilter performance. Starting from a concentration of 0.14 g/L, the N-concentration in the nutrient solution was increased to 1.0 g/L, and the optimum nitrogen concentration was found in due course to be located at around 0.75 g/L, for inlet loads of > 55 g/m³/h, and at around 0.5 g/L for inlet loads of ≤ 55 g/m³/h. Thus, as an example, within the inorganic based-bed biofilter, increasing the nitrogen concentration, from 0.14 to 0.75 g/L, led to an increase in the elimination capacity, from 8 to 36 g/m³/h, when the inlet load was maintained at 95 g/m³/h.

Further, the influence of phosphorus on the methane elimination has been studied, using the inorganic-based bed biofilter. The results reveal that phosphorus, at an appropriate concentration, is also an important nutrient, even if its impact on the elimination capacity, when varied between 0.3 and 6.1 g/L, is of lesser importance (e.g. 35 % increase in the EC
when the phosphorus concentration is varied between 0.3 and 3.1 g/L, at an inlet load of 75 g/m$^3$/h) than that resulting from the variation of the nitrogen concentration between 0.14 and 1.0 g/L (e.g. 260% increase in the EC when the nitrogen concentration is varied between 0.14 and 0.75 g/L, at an inlet load of 75 g/m$^3$/h). The increase of phosphorus concentration in the nutrient solution was accompanied by an increase of the biomass growth rates, thus causing an increase in the biofilter clogging rate and disturbing, therefore, its desired stability. For example, at the 0.3 g-P/L input rate, the biofilter can be operated for 1 year without any maintenance, while, at the 3.1 g-P/L charge, the biofilter clogs-up within 1 month. This explains why the optimized phosphorus concentration value, of 1.5 g/L, is proposed for the continuous operation of the biofilter over long periods (i.e. ≥ 1 year).

The influences of the addition of other nutrients such as potassium (concentration ≤ 3.8 g/L) and micronutrients such as copper (concentration ≤ 0.006 g/L), in the methane biofilter have been found to be minor. More specifically, for potassium, a concentration of 0.076 g/L has been identified to be sufficient enough, while for the copper, its addition into the nutrient solution, in the form of refined chemicals, was found to be unnecessary probably because it was already present, at sufficient levels, in the municipal tap water used to produce the nutrient solution.

The influence of the total gas flow rate on the methane biofiltration has also been determined, while separately, the impact of the phosphorus concentration on this parameter has also been investigated, for a level of nitrogen concentration fixed at 0.75 g/L. The results of these tests have shown that the gas flow rate is a very important parameter and that it affects the methane biofilter performance. The comparison of the gas flow rate parameter (when it is comprised of between 1 and 5.5 L/min) with the methane concentration parameter (comprised of between 1200 and 12000 ppmv) has confirmed that the first parameter is the more important, at least during the methane biofiltration. To illustrate this assertion, it is to be noted that the tripling of the gas flow rate, from 1 to 3 L/min, when the methane concentration is maintained at the 2500 ppmv level, caused a decrease in the value of the conversion by some 40%. At the same time, after tripling the methane concentration from 2500 to 7500 ppmv, the conversion decreased by only some 7%, for the gas flow rates of 1 or 3 L/min. This phenomenon has been observed at the 2 phosphorus concentrations tested; i.e. 0.3 and 1.5 g/L. In addition, it
was observed that, at both phosphorus concentrations (i.e. 0.3 and 1.5 g/L), the biofilter methane elimination capacities were almost the same, at gas flow rates of 4.2 and of 5.5 g/L.

The highest gas flow rate value found, that allowed biofilter conversions comprised of between 90 and 100 %, for methane concentrations < 12000 ppmv, was some 2 L/min, with the condition of optimizing the nutrient concentrations because, over this operational range, the reaction limitation was a more problematic one than the mass transfer limitation. On the other hand, as the gas flow rate increased above this limit value, the biofilter overall conversion decreased because of the more pronounced mass transfer limitation. Nevertheless, no significant effect of the total gas flow rate on the carbon dioxide production was noted.

The production rate of carbon dioxide (expressed in g/m³/h) is the biological indicator of the microbial activity occurring in aerated biofilters. In the organic-based bed, it was noted some biological reactions, which are not directly linked with the methane biodegradation, were responsible for more than 10 % of total carbon dioxide production. On the other hand, it is generally noted that the carbon dioxide production could be readily correlated with the methane elimination capacity, and that both curves followed similar trends in the inorganic-based bed biofilter. Also, within the same packing material, and because of the increased microbial growth rates, it was observed a decrease in the carbon dioxide production within the biofilter following the increase in the phosphorus concentration (e.g. 30 % decrease, on average, after increasing the phosphorus concentration present in the nutrient solution, from 0.3 to 1.5 g/L).

The determination of the particular microkinetic parameters, characterizing one continuous, steady-state methane biofilter, irrigated with a nutrient solution composed of nitrogen (0.75 g/L) and phosphorus (0.3 g/L), has been performed. The method consisted of studying the growth of microbial extracts, immobilized on bed pellets that were directly sampled from an operating biofilter having an inlet methane concentration of 7500 ppmv. The kinetic tests were performed in batch thermostated reactors by following the evolution of the headspace concentration of methane, and the mass of biomass versus time. A theoretical analysis related the obtained experimental data to the microbial specific growth rates. Two ranges of methane concentrations were identified. From 0.65 to 9.55 g.m⁻³, the Monod model, with $\mu_{\text{max}} = 0.43$
and $K_m = 5.37 \text{ g.m}^3$, was appropriate. On the other hand, for methane concentrations from 9.55 to 17.70 g.m$^3$, a transformed version of the Monod model, with $\mu_{\text{max}} = 1.09 \text{ d}^{-1}$ and $K'_{m} = 7.59 \text{ g.m}^3$, was found to characterize the real specific growth rates quite well.

Following this determination, a steady state model for predicting the biofilter performance and integrating important parameters such as the methane inlet concentration, the total gas flow rate and the filter bed average temperature, has been developed. In considering the conversion performance parameter, it was noted that the model gave results with a) less than 5 % error and b) of up to 10 % error, when the methane concentration was comprised of between 4500 and 10000 ppmv, and of < 4500 ppmv, respectively. The model estimations of the methane elimination capacity, of the carbon dioxide production and of the biofilter bed average temperature, gave very satisfactory results over the entire study range (methane concentration $\leq 10000$ ppmv).

The principle of biofiltration is simple and consists of micro-organisms, attached to an inert support, in contact with a gaseous pollutant which is further biodegraded after being transferred to the biofilm. However, the understanding of the methane biofiltration mechanisms is a challenge, as can be noted at the end of this study. The particular study undertaken here has cast more light into the operations of the methane biofilter and will certainly favor a better control of the biofiltration process.
7.1. Abstract

During their storage in landfills, wastes are biodegraded, which results in the production of biogas and leachate. Over recent years, the handling of the leachate product has become one of major concern. However, in the case of biogas product, elimination or valorization processes are applied in a smaller proportion, even if the methane emissions, directly related to landfills, are some 25 % of the total anthropogenic methane emissions. Indeed, many older or smaller landfills are deprived of gas collection systems, thereby making impossible the application of gas combustion and/or valorization methods. Therefore, other processes have to be considered, e.g., the biofiltration of methane. In this paper, the results of an experiment, undertaken to confirm the stability of the biofiltration system that has been developed at Université de Sherbrooke by the Biocom group, are presented. At a methane inlet concentration of around 7500 ppmv and a gas flow rate of 0.25 m³/h, the conversion of the biofilter can be maintained at 22 % unchanged for a period of 150 days or more. Even after the cessation of methane feeding and biofilter irrigation for some 2 weeks, the biofilter performance was able to be restored, in only one week, to the same operating level as it was maintained before the deliberate shutdown.

Résumé

Après l’élimination des déchets dans les sites d’enfouissement sanitaire débute leur biodégradation, ce qui occasionne la formation d’un biogaz et d’un lixiviat. Ces dernières
années, la gestion du lixiviat a suscité beaucoup d’intérêt, contrairement à celle du biogaz. Pour celui-ci, des procédés d’élimination ou de valorisation sont appliquées en faible proportion, même si les émissions de méthane, directement reliées au biogaz, correspondent à 25 % des émissions anthropogéniques. En effet, plusieurs sites d’enfouissement sanitaire de petites tailles ou âgés sont dépourvus de systèmes de collecte du biogaz, rendant impossible l’application des procédés de combustion, avec ou sans valorisation. Par conséquent, d’autres procédés, telle la biofiltration du méthane, doivent être considérés. Dans le présent écrit, les résultats d’une étude, menée afin de confirmer la stabilité d’un système de biofiltration du méthane développé à l’Université de Sherbrooke par le groupe de recherche Biocom, sont présentés. Lorsque la concentration initiale de méthane se situe autour de 7500 ppmv et pour un débit total gazeux de 0.25 m$^3$/h, la conversion dans le biofiltre peut être maintenue constante à environ 22 % pour une période excédant 150 jours. Même après une interruption de 2 semaines de l’alimentation du méthane et de l’irrigation de biofiltre, on a noté qu’un temps d’environ une semaine était requis pour permettre à la conversion du biofiltre de rejoindre le niveau précédant cet arrêt programmé.

7.2. Introduction

7.2.1. Wastes in Canada

During the last decade, it is to be noted that a continuous increase in the total amount of wastes generated in Canada took place. The total wastes, generated during the year 2004, was > 33 million metric tons (being 3 % higher than in 2002), of which around 10 million metric tons originated from residential sources. The remaining part arose from commercial and public institutions (50 %), and other sources. These wastes are mainly composed of organic materials (40 % m/m), papers (26 % m/m), plastics (9 %), glass, metals and others (Buchanan et al., 2007).

Various reasons are advanced to explain this situation: the population increase, the increases in goods’ consumption, caused in part by the higher levels of incomes, the changes in society that have resulted, for example, in increased need for non-reusable products, and the
continuous evolution of technologies (Cameron et al., 2005). Wastes can be substantially eliminated through recycling efforts (papers, plastics, metals and glass materials), composting and anaerobic digestion (organic wastes), thermal treatments (part of energy generation), and finally, by landfilling.

Increasingly, wastes are now being valorized through various recycling processes (e.g. 40-50 % of residential wastes may be recycled) but in Canada, the main way of disposing of wastes is still through landfilling, which affected, in 2005, around 75 % of the wastes arising during the same period. Indeed, about 10000 landfills (active and inactive, all of them requiring attention) presently exist in Canada (Nikiema et al., 2007). The majority of them (83 %) are public institutions but private landfills also exist. Public landfills receive around 56 % of the wastes, private landfills receive the remainder. It must also to be mentioned that most landfills are now rather old. Indeed, some 30 % of landfills had, in 2002, a remaining useful life of less than 10 years. However, these landfills were still receiving more than half of the currently generated wastes (Cameron et al., 2005).

7.2.2. The biogas and the leachate

During the degradation of wastes stored in landfills, a leachate and a biogas, both of which need to be handled, are generated. The quantities and compositions of these materials are influenced by various factors such as the types of wastes, their ages, etc. (Trebouet et al., 2001).

The leachate is mainly composed of water, in which soluble and solid pollutant particles, are present, including minerals, e.g. iron, and organic matters (COD, up to 70000 mg/L; BOD, up to 56000 mg/L and TKN, up to 2000 mg/L) (Sanphoti et al., 2006; Tränkler et al., 2005; Visvanathan et al., 2007). The leachate is generated during dehydration of the biodegrading wastes or when rain water passes through the wastes; this explains its wide variations in composition. In Canada, in 2000, 46 % of municipal landfills were equipped with membranes, limiting the infiltration of external water into the site, while 18 % of landfills had collection systems installed for the leachate. These two kinds of landfills handled some 75 % of the total of landfilled wastes arising in the same year (Cameron et al., 2005).
The other landfill product, the biogas, is a mixture of gases, composed principally of methane (30-70 % V/V), carbon dioxide (20-50 % V/V) (both greenhouse gases), along with various sulphur compounds, volatile organic compounds, and others. Because of its high heating value during the landfill's early years (usually half that of natural gas), the biogas can be valorized, if collected, as an energy source (Nikiema et al., 2007). In as much as is feasible, Canada Government policy encourages the energy recovery of biogas through combustion. There are some 50 landfills in Canada that collect their biogas and at least 30000 metric tons/day of methane are burned on each site. However, for the older or smaller landfills (i.e. < 200000 m$^3$ of capacity), these are frequently deprived of gas collection systems, and thus valorization methods cannot be reasonably applied. Therefore, in order to avoid important methane emissions to atmosphere, biological processes, such as biofiltration, may be applied.

### 7.2.3. The methane biofiltration

Biofiltration is performed within a triphasic reactor, packed with stationary filter material, in which growth of the micro-organisms is favored (Delhoménie and Heitz, 2005). Indeed, methanotrophs are able to biodegrade the methane pollutant, and then generate, as in all biological processes, new biomass, salts, water and carbon dioxide, the latter product to a lesser extent than occurs in chemical oxidation processes, as presented in Equation 7-1.

$$\text{CH}_4 + x\text{O}_2 \rightarrow y\text{CO}_2 + z\text{H}_2\text{O} + \text{Biomass} + \text{Salts} \quad \text{(Eq. 7-1)}$$

Experiments conducted to date have confirmed that biofiltration is deemed suitable for the direct elimination of methane on landfill sites. The Biomet group, located at Université de Sherbrooke (Sherbrooke, Canada), has for more than 5 years, conducted research on the problematic of the methane issuing from landfills. The main interest was to determine the relationship between the measured biofilter performance and some operating parameters, including the concentrations of inlet methane and the nitrogen present in the nutrient solution. For example, during previous experiments, the nitrogen concentration, required for the proper operation of the biofilter, has been optimized and appears to be 0.75 g/L for a methane inlet concentration of between 7000 and 7500 ppmv (Nikiema et al., 2005). The objective of this
present study has been to confirm the stability of the biofiltration system, and its capacity to remain as efficient as it was initially, even after a substantial period of time (nearly one year).

7.3. Materials and methods

The lab-scale biofiltration system employed in this study is presented in Figure 7-1. It is mainly composed of 3 sections: 1) the polluted air generation section (humidified air and pure methane (99 % V/V of purity); gas inlet temperature: ~ 20°C; inlet concentration of methane: 7500 ppmv; total gas flow rate: 0.25 m³/h); 2) the biofiltration system, which is composed of an up-flow biofilter (composed of two stages, each containing 33 cm of filtering material) and an irrigation system, and 3) the disposal of the exit gases and liquids.

Figure 7-1: Methane biofiltration set-up

It must be mentioned that the periodic bed irrigation (1 L/day for each biofilter) was performed using a nitrogen mineral salt solution, as described elsewhere (Delhoménie et al., 157
2007), containing 0.5 g/L of nitrogen. The filter bed used in the present study consists of an inorganic material having particles of around 5 cm mean diameter.

The following experimental results are expressed in terms of the inlet load, elimination capacity, carbon dioxide production and conversion, as described in Table 7-1.

<table>
<thead>
<tr>
<th>TABLE 7-1. PARAMETERS USED TO EXPRESS THE RESULTS</th>
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<tr>
<td><strong>Description</strong></td>
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<tr>
<td>Inlet load (g/m$^3$/h)</td>
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<tr>
<td>Elimination capacity (g/m$^3$/h)</td>
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<tr>
<td>Carbon dioxide production (g/m$^3$/h)</td>
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<tr>
<td>Conversion (%)</td>
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</table>

With: $C$: Concentration in g/m$^3$; $Q$: Gas flow rate in m$^3$/h and $V$: Bed volume in m$^3$.

7.4. Results

Figure 7-2 presents the conversion (%) and inlet load (g/m$^3$/h) in the inorganic-based biofilter, as a function of time (days). On day 0, the biofilter was inoculated with the lixiviate, being taken from another biofilter already treating methane (under similar operating conditions). At day 160, the biofiltration processing was stopped for a 2-week break period, during which the methane feed and biofilter irrigation ceased. However, the air feed was maintained for this period.
Figure 7-2: Conversion (%) and inlet load (g/m³/h) in the biofilter as a function of time (days).

During this study, the inlet load remained at around 120 g/m³/h. It was noted that, after the 6 months of operation, the biofilter was still as efficient as it was at the start-up. After the imposed 2-week interruption period, the biofilter restart procedure (this time without inoculation) was achieved within a week, the biofilter reaching its maximum conversion rate soon after. In addition, no difference was detected in the performance of the biofilter, either before or after the imposed interruption (conversion = 22 %). During the whole of the experimental period, the 2 stages of the biofilter exhibited similar methane conversion. Indeed, around 48 % and 52 % of the methane elimination were achieved in stage 1 (lower) and stage 2 (upper) respectively.

Figure 7-3 presents data on the elimination capacity (g/m³/h) for, and the carbon dioxide production (g/m³/h) within, the biofilter, as a function of time (days). During the first six months of operation, the average elimination capacity was estimated to be ~30 g/m³/h, while the average carbon dioxide production was ~ 60 g/m³/h. However, after the planned
interruption period, the average carbon dioxide production rate was decreased, by ~15 \%, indicating that the biomass growth rate was now at a higher value than that previously observed (Nikiema et al., 2005).

![Graph of elimination capacity and carbon dioxide production](image)

**Figure 7-3:** Elimination capacity (g/m³/h) and carbon dioxide production (g/m³/h) in the biofilter, as a function of time (days).

As reported for other methane treating biofilters, a good correlation can be observed between the methane elimination capacity and the carbon dioxide production, in the biofilter, except for the biofilter initial start-up, from day 0 to day 35. A possible explanation could be the multiplication rate of the micro-organisms; it is at its highest level at the start-up and then decreases with time until it becomes quite constant, when an equilibrium level is reached (consequently, CO₂ production keeps increasing until it reaches its maximum value, this being the phenomenon observed in the present biofilter). Another possible reason is the adsorption of methane on the biofilter's packing material. However, this possibility was later excluded because such phenomena would be reduced in intensity when the filter material is of an
inorganic origin (Devinny and Ramesh, 2005). It is to be mentioned that higher methane conversions (compared to the average value of 22 % reported for this study) can be obtained, e.g. when higher nitrogen concentration is used (data not shown).

7.5. Conclusion

Wastes result principally from the expansion of the needs of humans living and their activities on the Earth. Thus, for many years in Canada, the total of human generated wastes has never stopped increasing. Along with this increase are created the problems associated with the environment maintenance and safety during the disposal of these wastes. In the case of methane emissions control, from older and/or smaller landfills, biofiltration could be a technically reliable solution. During the lab-scale experiments some of the parameters involved were identified as being important, some of them already having been optimized; e.g. the concentration of the input nitrogen. Therefore, the particular aim of this present study has been to confirm the stability of the biofiltration system undergoing development, i.e. its capacity to give the same performance, continuously, even after several operating months including a substantial process interruption period. Following the experimental operating period (6 months), the biofilter was observed to be still as efficient as it was at the test period commencement. In addition, the restarting of the biofilter, following the 2-week interruption period was readily performed. Indeed, the biofilter reached its maximum conversion performance after only one week. There was essentially no difference between the filter performance, before and after this deliberate interruption, except for the carbon dioxide production level which was at a slightly lower level in the post interruption operating period. Finally, as reported for other methane treating biofilter systems, it was observed that there was a good correlation between the methane elimination capacity and the carbon dioxide production.
7.6. Acknowledgements

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8.2. Chapter 1


8.3. Chapter 2


8.4. Chapter 3

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8.5. Chapter 4


8.6. Chapter 5


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### 8.7. Chapter 6


### 8.8. Appendix


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