UNIVERSITÉ DE SHERBROOKE
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TRAITEMENT DES COMPOSÉS ORGANIQUES VOLATILS PAR BIOFILTRATION AVEC ET SANS PERCOLATION : ÉTUDES CINÉTIQUES ET DE CARACTÉRISATION DES BIOFILTRES

Treatment of volatile organic compounds by biofiltration with and without percolation: kinetic and characterization studies

Thèse de doctorat présentée pour l'obtention du grade
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Résumé

Les objectifs du présent travail sont relatifs à une étude cinétique et à la caractérisation des biofiltres avec et sans percolation garnis avec des matériaux inertes pour le traitement du méthanol, de l'éthanol et du toluène. La thèse est divisée en trois sections.

La première section est une introduction à la biofiltration, d'un point de vue théorique et expérimental. Il est démontré que l'éthanol peut être traité par biofiltration par percolation avec une faible concentration d'azote présent dans la solution nutritive en obtenant des rendements élevés. Cette étude a permis de développer des techniques d'entretien du biofiltre et de contrôle de la biomasse dans le lit garni.

La deuxième section comprend une série d'études pour caractériser des biofiltres avec et sans percolation pour traiter du méthanol. Des nouvelles méthodes expérimentales ont été développées. Par exemple, une méthode pour calculer l'accumulation de biomasse dans le lit garni du biofiltre a été mise au point. Pour le biofiltre percolateur, des méthodes pour obtenir le coefficient de partition du méthanol et le taux de production de la biomasse ont été développées. Les rôles du biofilm et de la solution nutritive dans la performance des biofiltres percolateurs ont également été analysés. Les deux études de cette section permettent d'approfondir la compréhension des mécanismes de biodégradation du méthanol.

La troisième section concerne des études cinétiques des biofiltres avec et sans percolation. La première étude propose une nouvelle méthode expérimentale pour calculer les paramètres microcinétiques reliés à la croissance microbienne. La deuxième étude compare les comportements microcinétique et macrocinétique lors du biotraitement du méthanol et du toluène. L'influence des conditions opératoires sur la croissance microbienne et la capacité d'élimination est analysée. L'étude comprend entre autres l'identification d'indicateurs énergétiques des biofiltres avec et sans percolation qui sont nécessaires lors de l'établissement des bilans d'énergie et de l'estimation de la température dans le lit garni.

Mots clés : Composés organiques volatils, biofiltration, biofiltre percolateur, microcinétique, macrocinetique, biofilm

Abstract

The objectives of this work are related to the kinetic study and characterization of air treatment biofilters with and without percolation which were packed with inert packing materials in order to treat methanol, ethanol and toluene vapours. The thesis is divided into three sections. The first section contains a bibliographic introduction to biofiltration and an experimental study. The review of experimental work shows that methanol, ethanol and toluene can be treated in biofilters with or without percolation. In the experimental study of this section, ethanol is treated in a biotrickling filter at low nitrogen concentrations in the nutrient solution and high removal efficiencies are obtained. In this study, experimental protocols for maintaining the biofilter and controlling the biomass content in the packing bed were developed.

The second section is composed of two experimental studies for characterizing biofilters with and without percolation in order to treat methanol. A methodology for calculating the biomass accumulated in the packing bed of a biofilter is among the new experimental protocols developed in this study. In the case of biotrickling filter, methodologies for determining the partition coefficient of methanol and the biomass production rate were developed. The role of the biofilm and the nutrient solution on bioflter performance was also analyzed. The studies of this section lead to a better comprehension of methanol biodegradation in biofilters.

The third section contains two kinetic studies for biofilters with and without percolation. In the first study, a new experimental methodology is proposed to calculate microkinetic parameters related to microbial growth in a biofilter. In the second study, the microkinetic and macrokinetic behaviors of methanol and toluene biodegradation are compared. The influence of operating conditions on microbial growth and elimination capacity is also analyzed. This study includes the identification of energy indicators of biofilters with and without percolation, which could be used in energy balances and for estimating the temperature of packing bed.

Key words: Volatile organic compounds, biofiltration, biotrickling filter, microkinetics, macrokinetics, biofilm

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Introduction générale

Le présent travail présente les résultats d'une recherche bibliographique et expérimentale sur la biofiltration avec et sans percolation de l'air pollué par des composés organiques volatils (COV). La section I est une introduction à la biofiltration avec et sans percolation. Cette section comprend le chapitre 1 qui définit l'état de l'art sur la biofiltration. Dans le chapitre 1, le principe d'opération des biofiltres ainsi que les facteurs qui affectent leur performance sont discutés. Les microorganismes présents à l'intérieur des biofiltres, les nutriments ajoutés aux biofiltres, les polluants à traiter et les garnissages utilisés sont également discutés. Les paramètres pour évaluer et suivre la performance des biofiltres sont expliqués. Le chapitre 1 aborde aussi les modèles biophysiques qui décrivent le fonctionnement du biofilm en termes des phénomènes de transport et des réactions qui ont lieu dans le biofilm. Les modèles mathématiques qui ont été développés pour simuler la performance des biofiltres ainsi que les modèles cinétiques de croissance microbienne et de biodégradation des polluants sont mentionnés.

Le chapitre 2 décrit la mise en marche et la caractérisation d'un biofiltre percolateur pour traiter des vapeurs d'éthanol. Ce chapitre permet de se familiariser avec les paramètres de performance caractéristiques d'un biofiltre percolateur, le contrôle de la biomasse, l'entretien de l'équipement et les mesures analytiques les plus courantes réalisées au laboratoire. Le chapitre 2 montre également l'étude expérimentale ayant comme but le traitement de l'air pollué avec de fortes charges d'éthanol. L'étude dépasse les seuils de concentration d'éthanol généralement utilisés dans des biofiltres traditionnels et ouvre la porte au débat sur le traitement des COV aux concentrations et charges réservées traditionnellement aux procédés physico-chimiques. L'étude a aussi eu comme but d'opérer un biofiltre percolateur à faibles concentrations de nutriments dans la solution nutritive, ce qui lui confère des avantages d'un point de vue économique.

Les sections II et III sont d'ordre expérimental. La section II comprend deux chapitres qui analysent le rôle du biofilm sur la performance des biofiltres avec et sans percolation. Le COV utilisé dans ces deux études est le méthanol. Le chapitre 3 décrit la biofiltration du méthanol dans des biofiltres garnis avec des matériaux inertes. L'étude analyse les effets des conditions d'opération sur la population microbienne, spécifiquement la dynamique des

microorganismes spécifiques (méthylotrophes) et non spécifiques au méthanol. D'autres facteurs contribuant à l'activité microbienne ont été étudiés, tels l'accumulation de biomasse et le contenu d'eau dans le lit garni. Afin de caractériser adéquatement le lit du biofiltre, des méthodes expérimentales ont été développées, telle celle relative au calcul de la moyenne pondérée de biomasse présente dans le lit filtrant, ce qui s'avère utile pour le bilan de carbone réalisé dans cette étude et pour le calcul des paramètres cinétiques du chapitre 6.

Le chapitre 4 est une étude relative au traitement du méthanol avec un biofiltre percolateur. Les effets des variables telles la concentration d'azote, le temps de résidence et la charge de méthanol sur la performance du biofiltre percolateur ont été étudiés. Ce chapitre montre le rôle de la solution nutritive dans l'enlèvement des polluants solubles dans l'eau à l'intérieur des biofiltres percolateurs. Dans cette étude a aussi été abordé le traitement du méthanol à hautes concentrations et charges. À la différence du chapitre 2, l'élimination du polluant par biotransformation en biomasse ou dioxyde de carbone ou par absorption dans la solution nutritive est analysée de façon détaillée. Les coefficients de rendement du méthanol en biomasse ou en dioxyde de carbone sont analysés, afin d'être utilisés dans le calcul des paramètres cinétiques du chapitre 6. Cette étude a permis de développer une nouvelle méthode pour la caractérisation du biofiltre percolateur : la détermination du coefficient de partition du méthanol pour un biofiltre percolateur en opération. Le coefficient de partition peut être utilisé dans des modèles mathématiques et des modèles cinétiques.

La section III est relative à la cinétique de la croissance microbienne et à la biodégradation des COV. Le chapitre 5 montre le développement d'une nouvelle méthode expérimentale pour calculer les paramètres cinétiques de croissance d'un biofilm développé dans un biofiltre traitant du méthanol. La méthode consiste en la détermination des paramètres cinétiques sous des conditions proches de celles auxquelles le biofilm est exposé dans un biofiltre opérant en régime quasi-permanent. Une procédure mathématique a été adaptée pour calculer les paramètres cinétiques à partir des concentrations de méthanol et de dioxyde de carbone dans la phase gazeuse d'un bioréacteur. La procédure mathématique établit une différence entre la quantité de méthanol absorbé et de méthanol biodégradé. Le chapitre 6 est une étude sur la cinétique des biofiltres avec et sans percolation pour traiter le méthanol et le toluène. Le calcul des paramètres cinétiques de croissance microbienne et de biodégradation des polluants permet de faire une comparaison entre le biofiltre percolateur et le biofiltre ainsi qu'entre les

polluants traités avec la biofiltration traditionnelle. Des modèles cinétiques pour calculer la croissance microbienne et la capacité d'élimination sous des conditions réelles d'opération sont testées pour des biofiltres présentant de l'inhibition liée à la concentration élevée du polluant. L'étude montre les effets des conditions d'opération sur la croissance microbienne ainsi que sur la capacité d'élimination. Une brève analyse d'indicateurs énergétiques utiles lors du calcul de transfert de chaleur et de la température dans le lit garni est présentée dans ce chapitre.

SECTION I. BIOFILTRATION AVEC ET SANS PERCOLATION DES COMPOSES ORGANIQUES VOLATILS

Chapitre 1. Biofiltration de l'air pollué.

Les composés organiques volatils (COV) sont issus de diverses industries, telles les usines pétrochimiques, pharmaceutiques ou de pâtes à papier. Ce sont des composés organiques, liquides ou solides (par exemple hydrocarbures, cétones et alcools), « ayant une pression de vapeur supérieure ou égal à 0.01 kPa à une température de 293.15 K ou ayant une volatilité correspondante sous des conditions d'utilisation particulières » (LE CLOIREC, 1998). Suite aux problèmes qu'ils génèrent sur l'environnement et la santé humaine, les émissions des COV sont de plus en plus contrôlées (COMMUNICATION CANADA, 2003). Selon l'Inventaire National des Rejets de Polluants (ENVIRONNEMENT CANADA, 2007), en 2006 au Canada les rejets du méthanol (16337 tonnes), des xylènes (5446 tonnes), du toluène (4359 tonnes) et du n-hexane (4358 tonnes) à l'air, totalisant 30500 tonnes, ont représenté presque un tiers (28 %) des 108910 tonnes des émissions atmosphériques totales des composés dangereux.

Pour faire face à cette problématique, il s'avère essentiel de développer des technologies capables de respecter les normes environnementales en vigueur, mais aussi compétitives au niveau coût par rapport aux technologies classiques existantes telles l'incinération, l'adsorption ou l'absorption. Pour le contrôle de grands débits volumiques d'air, de 100 à 1000000 m^3 h^{-1}, à faible concentration en COV, de 0.1 à 10 g m^{-3}, ces technologiques classiques se montrent particulièrement dispendieuses (IRANPOUR et coll., 2001; JORIO et coll., 1999; COOPER et coll., 2002). Une alternative intéressante par rapport aux technologies classiques est le biotraitement des émissions de COV. En général, les biotechnologies sont peu énergivores et peu consommatrices de produits chimiques et présentent des coûts d'opération moins élevés que ceux relatifs aux procédés traditionnels (KENNES et coll., 1998). Elles ont l'avantage de ne pas produire de rejets dangereux secondaires tels le monoxyde de carbone, les oxydes d'azote et les cendres.

1.1. Bioprocédés pour traiter de l'air pollué.

Il existe 3 systèmes biologiques à échelle industrielle pour traiter les COV : le biolaveur, le biofiltre et le biofiltre à percolation. Le mode opératoire de chaque procédé est décrit brièvement ci-dessous et les principales caractéristiques, ainsi que les avantages et les

inconvénients sont indiqués dans le Tableau 1.1. Pour compléter la description, les trois procédés sont présentés sur la Figure 1.1.

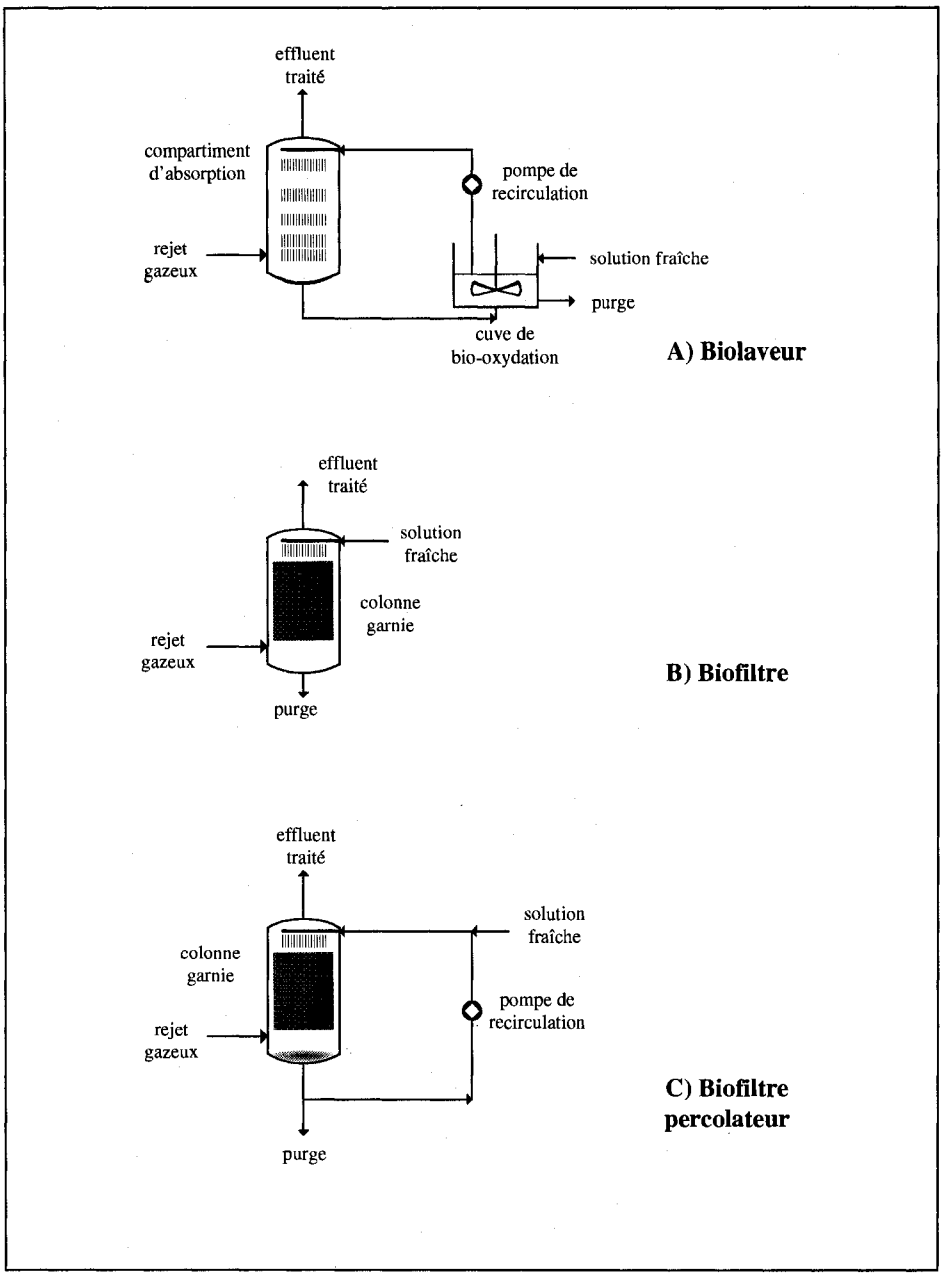


Figure 1.1. Représentation schématique des trois principaux types de bioréacteurs servant au traitement des effluents gazeux.

	Biofiltre	Biofiltre à percolation	Biolaveur
Biomasse	Immobilisée sur le lit filtrant	Immobilisée sur support	En suspension (en bioréacteur)
Phase liquide	Non mobile (eau ajoutée pour compenser l'évaporation)	Mobile (recirculation d'eau)	Mobile (tour d'absorption)
Concentration cible	< 1000 mg m^{-3}	< 500 mg m^{-3}	< 5000 mg m^{-3}
Taux d'enlèvement	80 – 99%	80 – 99%	< 99%
Constante d'Henry	< 10	< 1	< 0,01
Avantages	Rapport surface/volume élevé (~ 1000 m^2 m^{-3}); Facilité d'opération et d'entretien; Coûts d'exploitation faibles	Contrôle aisé des conditions d'opération (nutriments, pH); La biomasse n'est pas affectée par le débit de la solution nutritive	Contrôle aisé des conditions d'opération (nutriments, pH); Unité compacte; Faible perte de charge
Inconvénients	Difficulté de contrôler les paramètres d'opération; Occupe une grande surface; Réponse lente des microorganismes à la suite d'une surcharge en polluant.	Faible surface d'échange du lit (de 100 à 300 m^2 m^{-3}); Il faut traiter les boues générées; Démarrage complexe; Coûts d'exploitation relativement élevés.	Deux unités de traitement; Lessivage des micro-organismes et génération de boues; Supporte difficilement un arrêt prolongé; Démarrage difficile; Coûts élevés.

Source: JORIO et coll., 1999.

Tableau 1.1. Principales caractéristiques des unités de biotraitement des effluents gazeux.

1.1.1. Biolaveur.

Ce procédé est recommandé pour des composés très solubles dans l'eau qui présentent un coefficient d'Henry inférieur à 0.01. Celui-ci est défini comme le rapport de la concentration du composé dans la phase gazeuse sur la concentration du composé dans la phase liquide. Le biolaveur est constitué de deux étapes : une étape d'absorption suivie d'une étape d'oxydation biologique. Dans l'étape d'absorption, le gaz pollué est mis en contact dans une colonne

d'absorption avec un liquide « absorbeur » tel une solution aqueuse. À la sortie de cette unité, le liquide est envoyé dans un bioréacteur afin de bioconvertir les polluants absorbés en dioxyde de carbone, en eau et en biomasse. L'unité d'absorption est alimentée en continue par la phase liquide. Grâce au renouvellement constant de la solution nutritive, divers paramètres d'opération sont contrôlés dans le biolaveur, comme le pH et la concentration des nutriments. Ce procédé est le plus cher des trois biotraitements parce qu'il requiert plus d'équipements que les deux autres et il consomme aussi plus d'énergie pour son fonctionnement.

1.1.2. Biofiltre.

Les composés à traiter par biofiltration doivent posséder un certain degré de solubilité dans l'eau; ils ont en général un coefficient d'Henry qui n'excède pas 10. Ce procédé est le plus simple et le moins cher des trois systèmes biologiques. C'est un réacteur rempli de matériaux solides, généralement d'origine organique (compost, tourbe, copeaux de bois, morceaux de racines, etc.). L'avantage d'utiliser un matériel organique est l'apport de nutriments intrinsèques au lit filtrant et d'une microflore indigène, laquelle peut être développée et acclimatée aux polluants. Le biofiltre est opéré en passant un débit d'air pollué au travers du lit. Un biofilm se développe sur la surface du lit, dégrade les polluants et libère des déchets cellulaires et des produits issus de la bioréaction : dioxyde de carbone, eau et sels. Des nutriments sont ajoutés périodiquement par l'intermédiaire de la solution nutritive sur le lit afin de favoriser la réaction de biodégradation.

1.1.3. Biofiltre à percolation.

Les composés ayant un coefficient d'Henry inférieur à 1 sont bien dégradés par la biofiltration par percolation. Le principe d'opération d'un biofiltre percolateur consiste à faire diffuser de l'air pollué par des COV à travers un lit garni de particules solides synthétiques humides. Sur le garnissage sont immobilisés des microorganismes agissant comme catalyseurs de biodégradation des polluants. Comme dans les autres procédés biologiques, les microorganismes utilisent les COV comme source de carbone et d'énergie. L'air pollué est injecté dans le bioréacteur et les polluants diffusent ensuite de la phase gazeuse vers le biofilm, dans lequel ils sont absorbés et biodégradés. Les déchets cellulaires volatils passent

dans la phase gazeuse et sont transportés par convection vers la sortie du réacteur. Le COV n'est transformé que s'il est absorbé dans le biofilm, ce qui explique que la biodégradabilité des COV varie selon la solubilité du COV dans l'eau.

En plus du carbone, les microorganismes requièrent la présence d'éléments nutritifs tels que l'azote, le phosphore, le soufre et le potassium, ces derniers éléments étant fournis par l'intermédiaire de la solution nutritive, laquelle est ajoutée continuellement sur le garnissage pour assurer une alimentation adéquate en nutriments, indispensables au bon fonctionnement des microorganismes.

1.2. Facteurs qui affectent la biofiltration avec et sans percolation.

1.2.1. Microorganismes.

Les microorganismes constituent le cœur d'un procédé biologique. Ils dégradent les molécules de COV pour se nourrir et utiliser l'énergie reliée à la dégradation. Cette énergie est employée pour satisfaire leurs besoins métaboliques.

Dès que les microorganismes sont adaptés aux conditions du biofiltre, ils croissent sur la surface solide du garnissage en formant une biopellicule. La biopellicule ou biofilm augmente d'épaisseur grâce au développement des nouvelles couches microbiennes qui viennent s'agencer sur les précédentes. La partie extérieure du biofilm est nettement aérobie suite au contact constant avec le courant gazeux qui contient l'oxygène. À l'intérieur de la couche les microorganismes meurent à cause de l'absence d'oxygène et de nutriments et leur décomposition a lieu. Ces microorganismes servent de nutriments pour les microorganismes externes et participent aussi à l'épaississement du biofilm. Comme ils ne sont plus capables de produire des biomolécules extracellulaires, ils perdent leur capacité d'adhésion ce qui provoque leur détachement de la biopellicule. Dans un biofiltre sans percolation, la biomasse s'accumule jusqu'à colmater le lit garni en obstruant les voies d'écoulement du gaz et du liquide. Dans un biofiltre percolateur, les agglomérats de biomasse détachée sont transportés par la solution nutritive dans le réservoir de solution nutritive, les plus grands agglomérats sédimentent en formant les boues, et peuvent être ainsi séparés par sédimentation et enlevés par un courant de « purge ». Les petits agglomérats restent en suspension dans la solution nutritive et possèdent une activité biologique. COX et coll. (2000b) ont observé, en travaillant

avec le toluène, que ces agglomérats participent à la biodégradation du COV de façon considérable.

Inoculum ou microorganismes	**Polluant traité**	**Référence**
Boues provenant d'un biofiltre qui traite le même polluant	Toluène	SMITH et coll., 2002 COX et coll., 2000b
Garnissage d'un biofiltre qui traite le même polluant	Toluène	SMITH et coll. 1996
Boues acclimatées au polluant :		
- d'une cabine de peinture pour les automobiles	Benzène polyalkylé	HEKMAT et coll., 1997
- d'un étang de boues activées	Styrène	CHOU et coll., 1998
- dans un laboratoire de façon aérobie	Éther diéthylique	ALONSO et coll., 2000 RIHN et coll., 1997
Souches pures :		
- *Rhodococcus* sp. et *P. fluorescens*	Acétate d'éthyle, acétone et 1- et 2-propanol	KIRCHNER et coll., 1996
- *Hyphomicrobium* sp. GJ21	Dichlorométhane	DIKS et coll., 1994
- *Rhodococcus erythropolis*	Styrène	TRESSE et coll., 2002
Sources diverses :		
- Consortium d'une culture méthanotrophique	Isobutane et n-pentane	BARTON et coll., 1997
- Consortium adapté dans une usine pilote pour dégrader le polluant	Disulfure de carbone	ALCANTARA et coll., 1999
- Adaptation de microorganismes présents dans l'eau	Méthyléthylcétone	CHOU et coll., 1997
- Microorganismes du lixiviat généré par le compostage	Éthanol	COX et coll., 2001
- Terre et eau souterraine polluées par le polluant à traiter	Éther de méthyle tert-butyle (MTBE)	FORTIN et coll., 1999

Tableau 1.2. Microorganismes inoculés ou identifiés dans certains biofiltres percolateurs.

Presque tous les microorganismes utilisés lors de la biofiltration doivent s'acclimater pour être capables de survivre et de grandir sous des nouvelles conditions d'opération. L'inoculation

permet d'initier la formation de la biopellicule et/ou d'améliorer la performance d'un biofiltre présentant des problèmes d'acclimatation ou un faible taux de dégradation. Plusieurs auteurs rapportent l'utilisation d'inoculum issu de sites pollués. En général il est ajouté directement sur le garnissage du biofiltre ou dans la solution nutritive (FORTIN et coll., 1999 ; HEKMAT et coll., 1997 ; COX et coll., 2001). Les boues des usines de traitement des eaux usées constituent une autre source d'inoculum, en particulier celles qui reçoivent des eaux contenant le polluant d'intérêt (CHOU et coll., 1998; RIHN et coll., 1997). Cependant la source la plus commune sont les boues qui proviennent de biofiltres traitant le même polluant (SMITH et coll., 2002; COX et coll., 1999; COX et coll., 2000a). Il existe cependant quelques études sur l'utilisation de souches pures pour traiter de l'air par biofiltration (DIKS et coll., 1994; TRESSE et coll., 2002). Le Tableau 1.2 mentionne les microorganismes répertoriés dans divers biofiltres sous forme de consortium ou de monocultures.

1.2.2. Garnissage.

Les caractéristiques suivantes définissent le choix d'un matériau pouvant être utilisé comme lit filtrant :

- **Surface spécifique**. La surface spécifique du garnissage joue un rôle dans le transfert de composés entre le gaz et le biofilm. De grandes valeurs affectent ainsi positivement la diffusion des polluants, de l'oxygène et des nutriments vers le biofilm. Les valeurs de surface spécifique varient entre $28x10^3$ et $380x10^3$ m^2 m^{-3} (KENNES et coll., 1998).
- **Volume massique**. Un matériau de faible volume massique est facile à manipuler. Il exerce peu de pression sur le garnissage et il est susceptible de se comporter comme un lit fluidisé pendant le lavage, ce qui permet d'obtenir une friction entre les particules de garnissage en provoquant l'enlèvement d'une certaine quantité de biomasse. Le volume massique de différents matériaux filtrants est compris en général entre 0.09 et 0.33 g cm^{-3} (KENNES et coll., 1998).
- **Porosité**. Une grande porosité interne du garnissage, de 85% à 95% (LI et coll., 2001), permet de diminuer la perte de charge et les problèmes d'obstruction liés à la croissance de la biomasse. Elle permet également aux gaz de circuler de façon uniforme et sans restriction (JORIO et coll., 1999).

- **Propriétés mécaniques**. Une stabilité structurale est recommandée pour éviter la déformation et le possible compactage du lit. En outre, une grande résistance à la compression permet de supporter la force exercée par les couches supérieures du garnissage sur les couches inférieures (LI et coll., 2001). Un matériau dur peut mieux résister à l'effet d'abrasion relatif à l'écoulement de la solution nutritive et au lavage du garnissage.
- **Propriétés chimiques**. Le matériau du garnissage doit être inerte. Il ne doit pas libérer des composés qui peuvent être toxiques pour les microorganismes ou des composés qui peuvent présenter un nouveau problème de pollution. Si le garnissage libère des composés, ceux-ci doivent être bénéfiques au système, par exemple un composé qui fonctionne comme tampon pour le contrôle du pH. Certains matériaux peuvent adsorber les polluants. Si c'est le cas, le lit peut réduire l'effet des fluctuations de charge du polluant sur la performance du biofiltre.

La géométrie des particules qui constituent le garnissage est très variée : des cubes, des cylindres, des anneaux, des sphères ou des figures non géométriques. Des exemples de diverses sortes de garnissage sont donnés dans le Tableau 1.3.

1.2.3. Nutriments.

Les microorganismes qui constituent le biofilm ont besoin de certains nutriments pour former les biomolécules nécessaires telles les enzymes. Les éléments les plus importants après le carbone sont l'azote et le phosphore. Le ratio massique C:N:P recommandé pour le traitement d'air pollué est de 100:5:1 (EDWARDS et coll., 1996; HOLUBAR et coll., 1999). Dans un biofiltre à percolation, la source de carbone et d'énergie est le COV à traiter. Les autres éléments nutritifs sont fournis par la solution nutritive qui contient aussi du soufre, du potassium et des micronutriments, comme le manganèse, le zinc ou le cuivre.

Azote

Le rôle de l'azote est très important dans le métabolisme des microorganismes. Il constitue une partie essentielle de certains acides aminés, comme la glutamine, et il joue un rôle fondamental dans la structure des protéines (LEHNINGER et coll., 1993). L'azote peut être

assimilé sous forme inorganique, comme le nitrate ou l'ammonium, ou sous forme organique, la plus simple étant l'urée. L'azote sous forme de nitrate est plus difficile à métaboliser que sous forme d'ammonium ou sous forme d'urée, parce que le nitrate doit d'abord être transformé en ammonium pour pouvoir être incorporé dans les biomolécules, ce qui entraîne une dépense énergétique pour l'assimiler (SMITH et coll., 1996; SCHÖNDUVE et coll., 1996). SMITH et coll. (1996) ont essayé diverses formulations nutritives, avec du nitrate et de l'ammonium, pour la biofiltration du toluène. Ils ont trouvé que les deux formes d'azote génèrent des populations similaires de microorganismes, capables de dégrader le toluène.

Polluant	**Matériau du garnissage (dimensions)**	**Dimensions du lit (m)**	**Références**
Éthanol	Anneaux Pall au polypropylène (2.5 cm)	H = 1.3, D = 0.15	COX et coll., 2001
Éther méthyl-*tert*-butylique (EMTB)	Pierre de lave (1-3 cm)	H = 0.5, D = 0.15	FORTIN et coll., 1999
Éther diéthylique	Terre de diatomées (0.6 cm)	H = 0.1, D = 0.08	ALONSO et coll., 2000
Toluène	Terre de diatomées (0.6 cm)	H = 1.1, D = 0.15	SMITH et coll., 1996
Disulfure de carbone	Feuilles ondulées angle de 60°	H = 2.5, D = 0.29	ALCANTARA et coll., 1999
Sulfure d'hydrogène et méthanol	Anneaux Pall en polypropylène (1.6 cm)	H = 0.5, D = 0.15	ALLEN et coll., 2000
m-Chlorobenzène et o-Dichlorobenzène	Selles Intalox en céramique (1.25 cm)	H = 0.8, D = 0.15	BALTZIS et coll., 2001
Toluène et m-crésol	Anneaux en polypropylène (0.15 cm et 0.25 cm)	H = 1.2, D = 0.15	GAI et coll., 2001
Toluène et n-heptane	Cubes en polyéther (0.1 cm)	H = 0.8, D = 0.15	HOLUBAR et coll., 1999
Acétate de méthyle	Particules de carbone (2.1 cm)	H = 0.8, D = 0.14	LU et coll., 2001a
Dichlorométhane	Selles Super Torus en polypropylène (2.5 cm)	H = 1.0, D = 0.23	OKKERSE et coll., 1999a

Tableau 1.3. Caractéristiques du garnissage et dimensions du biofiltre percolateur.

Polluant	Forme d'azote utilisé dans la solution nutritive	Concentration du composé ($g\ L^{-1}$)	Référence
Éthanol	KNO_3	1.4 et 2.0	COX et coll., 2001
Acétate d'éthyle et xylène	KNO_3	3.0	CHANG et coll., 2001
	$(NH_4)_2SO_4$	2.0	
Toluène	KNO_3	5.0	COX et coll., 2000a
Benzène, toluène, éthylbenzène, xylène	KNO_3	6.6 - 18.2	LU et coll., 1999
	$(NH_4)_2SO_4$	4.4 - 12.1	
Acrylonitrile et styrène	KNO_3	3.0	LU et coll., 2002
	$(NH_4)_2SO_4$	2.0	
n-Pentane et isobutane	KNO_3	1.0	BARTON et coll., 1999
	NH_4Cl	0.1	
Butanal	$(NH_4)_2SO_4$	1.0	WECKHUYSEN et coll., 1993
Monochlorobenzène	NH_4NO_3	1	MPANIAS et coll., 1998a
Dichlorométhane	$(NH_4)_2SO_4$	3	OKKERSE et coll., 1999a
Sulfure d'hydrogène et méthanol	NH_4Cl	1.5	ALLEN et coll., 2000
Toluène	NH_4NO_3	3	PEIXOTO et coll., 1998
	$(NH_4)_2SO_4$	2.5	
Sulfure de diméthyle, sulfure d'hydrogène et méthanethiol	NH_4Cl	0.4	RUOKOJÄRVI et coll., 2000
Toluène	$(NH_4)_2SO_4$	3.0	WÜBKER et coll., 1997
Benzène poly-alkylé	$(NH_4)_2SO_4$	1.0	HEKMAT et coll., 1997
1,3-Butadiène	Lisier de porc	410	CHOU et coll., 1998

Tableau 1.4. Formes d'azotes plus utilisées et leurs concentrations dans la solution nutritive.

Un mélange de sels de nitrate et d'ammonium a été utilisé dans plusieurs travaux expérimentaux (CHANG et coll., 2001; LU et coll., 2001a; LU et coll., 2000; LU et coll., 1999). Les chercheurs n'expliquent pas la raison du mélange de sels. Une conclusion

suggérée est qu'une solution nutritive avec ces deux formes d'azote garantit des nutriments suffisants et disponibles pour satisfaire les fonctions métaboliques avec une faible production de biomasse. Le Tableau 1.4 présente les formes d'azote les plus utilisées et leurs concentrations respectives dans la solution nutritive.

Les biofiltres percolateurs peuvent être opérés pendant plusieurs jours même si un des nutriments est absent de la solution nutritive (limitation). La limitation en nutriments a pour effet de réduire la vitesse de formation de la biomasse et n'affecte pas la conversion du polluant, mais il faut préciser que cette limitation n'enlève pas la biomasse déjà formée. HOLUBAR et coll. (1999) recommandent d'arrêter l'alimentation en azote une fois que le biofiltre est stable. Lorsque la conversion commence à diminuer, ils recommandent de faire un lavage et de recommencer l'alimentation d'azote. De cette façon, la quantité d'azote fournie est minimisée et la conversion du polluant ainsi que la stabilité du biofiltre percolateur sont maintenues dans des intervalles appropriés.

Phosphore

Le phosphore est un élément constituant des molécules d'acide nucléique tels l'ADN et l'ARN (LEHNINGER et coll., 1993). Le phosphore est fourni sous forme de phosphate ou d'orthophosphate. Même si, d'un point de vue du métabolisme cellulaire, le phosphore est aussi important que l'azote, son effet sur la performance des biofiltres percolateurs est moins étudié.

La disproportion d'un nutriment, soit en excès, soit en déficit, produit des déséquilibres dans la composition de la biomasse. Par exemple, l'excès de phosphate peut conduire à une accumulation de phosphore intracellulaire sous forme de polyphosphate (KORNBERG, 1995). La limitation en phosphore conduit à la réduction de la génération d'énergie par unité de masse cellulaire sèche et par conséquence la conversion et la capacité d'élimination sont réduites (WÜBKER et coll., 1996).

SORIAL et coll. (1997) ont étudié la relation entre la production de biomasse et la limitation en phosphore. Ils trouvent lorsque le phosphore n'est pas limitant qu'une conversion de 99% est atteinte dans le premier tiers du biofiltre. Mais si le phosphore est l'élément limitant, tout le lit est nécessaire pour obtenir une conversion similaire. D'autre part, quand le système est mis en limitation de phosphore, il peut rester stable jusqu'à 14 jours consécutifs. Les auteurs

suggèrent de soumettre le biofiltre percolateur à des limitations périodiques de phosphore pour diminuer la croissance bactérienne et par conséquence la fréquence des lavages pour enlever l'excès de biomasse.

Soufre et potassium

Le soufre et le potassium sont deux éléments considérés comme des macronutriments, par la quantité à laquelle ils sont consommés et par leur importance biologique (LEHNINGER et coll., 1993). Le soufre joue un rôle très important dans le fonctionnement des enzymes et des protéines. La capacité de former des liaisons de type d'hydrogène entre les acides aminés contenant du soufre contribue à la définition de la structure tertiaire et quaternaire des polypeptides. Quant au potassium, il intervient dans le contrôle de la pression osmotique des microorganismes.

WÜBKER et coll. (1996) ont étudié l'impact de la limitation en potassium sur la production de biomasse dans un biolaveur. Ils trouvent que celle-ci diminue la quantité de carbone transformée en biomasse. Malheureusement, il n'existe pas de recherche sur les effets de ces deux nutriments au niveau de la performance des biofiltres percolateurs.

1.2.4. Débit de la solution nutritive dans un biofiltre percolateur.

Le débit de la solution nutritive permet d'apporter de façon continue des nutriments et de fournir au biofilm l'humidité nécessaire, de diluer les sous produits métaboliques formés ainsi que de contrôler le pH et la diffusion de l'oxygène (HOLUBAR et coll., 1999; SORIAL et coll., 1997). Le débit dépend aussi des dimensions du biofiltre (diamètre et hauteur du lit), de l'activité biologique de la biomasse, etc. BALTZIS et coll. (1996) montrent que l'augmentation du débit de recirculation de la solution nutritive entraîne une amélioration de la performance du biofiltre percolateur qui traite des xylènes. Les études issues de la littérature montrent une grande variation de ce paramètre, telles les valeurs du débit de la solution nutritive présentées dans le Tableau 1.5 qui sont compris dans une gamme de 0.04 à 144 $L\,h^{-1}$.

Polluant	Débit d'air pollué ($m^3 h^{-1}$)	Concentration de polluant ($g m^{-3}$)	Débit de la solution nutritive ($L min^{-1}$)	Références
Éthanol	1.5	2	2.4	COX et coll., 2001
Styrène	0.9-2.1	0.2-2.5	2.0	CHOU et coll., 1998
Toluène	1.5	1-2	2.4	COX et coll., 2000b
Éther diéthylique	0.4	0.2-0.4	0.0007	RIHN et coll., 1997
p-Xylène et m-Xylène	0.06	1.0 - 10.0	0.25, 0.375 et 0.5	BALTZIS et coll., 1996
m-Chlorobenzène o-Dichlorobenzène	0.14, 0.19 et 0.26	0.44 à 3.8	0.1	BALTZIS et coll., 2001
Disulfure de carbone	3400 - 4080	1.7 - 2.4	210 - 340	HUGLER et coll., 1999
Sulfure d'hydrogène et méthanol	1.2	H_2S : 0.07 Méthanol : 0.06	0.25 - 0.5	ALLEN et coll., 2000
Dichlorométhane	20.0	2.0	0.045	OKKERSE et coll., 1999b
Acétate d'éthyle	0.2 - 0.8	0.6 - 14.4	0.0024	LU et coll., 2001c
Acrylonitrile	0.07 - 0.26	0.3 - 13.0	0.0022	LU et coll., 2000
Éther de méthyle tert-butyle (MTBE)	0.36 - 0.6	0.7 - 1.3	2.5	FORTIN et coll., 1999
Méthanol et α-pinene	0.17	0.7 - 2.1	1.0	KONG et coll., 2001

Tableau 1.5. Débits d'air pollué et débits des solutions nutritives dans des biofiltres percolateurs.

1.2.5. Biodégradabilité du polluant.

Une grande variété de composés chimiques peut être oxydée dans les biofiltres percolateurs avec une conversion de 50 à 100%. La majorité des études sur les biofiltres percolateurs montrent que les composés aromatiques, principalement ceux du groupe BTEX (benzène, toluène, éthylbenzène et xylène) ainsi que le styrène, sont les COV les plus étudiés (Tableaux 1.2 à 1.6). L'autre groupe de polluants très étudié est celui des organochlorés tel le

dichlorométhane. Les études sur la dégradation des mélanges de polluants dans des biofiltres percolateurs sont nombreuses (ALLEN et coll., 2000 ; BALTZIS et coll., 1996 ; FORTIN et coll., 1999 ; KONG et coll., 2001). Les mélanges sont très variés mais le groupe BTEX est le plus commun. Il y a peu d'études sur les alcools, les aldéhydes, les paraffines de faible masse molaire, les alcanes, etc.

Les polluants d'intérêt pour la présente recherche sont l'éthanol, le méthanol et le toluène. La dégradation de ces composés est plus étudiée par biofiltration sans percolation qu'avec percolation. En particulier l'éthanol et le toluène sont souvent considérés comme modèle du fait de leur grande biodégradabilité. Les sujets d'étude sont divers et comprennent : l'effet de l'ajout de sels sur la performance du biofiltre (CHRISTEN et coll., 2001 ; DELHOMÉNIE et coll., 2001 ; TERAN PEREZ et coll., 2002), l'effet du garnissage (CHRISTEN et coll., 2002 ; DELHOMÉNIE et coll., 2002 ; KIARED et coll., 1997 ; HODGE et coll., 1994 ; RAMIREZ-LOPEZ et coll., 2000), l'effet de paramètres d'opération tels l'humidité (AURIA et coll., 1998 ; KIARED et coll., 1996) le temps de résidence de l'air pollué (ARULNEYAM et coll., 2000), l'utilisation de cultures pures lors de la dégradation de l'éthanol (LIM et coll., 2004), le co-traitement d'éthanol et de toluène (LIM, 2005), les voies métaboliques lors de la dégradation de l'éthanol (DEVINNY et coll., 1995) et la modélisation de la biofiltration (NUKUNYA et coll., 2005 ; HODGE et coll., 1997 ; HODGE et coll., 1995 ; HODGE et coll., 1991). Les études du méthanol sont moins nombreuses et elles sont axées sur la modélisation (SOLOGAR et coll., 2003 ; KRAILAS et coll., 2002 ; KRAILAS et coll., 2000a ; BALTZIS et coll., 1992) et les effets des paramètres d'opération (ALLEN et coll., 2000 ; KRAILAS et coll., 2000b ; SHAREEFDEEN et coll., 1993).

L'étude de ces deux composés par biofiltration par percolation se limite dans le cas du méthanol au travail fait par KONG et coll. (2001). Ils ont analysé les performances du biofiltre percolateur pour des températures comprises entre 50 et 70 °C (conditions thermophiliques) lors du co-traitement du méthanol avec l'α-pinène. Dans le cas de l'éthanol les travaux existants sont ceux de : COX et coll. (2001) qui ont étudié la dégradation en conditions thermophiliques, CIOCI et coll. (1997) qui ont utilisé un garnissage particulier consistant en des capsules emprisonnant les microorganismes, et FANG (2002) qui a optimisé les conditions d'opération d'un biofiltre percolateur traitant de l'éthanol.

Polluant	But de l'étude	Conversion (%)	Capacité d'élimination ($g\ m^{-3}\ h^{-1}$)	Références
Éthanol	Dégrader l'éthanol en conditions thermophiliques	67 100	230 70	COX et coll., 2001
Benzènes polyalkylés	Analyser l'effet de la limitation en azote	26	27	HEKMAT et coll., 1997
Benzène, toluène, éthylbenzène, xylène	Contrôler la formation de biomasse en limitant le phosphore	99	75	SORIAL et coll., 1997
Sulfure d'hydrogène et méthanol	Traiter des gaz non condensables émis par le procédé Kraft	90	8.0	ALLEN et coll., 2000
Éther méthyl-*tert*-butylique (EMTB)	Identifier l'étape qui limite le biofiltre percolateur	95 97	50 41	FORTIN et coll., 1999
Styrène	Étudier la dégradation du styrène	90 80	32 55	LU et coll., 2001b
Monochloro-benzène	Comparer la biofiltration avec et sans percolation	jusqu'à 94	8.9 à 62	MPANIAS et coll., 1998b
Toluène	Analyser une variante de biofiltre percolateur	50 à 67	80	COX et coll., 2000a
Disulfure de carbone	Traiter les composés soufrés provenant d'une usine	90	220	HUGLER et coll. 1999
N,N-diméthylacetamide	Traiter les rejets gazeux d'une usine	90 80	20.2 27.6	LU et coll., 2001c
p-Xylène et m-Xylène	Étudier les facteurs qui affectent la dégradation du xylène	p-X : 46 - 98 m-X : 94	68 - 14 120	BALTZIS et coll., 1996

Tableau 1.6. Conversion et capacité d'élimination pour divers polluants.

1.2.6. Débit d'air pollué.

Le débit d'air pollué dans des biofiltres traitant des émissions industrielles varie de 5000 à 1000000 $m^3\ h^{-1}$ (KENNES et coll., 1998). Le tableau 1.5 montre diverses valeurs de débit d'air utilisées à échelle pilote.

Le débit d'air et le volume du bioréacteur dans la section du lit filtrant définissent le temps de résidence de l'air pollué dans le système. Le temps de résidence est évalué par l'équation suivante :

$$EBRT = \frac{V_f}{Q}$$

EBRT = temps de résidence en fût vide, h

V_f = volume du lit filtrant vide, m^3

Q = débit volumique d'air, $m^3\ h^{-1}$

La valeur du temps de résidence en fût vide (EBRT) est directement liée à la conversion du polluant (LU et coll., 2000 ; LU et coll., 2001c). Avec un temps de résidence élevé, des taux de conversions de l'ordre de 100% sont obtenus (COX et coll., 2001 ; KONG et coll., 2001). L'explication est donnée par plusieurs auteurs, entre autres LOBO et coll. (1999), qui mentionnent que le biofiltre percolateur est contrôlé par deux mécanismes : le transfert de masse du polluant qui va de la phase gazeuse à la phase liquide et les phénomènes qui ont lieu dans le biofilm (i.e. les transferts de masse des composés dans une matrice complexe et les bioréactions).

1.2.7. Concentration du polluant.

La concentration du polluant ne peut être élevée à cause des effets inhibiteurs des hautes concentrations sur les microorganismes. Les concentrations oscillent en général entre 0,1 et 10 $g\ m^{-3}$ (COOPER et coll., 2002 ; POPOV et coll., 1999). Par exemple, lors de la biofiltration de l'éthanol, on observe une acidification du lit quand la concentration dépasse 1.0 $g\ m^{-3}$ (DEVINNY et coll., 1995 ; LESON et coll., 1995 ; DASTOUS et coll., 2005). Les concentrations en biotraitement sont faibles en comparaison avec celles utilisées dans les traitements traditionnels, comme l'incinération (de 10 à 120 $g\ m^{-3}$). Par contre, le fait de

pouvoir traiter de faibles concentrations de COV représente un avantage sur les traitements traditionnels. Dans les traitements traditionnels, la relation énergie consommée et concentration de polluant n'est pas proportionnelle, l'énergie ne changeant pas beaucoup si la concentration de polluant diminue tout en maintenant un débit d'air constant. Cette particularité a pour conséquence que les traitements traditionnels pour des faibles concentrations de COV s'avèrent très coûteux, par exemple pour l'incinération, le coût moyen de traitement d'air pollué est de 10 US \$/1000 m^3 d'air traité par rapport à 3.5 US \$/1000 m^3 d'air traité pour la biofiltration (KENNES et coll., 1998).

1.2.8. Charge à l'entrée de polluant.

La charge à l'entrée du polluant indique la masse nette de polluant qui entre dans le biofiltre par unité de volume du lit et par unité de temps. Elle est obtenue en multipliant le débit d'air par la concentration de polluant à l'entrée et en divisant par le volume du lit filtrant.

$$CI = \frac{Q \quad C_{go}}{V_f}$$

CI = charge de polluant à l'entrée du bioréacteur, g m^{-3} h^{-1}

C_{go} = concentration du polluant, g m^{-3}

V_f = volume du lit filtrant vide, m^3

Q = débit volumique d'air, m^3 h^{-1}

La performance du biofiltre est limitée par la charge du polluant. Un diagramme de la capacité d'élimination en fonction de la charge permet de déterminer les conditions auxquelles le biofiltre est limité par la cinétique microbienne ou par les phénomènes de diffusion.

1.3. Paramètres qui indiquent la performance d'un biofiltre avec et sans percolation

Le but d'un biotraitement d'air pollué est d'enlever les polluants du courant gazeux. Les paramètres qui indiquent le niveau auquel est atteint ce but sont la quantité de polluant dégradé ainsi que le pourcentage de polluant enlevé. Ces deux paramètres sont nommés respectivement capacité d'élimination et taux de conversion.

Tous les travaux expérimentaux étudiant les variables qui affectent la performance des biofiltres percolateurs utilisent ces deux paramètres comme indicateurs. Le Tableau 1.6 montre une grande variété d'objectifs dans les travaux de recherche évalués avec ces deux paramètres.

1.3.1. Capacité d'élimination.

De façon similaire à la charge volumique à l'entrée, la capacité d'élimination est aussi une quantité de masse nette de polluant. Elle indique la masse de polluant transformé du courant gazeux par unité de volume du lit et par unité de temps. La façon de calculer la capacité d'élimination est la suivante :

$$CE = \frac{Q\ (C_{go} - C_{gf})}{V_f}$$

CE = capacité d'élimination, g m^{-3} h^{-1}

C_{go} = concentration du polluant à l'entrée, g m^{-3}

C_{gf} = concentration du polluant à la sortie, g m^{-3}

V_f = volume du lit filtrant vide, m^3

Q = débit volumique d'air, m^3 h^{-1}

1.3.2. Taux de conversion.

Le taux de conversion du polluant indique l'efficacité d'un système à dégrader un composé. Elle est évaluée comme suit :

$$X = \frac{(C_{go} - C_{gf})}{V_f} \quad 100$$

X = conversion, (%)

C_{go} = concentration du polluant à l'entrée, g m^{-3}

C_{gf} = concentration du polluant à la sortie, g m^{-3}

La capacité d'élimination et/ou la conversion montrent le comportement d'un biofiltre percolateur. La première indique la quantité de polluant qui peut être dégradée, alors que la

deuxième indique l'efficacité du biofiltre percolateur. Lorsque les deux sont utilisés, elles donnent une idée plus précise du bioréacteur.

1.3.3. Production de biomasse.

La production de biomasse est une indication de la performance du biofiltre. Le taux de production de biomasse dépend des conditions d'opération et de l'adaptation des microorganismes au polluant. L'indicateur le plus précis de l'adaptation des microorganismes est la quantité de microorganismes spécifiques au polluant présente dans la biomasse. ARCANGELI et coll. (1992), SPEITEL et coll. (1993) aussi que PEDERSEN et coll. (1999) rapportent que 10 % de la biomasse totale est capable de dégrader les polluants et que cette quantité peut supporter la croissance des autres microorganismes présents dans le biofiltre. ALONSO et coll. (1997) indiquent que le taux de conversion n'est pas fonction de la quantité de biomasse présente dans le biofiltre. Ces auteurs indiquent qu'un biofilm mince et actif produit des taux de conversion élevés.

1.3.4. Production de dioxyde de carbone.

Le taux de production de dioxyde de carbone est un autre indicateur de la performance du biofiltre. Une fois que le système arrive à un taux de conversion stable, le taux de production de dioxyde de carbone varie dans une petite gamme de valeurs. DIKS et coll. (1994) suggèrent l'existence d'un équilibre entre les divers microorganismes présents dans le biofilm, ce qui signifie que la production de dioxyde de carbone est stable. D'autres auteurs relient la variation de la production de dioxyde de carbone avec la demande d'énergie des microorganismes (HOLUBAR et coll., 1999) ou avec des conditions d'opération extrêmes (COX et coll., 2001).

1.3.5. Rendements en biomasse et en dioxyde de carbone.

Les composes organiques volatils sont transformés par les microorganismes présents dans le biofiltre en biomasse, dioxyde de carbone et eau suite à la réaction globale suivante :

$$COV + O_2 + nutriments \xrightarrow{microorganismes} biomasse + CO_2 + H_2O + sels$$

La conversion du COV en biomasse ou dioxyde de carbone peut être suivie par l'intermédiaire des rendements de ces deux composés (JORIO et coll., 2005). Le rendement de biomasse ou de CO_2 est défini comme la masse formée de biomasse ou de CO_2 par unité de masse du COV consommée. La valeur des rendements permet d'avoir une idée des réactions qui prédominent à l'intérieur d'un biofiltre et permet d'évaluer plusieurs paramètres, tels la vitesse de croissance des microorganismes et la vitesse de consommation des COV (JORIO et coll., 2005 ; DELHOMÉNIE, 2002).

1.4. Comparaison entre le biofiltre et le biofiltre percolateur.

La solution nutritive est fournie de façon intermittente au biofiltre et continuellement au biofiltre percolateur. Étant donné que la phase liquide influence les phénomènes de transfert de masse (ZHU et coll., 1998) et que ces derniers ont des effets sur les réactions biologiques et le contenu d'eau dans le biofilm, la périodicité d'arrosage cause plusieurs différences entre les deux biotechnologies. Par exemple, le biofiltre percolateur est opéré en général à des temps de résidence 50 à 70% plus courts que le biofiltre. Les taux de conversion sont cependant similaires à celles du biofiltre et varient de 30 à 100%, mais la capacité d'élimination est de 2 à 3 fois plus élevée dans le biofiltre percolateur (IRANPOUR et coll., 2001).

1.4.1. Transfert de masse et bioréactions dans le biofiltre.

La biodégradation des polluants à l'intérieur d'un biofiltre est le résultat de divers phénomènes simples qui ont lieu de façon simultanée. Les phénomènes présentés dans les modèles biophysiques de la Figure 1.2 sont considérés comme étant les plus importants :

i) Transfert du polluant et de l'oxygène de la phase gazeuse vers l'intérieur du biofilm. Étant donné que le biofiltre est arrosé de façon intermittente, la couche liquide qui couvre le biofilm est très mince et parfois inexistante. La résistance au transfert de masse de la couche liquide est en général négligée par plusieurs auteurs qui considèrent la couche liquide et le biofilm comme une seule phase homogène. De cette façon le premier modèle biophysique proposé pour la biofiltration (OTTENGRAF, 1986) considère trois phases : gaz, biofilm (liquide) et solide (garnissage). Le transfert de masse du gaz vers le biofilm est le suivant : les composés transportés par convection dans la phase gazeuse au moment d'entrer en contact avec la surface du biofilm sont

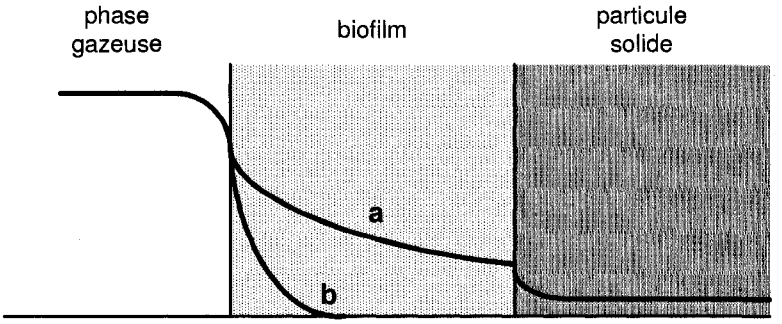
absorbés, puis à l'intérieur du biofilm les composés sont transportés par diffusion et dégradés. Les microorganismes en consommant des COV maintiennent toujours un gradient de concentration entre le gaz et le biofilm qui est la force motrice pour le transfert de masse entre les deux phases. Le modèle biophysique considère que la phase solide est inerte et qu'elle n'intervient pas dans le transfert de masse. Ce modèle biophysique est le plus simple. Par la suite, plusieurs auteurs ont développé des modèles mathématiques de biofiltration soit en régime permanent soit en régime dynamique (SHAREEFDEEN et coll., 1993 ; HODGE et coll., 1995 ; MOHSENI et coll., 2000 ; KRAILAS et coll., 2002).

ii) Transfert de nutriments de la phase liquide et de la phase solide vers le biofilm. La Figure 1.2-A montre que les COV non dégradés peuvent passer à l'intérieur des particules solides s'il existe un gradient de concentration (DESHUSSES et coll., 1995b). Les produits issus du métabolisme des microorganismes, tel l'acide acétique formé pendant la dégradation de l'éthanol (DEVINNY et coll., 1995), peuvent migrer vers l'intérieur des particules suite au gradient de concentration. À notre connaissance, le transfert des nutriments de la solution nutritive vers le biofilm n'a pas encore été considéré dans la littérature. On peut supposer que pendant l'absorption du liquide par le biofilm, les nutriments dissous sont également absorbés. La Figure 1.2-B montre des particules solides poreuses et hydratées qui contiennent des nutriments solubles dans l'eau. Ces nutriments diffusent vers la surface des particules où ils sont dégradés par des microorganismes (SWANSON et coll., 1997).

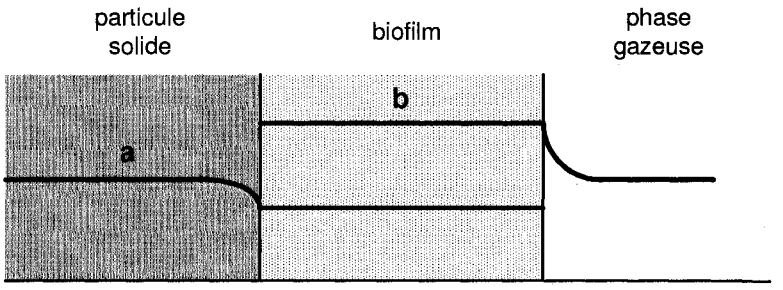
iii) Réactions biologiques dans le biofilm. La réaction générale est la transformation du COV en dioxyde de carbone, eau et biomasse. Cette réaction est en réalité l'addition de plusieurs réactions individuelles qui ont lieu dans le biofilm, telles la formation de composés intermédiaires (LOBO et coll., 1999 ; DIKS, 1992 ; DEVINNY et coll., 1995), la production de polysaccharides (FARRUGIA, 1999), la génération et la consommation de biomasse (OKKERSE et coll., 1999b).

iv) Transfert des produits issus du métabolisme microbien à partir du biofilm et vers la phase gazeuse. Cette étape est en général négligée pendant le développement de modèles biophysiques et mathématiques. Les composés qui ont été considérés dans quelques modèles sont l'eau et le dioxyde de carbone (KRAILAS et coll., 2000a). Étant

donné que les bioréactions d'oxydation sont exothermiques, le lit subit une augmentation de la température, ce qui provoque l'évaporation de l'eau à la surface du biofilm et des particules non couvertes par le biofilm (MORALES et coll., 1998).



A. Transfert de masse des COV et de l'oxygène de la phase gazeuse vers le biofilm.
Cas a) ni le COV ni l'oxygène sont consommés complètement, le taux de réaction limite la cinétique qui est de premier ordre.
Cas b) le COV ou l'oxygène est consommé complètement, le transfert de masse limite la cinétique qui est d'ordre zéro.



B. Transfert de masse qui n'est pas considéré dans les modèles mathématiques.
a) Transfert des nutriments, de la particule solide vers le biofilm.
b) Transfert du dioxyde de carbone et de l'eau, du biofilm vers la phase gazeuse.

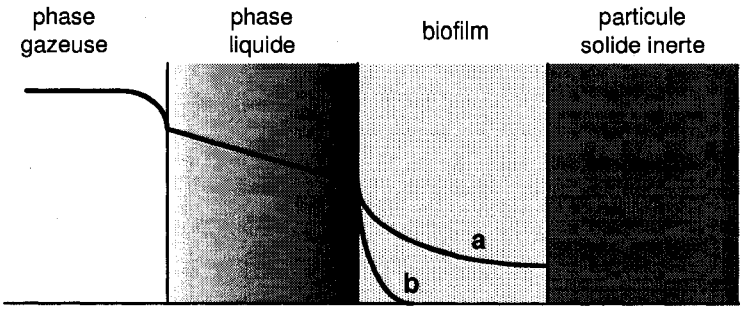
Figure 1.2. Modèle biophysique pour le transfert de masse dans un biofiltre. A montre le transfert de masse dans le sens de la phase gazeuse vers la particule solide, tandis que B montre le transfert de masse en sens inverse.

1.4.2. Transfert de masse et bioréactions dans le biofiltre percolateur.

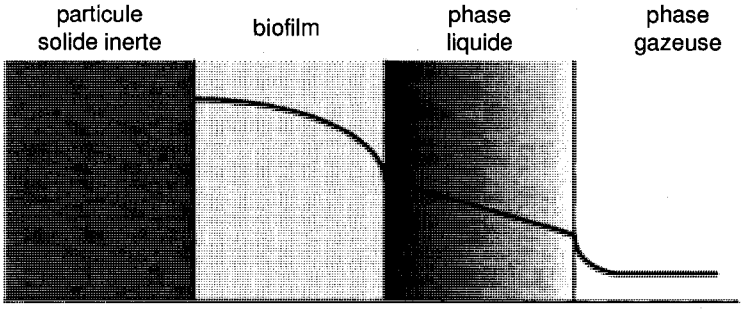
La biodégradation des polluants à l'intérieur d'un biofiltre percolateur est le résultat de la présence simultanée de divers phénomènes simples. Ces derniers sont montrés dans les

modèles biophysiques de la Figure 1.3. Les phénomènes décrits ci-dessous sont considérés comme les plus importants :

i) Transfert du polluant et de l'oxygène de la phase gazeuse vers l'intérieur du biofilm. Le premier modèle biophysique, proposé par DIKS et coll. (1991), contient 3 phases : le gaz, le liquide (solution nutritive) et le biofilm. Dans ce modèle, le biofilm est considéré comme une phase liquide homogène, de façon similaire au biofiltre. À l'exception de SMITH et coll. (2002), qui proposent un modèle avec deux phases : la phase gazeuse et le biofilm, épais et rugueux, tous les modèles considèrent trois phases. Les modèles biophysiques triphasiques ont été utilisés pour développer des modèles mathématiques pour la biofiltration par percolation en régime permanent, en régime dynamique, pour un seul COV, ou pour un mélange de COV (ZHU et coll., 2001 ; BALTZIS et coll., 2001 ; ALONSO et coll., 1999 ; LOBO et coll., 1999 ; MPANIAS et coll., 1998a ; HEKMAT et coll., 1994 ; OCKELOEN et coll., 1992). Le transfert des COV et de l'oxygène de la phase gazeuse vers le biofilm se fait par la voie montrée dans la Figure 1.3-A. À l'interphase gaz-liquide, l'oxygène et les COV sont absorbés, ils diffusent ensuite dans le liquide et sont finalement absorbés par le biofilm, où ils diffusent et sont dégradés. Comme dans le biofiltre, il existe un gradient de concentration entre le gaz et le biofilm qui représente la force motrice pour le transfert de masse.
ii) Transfert de nutriments de la phase liquide vers le biofilm. Les nutriments présents dans la solution nutritive (phase liquide du modèle biophysique) sont absorbés par le biofilm. À l'intérieur du biofilm, ils sont transportés par diffusion. Des études récentes montrent d'autres formes de transfert des composés à l'intérieur du biofilm, tels des conduits spécialisés pour le transfert de l'oxygène et de l'azote (ZHU et coll., 2001).
iii) Transfert des produits issus du métabolisme microbien vers la phase gazeuse. La Figure 1.3-B montre le transfert de composés vers la phase gazeuse. Cette étape est en général négligée et les modèles existants n'expliquent pas la libération de ces composés par le biofilm.
iv) Réactions biologiques dans le biofilm. En général, les auteurs proposent les mêmes réactions et considérations pour le biofiltre et le biofiltre percolateur.



A. Transfert de masse des COV et de l'oxygène de la phase gazeuse vers le biofilm.
Cas a) ni le COV ni l'oxygène sont consommés complètement, le taux de réaction limite la cinétique qui est de premier ordre.
Cas b) le COV ou l'oxygène est consommé complètement, le transfert de masse limite la cinétique qui est d'ordre zéro.



B. Transfert de masse de dioxyde de carbone, d'eau et d'autres produits métaboliques du biofilm vers la phase gazeuse.

Figure 1.3. Modèle biophysique pour le transfert de masse dans un biofiltre percolateur. A montre le transfert de masse de la phase gazeuse vers le biofilm. B montre le transfert de masse du biofilm vers la phase gazeuse.

v) Réactions biologiques dans la phase liquide. Étant donné que la biomasse se détache du garnissage et que la solution nutritive est en recirculation constante, les microorganismes présents dans la biomasse détachée sont capables de se multiplier. Dans certains cas, pour des composés très solubles, une densité cellulaire élevée dans la phase liquide a été observée (COX et coll., 2001). En travaillant avec le toluène, un COV peu soluble, COX et coll. (2000b) rapportent des taux de conversion d'environ 20 % pour le toluène dans la phase liquide. L'addition d'émulsifiants dans la phase liquide augmente le

transfert des composés peu solubles dans l'eau et améliorent la performance du biofiltre percolateur (DUMONT et coll., 2005 ; GROENESTIJN et coll., 1999).

1.4.3. Effet de la phase liquide sur la population microbienne et la performance dans le biofiltre et dans le biofiltre percolateur.

Dans les deux systèmes, la phase liquide garanti le taux d'humidité dans le biofilm, ce qui est essentiel pour la diffusion des composés et pour le fonctionnement des microorganismes. Dans le biofiltre il existe un gradient d'humidité qui affecte la densité microbienne (KRAILAS et coll., 2000b) et qui peut être lié avec le gradient de la capacité d'élimination observé en fonction de la hauteur du biofiltre (PRADO et coll., 2005).

À notre connaissance, il n'existe pas d'études comparatives entre les populations de ces deux biotechnologies. Un indicateur de la différence entre les populations peut être le taux de production de dioxyde de carbone, lequel est 2 ou 3 fois plus élevé dans le biofiltre que dans le biofiltre percolateur. L'effet du lavage du biofilm par la phase liquide mobile peut expliquer ce comportement. Le lavage de la surface du biofilm évite l'accumulation des produits métaboliques inhibiteurs ou non (DIKS et coll., 1991). Les produits passent dans la phase liquide où ils sont dilués. Ils sont ensuite retirés du système par la purge du lixiviat. Dans le biofiltre, ces produits restent disponibles pour être consommés par d'autres microorganismes différents des spécifiques au polluant. Ceci augmente le taux de minéralisation des COV (ARCANGELI et coll., 1992 ; SPEITEL et coll., 1993 ; PEDERSEN et coll., 1999).

Par ailleurs, les populations varient avec le temps dans un système (KRAILAS et coll., 2000b). Certains microorganismes disparaissent parce qu'ils ne se sont pas adaptés ou parce qu'ils ont été déplacés. Les changements dans la population provoquent aussi des variations dans la structure du biofilm (TRESSE et coll., 2002). Selon les conditions d'opération, le biofiltre et le biofiltre percolateur peuvent arriver à un régime pseudo-permanent en termes d'accumulation de biomasse dans le lit (DIKS et coll., 1994) et à une stabilité de la structure du biofilm (TRESSE et coll., 2002).

1.5. Modèles mathématiques applicables à la biofiltration.

L'utilisation d'un modèle mathématique qui décrit la performance d'un système quelconque permet de : mieux connaître le système, de prédire les réponses du système face aux variations des conditions d'opération, d'optimiser le système en terme de coûts et de performance, de faciliter l'automatisation et la mise en échelle du système.

Divers modèles mathématiques ont été développés pour décrire la biofiltration. Les approches des modèles sont diverses. OTTENGRAF et coll. (1983) ont été les premiers à proposer un modèle mathématique pour un biofiltre. Le modèle considère que les concentrations du polluant dans la phase gazeuse et le biofilm sont à l'équilibre. SHAREEFDEEN et coll. (1993) proposent un modèle plus élaboré pour des biofiltres opérant en régime permanent. Ils introduisent des termes de limitation d'oxygène et d'inhibition du polluant. HODGE et coll. (1995) ont développé un modèle qui considère le biofiltre opérant en régime transitoire. Les modèles ont évolué et sont devenus plus complexes, afin de prédire le plus de phénomènes possible. De cette façon, il y a des modèles qui considèrent trois phases dans le biofiltre (SHAREEFDEEN et coll., 1994 ; AMANULLAH et coll., 1999), des modèles qui considèrent la biofiltration d'un mélange des composés (ZAROOK et coll., 1997) ou des modèles qui essaient de prédire l'influence des pores du garnissage (NUKUNYA et coll., 2005).

Par rapport au biofiltres percolateurs, DIKS et coll. (1991) ont été les premiers à proposer un modèle pour la biofiltration par percolation appliquée au traitement d'air pollué. C'était un modèle simple, d'ordre zéro pour la cinétique de dégradation du dichlorométhane dans le biofilm. OCKELOEN et coll. (1992) ont modifié le modèle de DIKS et coll. (1991), en adaptant le modèle à une cinétique de type Monod, qui consiste en une cinétique d'ordre 1 a faibles concentrations et qui devient d'ordre zéro en augmentant la concentration. Ils ont montré avec des simulations que la dégradation des COV est liée à leur solubilité dans l'eau. HEKMAT et coll. (1994) ont proposé un modèle avec une cinétique de type Monod dans le biofilm, dont l'ordre de réaction peut être zéro ou un, selon le polluant et sa concentration. Leur modèle a été validé avec des donnés expérimentales de trois polluants de nature chimique différente, tels l'éthanol, un mélange de benzènes polyalkylés et le dichlorométhane. Ils ont introduit un facteur d'effectivité biocatalytique dans le modèle pour déterminer quel phénomène limitait la vitesse de biodégradation : le transfert du polluant ou la bioréaction dans le biofilm. Les modèles antérieurs développés pour des biofiltres percolateurs en régime

permanent ou en régime dynamique (DESHUSSES et coll., 1995a ; SHAREEFDEEN et coll., 1995 ; ZAROOK et coll., 1997), ne considèrent pas l'accumulation de la biomasse dans le lit. Ils assument un biofilm homogène en termes d'épaisseur, de densité et de diversité microbienne. Par contre, ALONSO et coll. (1997) ont présenté un modèle qui considère que la surface spécifique du lit n'est pas constante, étant donné que l'accumulation de la biomasse provoque une variation de l'épaisseur du biofilm tout au long du lit, ce qui diminue la fraction de vide du lit et l'aire spécifique du garnissage. OKKERSE et coll. (1999b) ont développé un modèle qui prédit l'accumulation de la biomasse, ce qui est important pour définir le temps d'opération du biofiltre percolateur avant qu'il présente des problèmes de colmatage, de formation de chemins préférentiels pour les écoulements, etc. LOBO et coll. (1999) ont développé un modèle dynamique et ont montré que les dimensions du biofiltre percolateur sont fonction : du phénomène qui limite la vitesse de dégradation du polluant, de l'absorption du polluant et du mode de contact entre les écoulements d'air et de liquide. Tous ces modèles nommés préalablement, ont été conçus pour traiter un seul polluant. BALTZIS et coll. (2001) ont développé un modèle qui s'applique aux mélanges de polluants et qui tient compte de leur interaction cinétique.

Tous les modèles ont été développés avec une série de restrictions, de telle façon que chaque auteur arrive à un modèle qui décrit très bien un biofiltre percolateur particulier. Mais ce modèle doit être ajusté quand le polluant ou les conditions d'opération du biofiltre percolateur ne sont pas celles pour lesquelles il a été conçu. Pour l'utiliser sous des conditions différentes, il faut faire des ajustements et calculer ou évaluer expérimentalement certains paramètres du modèle.

1.6. Macrocinétique ou cinétique de la biodégradation des composés organiques volatils.

Le taux de biodégradation des COV dans un biofiltre avec ou sans percolation est en fonction des conditions d'opération et des microorganismes présents dans le biofilm. Le taux de biodégradation peut être défini par la capacité d'élimination et le comportement cinétique. Les modèles macrocinétiques ont été développés en fonction de la concentration de polluant dans la phase gazeuse. Ces modèles font partie des modèles mathématiques plus complexes mentionnés ci-dessus. Les modèles cinétiques de biodégradation des COV sont similaires à

ceux des réactions chimiques ou biologiques. Le plus simple est le modèle de premier ordre, similaire à une réaction chimique qui dépend de la concentration du réactif (JONES et coll., 2004). Ce modèle s'ajuste bien à la cinétique que présentent des biofiltres avec ou sans percolation qui ne sont pas inhibés par les COV et qui opèrent à de faibles concentrations des COV. Dans le cas des polluants présents à des concentrations plus élevées et qui ne présentent pas d'inhibition, la cinétique de biodégradation des polluants suit en général un ordre mixte et est défini par des modèles qui ont une structure mathématique similaire à l'équation de Michaelis-Menten de base, qui décrit une cinétique de deux ordres tel que le modèle de Monod (HIRAI et coll., 1990 ; KRAILAS et coll., 2002 ; SOLOGAR et coll., 2003 ; STRESSE et coll., 2005 ; WANI et coll., 1999). Les COV inhibent les microorganismes à partir d'un certain seuil de concentration, pour des concentrations supérieures à ce seuil la cinétique de biodégradation ne s'adapte pas aux modèles basés sur l'équation de Michaelis-Menten de base et cette équation doit être modifiée ou des nouveaux modèles cinétiques sont à utiliser ou à développer.

1.7. Microcinétique ou cinétique de la croissance microbienne.

Les paramètres cinétiques qui décrivent la croissance microbienne sont indispensables lors de l'élaboration d'un modèle mathématique pour simuler la performance d'un biofiltre. Généralement, la croissance microbienne est bien représentée par l'équation de Monod (LIU, 2007), qui exprime la vitesse spécifique de croissance microbienne en fonction de la concentration du COV dans la phase où se trouvent les microorganismes. De cette façon, les paramètres cinétiques de croissance microbienne sont calculés par l'intermédiaire de l'équation de Monod. La majorité des études de croissance microbienne sont faites avec des souches pures ou des microorganismes isolés d'un consortium microbien qui présente une activité de biodégradation envers un polluant. Traditionnellement, les microorganismes sont cultivés en suspension dans un milieu de culture liquide. Les paramètres cinétiques ainsi obtenus sont appliqués dans des modèles mathématiques pour simuler des biofiltres qui contiennent des consortiums microbiens suspendus dans une phase solide. Dernièrement, il y a plusieurs études qui portent sur la détermination des paramètres cinétiques de croissance microbienne sous des conditions plus proches de celles auxquelles est soumis le biofilm qui se

trouve à l'intérieur d'un biofiltre en opération (DELHOMÉNIE, 2002 ; GOVIND et coll., 1997).

Quand le COV inhibe les microorganismes, le modèle de Monod ne s'ajuste pas aux données expérimentales. L'utilisation d'un modèle avec un terme d'inhibition, tel que le modèle d'Haldane, permet de mieux appréhender cette cinétique (DELHOMÉNIE, 2002 ; OKPOKWASILI et coll., 2005 ; SHAREEFDEEN et coll., 1993). Dans la littérature, il n'existe pas de recherche sur la détermination des paramètres cinétiques associés à la croissance microbienne qui utilisent directement des données de production de biomasse du lit filtrant. Cette approche pourrait à notre avis faciliter la détermination des ces paramètres cinétiques qui seraient ainsi calculés sous des conditions d'opération réelles.

1.8. Structure du biofilm et ses effets sur la performance des biofiltres.

Les microorganismes qui forment le consortium microbien sont suspendus dans une phase solide nommé biofilm. Les unités catalytiques responsables de la biodégradation des COV dans un biofiltre sont des microorganismes. Leurs interactions, leurs densités cellulaires dans le biofilm et les effets des conditions d'opération sur le biofilm, sont des facteurs qui déterminent la performance d'un biofiltre. En général, les études qui analysent les biofilms dans des biofiltres avec et sans percolation montrent la prédominance des microorganismes spécifiques aux polluants traités (FARRUGIA, 1999 ; SONG et coll., 2000). Par contre, ces études n'analysent pas en général en profondeur l'effet des conditions d'opération sur la dynamique microbienne.

Par rapport à la composition du biofilm, les études démontrent que le biofilm est un microcosme en changement constant (ACUÑA et coll., 1999 ; DIKS et coll., 1994). Une petite variation des conditions d'opération, soit la température, soit la concentration des nutriments, induit de grandes modifications dans la distribution des espèces chimiques dans le biofilm (JUTEAU, 1997 ; TRESSE et coll., 2002). Les composés dont il faut tenir compte sont les exo-polysaccharides, qui sont capables d'intervenir dans la régulation d'humidité et la rétention des composés solubles dans l'eau à l'intérieur du biofilm (FARRUGIA, 1999).

Chapitre 2. Démarrage, entretien et caractérisation d'un biofiltre percolateur pour le traitement de l'air pollué avec vapeurs d'éthanol

Article « *Biotrickling filtration of air contaminated with ethanol* », qui a été publié dans le « Journal of Chemical Technology and Biotechnology », Vol. 82, no. 2, pp. 149-157 (2007).

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Résumé

Une biofiltre percolateur pour traiter des vapeurs d'éthanol a été opéré. Le but de l'étude a été l'analyse des effets des conditions d'opération sur la performance du biofiltre percolateur. L'étude a permis aussi de se familiariser avec les paramètres de performance caractéristiques d'un biofiltre percolateur, le contrôle de la biomasse, l'entretien de l'équipement et les mesures analytiques les plus courantes réalisées au laboratoire.

Le biofiltre percolateur a été opéré dans une gamme de concentrations d'éthanol variant entre 0.2 à 15.0 g m^{-3}, ce qui excède les concentrations d'éthanol généralement utilisées dans des biofiltres traditionnels. Le biofiltre percolateur a opéré également à de faibles concentrations d'azote dans la solution nutritive, soit 0.005 gN L^{-1}. Trois temps de résidence ont été testés : 30, 65 et 130 s.

Le taux de conversion a diminué avec la concentration d'éthanol et a augmenté avec le temps de résidence (variation entre 60 à 100 % selon les conditions opératoires). Une méthode de lavage du lit filtrant a été développée pour contrôler le contenu en biomasse. Le lavage périodique a stabilisé la performance des biofiltres. Une capacité d'élimination maximale de 970 g m^{-3} h^{-1} a été obtenue pour une charge d'éthanol de 1610 g m^{-3} h^{-1}, valeur supérieure à celle reportée dans la littérature. L'étude démontre que les biofiltres percolateurs peuvent traiter efficacement l'air pollué avec des vapeurs d'éthanol en utilisant des solutions nutritives peu complexes.

2. Biotrickling filtration of air contaminated with ethanol

Abstract

A biotrickling filter (BTF) for treating high ethanol loads was operated for one year and the effect of operating conditions was studied. The BTF was operated in a range of ethanol inlet concentrations of 0.2 to 15.0 g m^{-3} and at three different residence times (30 s, 65 s and 130 s). The experiments show that removal efficiency decreased with increasing ethanol inlet concentration and decreasing air residence time. Removal efficiency varied in the range of 60 to 100 %. A maximum elimination capacity of 970 g m^{-3} h^{-1} was obtained for an inlet load of 1610 g m^{-3} h^{-1}. At a constant residence time, the carbon dioxide (CO_2) production rate varied with ethanol inlet concentration. BTF presented the maximum CO_2 production rate in the range of inlet concentration of 3.0 to 7.0 g m^{-3}. Two strategies for controlling biomass accumulation were applied. One consisted in periodical washing. The other one combined periodical washing with nutrient starvation by consuming less water and energy. Both strategies led to maintaining the BTF stable, with high adaptability and reproducibility.

2.1. Introduction.

2.1.1. Removal of Volatile organic compounds from gaseous effluents.

The development of reliable and cost effective ways of eliminating volatile organic compounds (VOC's) from gaseous industrial emissions continues to be a crucial endeavour for a better environment. There are a number of physicochemical options including absorption, adsorption, thermal oxidation and catalytic oxidation. These processes work well for VOC concentrations up to 5.0 g m^{-3} and air flow rates less than 80000 m^3 h^{-1} (COOPER and coll., 2002; DELHOMÉNIE and coll., 2005b; JORIO and coll., 1999).

The characteristics of gas effluents described above are common in industry but there is a pressing need for efficient and cost effective processes for low concentrations and high flow rates. Biological processes are often very appropriate options for these situations and their operating costs are generally much lower than for physicochemical processes. In addition, biological processes can, if appropriately designed, be simpler to control and operate than physicochemical processes.

2.1.2. Biotrickling filtration.

One of the most promising options for the treatment of industrial gaseous effluents is the biotrickling filter (BTF). The process consists of passing the polluted gas through a bed, where the immobilized microorganisms transform the pollutants to non-hazardous end-products. The bed is irrigated continuously with an aqueous nutrient solution which provides the necessary nutrients to the microorganisms. The nutrient solution also keeps the bed properly humidified in order to give the microorganisms the best possible conditions to develop (KENNES and coll., 1998; EDWARDS and coll., 1996). This trickling controls some operating parameters in the BTF, for example the pH and the biomass content in the bed. If the pollutant is water-soluble, the trickling nutrient stream improves the transfer of the pollutant from the gas phase to the microorganisms.

2.1.3. Ethanol pollution.

Ethanol is a water-soluble VOC with a great diversity of applications. Ethanol is released in production processes of solvents, fuels, beverages, bread, etc. Ethanol emission rates of a typical installation could be considered not significant because they are generally below 100 tons per year (SMITH, 1999), but the number of installations that release ethanol may be so high that the total amount emitted in a geographic area must be taken in count. For example, in 1993, commercial activities in the European Community emitted 151 000 tons of ethanol to the atmosphere in the following processes: baking, brewing, spirit production and wine-making (PASSANT and coll., 1993). In Los Angeles, in the same year, commercial bakeries emitted 2400 ton $year^{-1}$ of VOC's, principally ethanol (COX and coll., 2001).

In spite of the magnitude of these emissions, they are usually neglected, because ethanol is considered non-toxic and highly biodegradable. This situation is well illustrated with this two examples: 1) The occupational exposure limits for ethanol concentration in air is high, it is 2.0 g m^{-3} per 10-hour working period (MATHESON TRI-GAS, 2004); 2) There are no legal limits for air quality for long term exposition to ethanol either from the industrial health point of view or for people who live near installations like breweries or bakeries which constantly emit ethanol.

Regulation of ethanol emissions was recently introduced in several environmental laws. In Canada, the Canadian Environment Protection Act was modified in 2003 to better regulate

VOC emissions and a detailed list of 60 VOC's was published with ethanol included in the list (COMMUNICATION CANADA, 2003). Ethanol emissions are established in terms of mass rates in several countries such as Australia, Canada and United States (ENVIRONMENT AUSTRALIA, 2006; COMMUNICATION CANADA, 2003; ENVIRONMENTAL PROTECTION AGENCY, 1992), where the threshold of emissions is generally 10 tons per year for an industrial installation.

2.1.4. Control of ethanol emissions by biofiltration with and without percolation.

In some countries such as the U.S. and Australia, large industries are required to control ethanol emissions. In those cases biofiltration was the bioprocess most recommended and applied (ENVIRONMENTAL PROTECTION AGENCY, 1992; ENVIRONMENT AUSTRALIA, 2006). Studies show that the biofilter achieves removal efficiencies greater than 90% (LE CLOIREC and coll., 2001; LESON and coll., 1993; LESON and coll., 1992) when ethanol concentration is lower than 2.0 g m^{-3} and for an empty bed residence time (EBRT) of 60 s. But, biofilter performance deteriorates when at the same EBRT the ethanol concentration exceeds 2.0 g m^{-3} because the filter bed is irreversibly affected by the accumulation of acetic acid and other toxic metabolites (DEVINNY and coll., 1995; LESON and coll., 1995).

Ethanol can also be eliminated by biotrickling filtration, which presents in general a better performance than biofiltration when the pollutants tend to acidify the bed. CIOCI and coll. (1997) show that removal efficiency of 80 % can be obtained when the biotrickling filter (BTF) operated at an ethanol inlet concentration of 2.0 g m^{-3} and an EBRT of 50 s. In another study, COX and coll. (2001) showed that ethanol can be oxidized by mesophilic (22 °C) and thermophilic (53 °C) microorganisms. The BTF operated at an inlet concentration of 2.0 g m^{-3} and an EBRT of 57 s, provided a removal efficiency of 75% for both temperatures, demonstrating that thermophilic microorganisms could be used without any performance reduction.

2.1.5. Washing of trickling bed.

In the BTF, the biomass which is generated may cause such difficulties as clogging of the bed and distribution piping systems. Moreover, the biomass requires treatment and final disposal which represents an additional high unit cost (DELHOMÉNIE and coll., 2005b; JORIO and coll., 1999; POPOV and coll., 1999). The amount of biomass in the BTF can be controlled by a number of operations including predation of the biofilm by protozoa and fly larva (COX and coll., 1999a); the washing of the trickling bed with water solutions of sodium hydroxide, sodium hypochlorite and hydrogen peroxide (COX and coll., 1999b); the backwash of the packing (SMITH and coll., 1998); the washing of the packing with air bubbles (OKKERSE and coll., 1999a); or the reduction of the nutrient content in the solution (HOLUBAR and coll., 1999; SORIAL and coll., 1997; ZHU and coll., 1996). In the cases of washing with air bubbles and backwashing, OKKERSE and coll. (1999a) and SMITH and coll. (1998) respectively, show that these strategies did not affect the activity of microorganisms.

2.1.6. Objectives.

The present paper is an experimental study of biotrickling filter application for controlling ethanol gaseous emissions. The research has the following objectives: a) analyze the effects of high ethanol concentrations (more than 2.0 g m^{-3}) on biotrickling filter performance, b) analyze the effects of empty bed residence time on biotrickling filter performance, and c) analyze the effect of applying air bubble washing and nutrient starving for controlling biomass accumulation.

2.2. Materials and methods.

2.2.1. Biotrickling filter.

The experiments were done using two identical biotrickling filters designated as BTF1 and BTF2. Both of them were operated at ~ 24°C. The experimental setup is shown on Figure 2.1. The setup consisted of a pollutant supply unit (PSU), a biotrickling filter (BTF) and a liquid recycling unit (LRU). The shell of BTF was a Plexiglas column with an internal diameter of 0.15 m. The packed bed was 1 meter high, divided in 3 sections of 0.33 m each. The packing

was polypropylene spheres (Jaeger Tri-Packs®, Fabco Plastics, Ontario, Canada) of 0.025 m diameter, 280 m^2 m^{-3} specific surface and 90% void space.

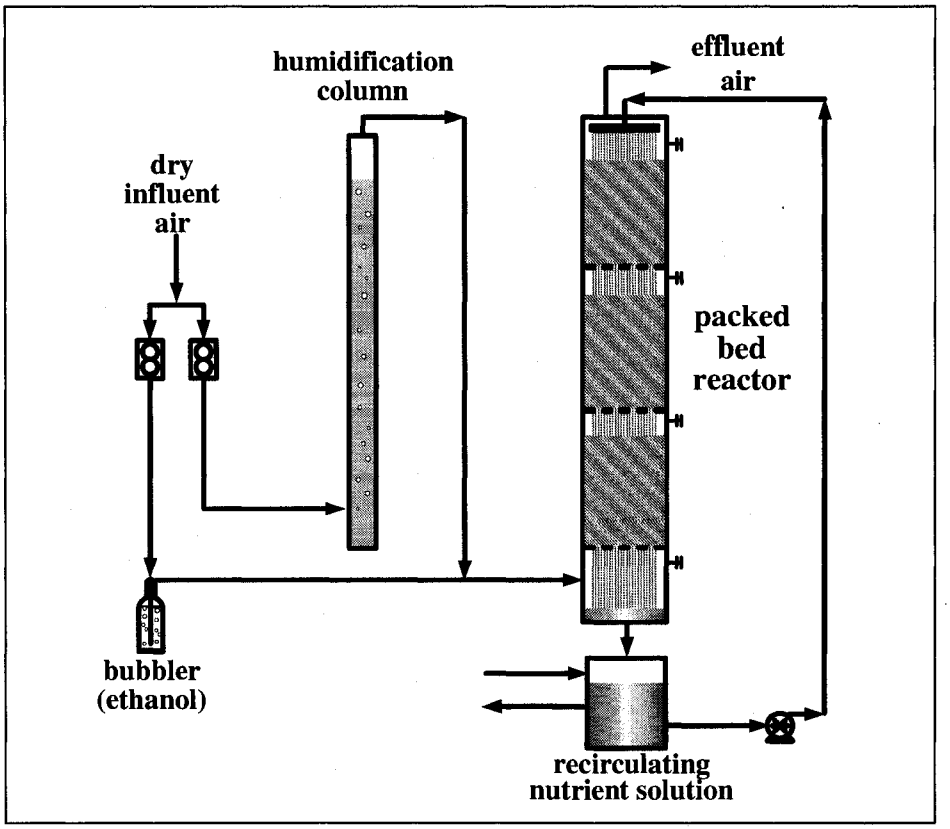

Figure 2.1. Schematic representation of biotrickling filter.

2.2.2. Inoculum.

BTF1 was inoculated with a lixiviate obtained from a biofilter which had treated ethanol vapours (DASTOUS and coll., 2005). The lixiviate was thickened and then added to the recycle tank of BTF1. The operational conditions used for starting-up the biofilm were: 1.0 m^3 h^{-1} of air flow rate, 8.0 g m^{-3} of ethanol inlet concentration, 1.0 L min^{-1} of recycled nutrient solution flow rate and 2.5 g L^{-1} of nitrogen present as urea in the nutrient solution. BTF2 was inoculated with packing obtained from BTF1, which had operated for 8 months.

2.2.3. Nutrient solution.

The nutrient solution was fed into the BTF at a rate of 1.5 L/min with a centrifugal pump (model 1212-2AA-121, SHURflo, West Sussex, UK). The nutrient solution in the storage tank (16 L) was renewed daily. The nutrient solution contained urea as the nitrogen source and other macro and micro-nutrients, which are listed in Table 2.1.

Compound	Concentration ($g\ L^{-1}$)
Nitrogen (from urea)	0.005
Phosphorus (from H_3PO_4, neutralized with NaOH)	0.005
Potassium (from K_2SO_4)	0.0016

Table 2.1. Composition of nutrient solution (made with tap water).

2.2.4. Inlet air.

Inlet air was dry and particle (solids, grease, microorganisms, etc.) free. Dry air was separated in two streams, which were controlled by means of two gas flow meters. One flow was bubbled through the water into a humidification column. The other one was passed through a bubbler containing ethanol at 95 % w/w (Commercial Alcohols Inc., Brampton, CA) which was placed in constant temperature bath at 20°C. The air flow rate of two streams was arranged to obtain the ethanol concentration specified for each experiment. The two air streams were mixed before entering at the base of BTF. Three air flow rates were tested: 0.5 $m^3\ h^{-1}$, 1.0 $m^3\ h^{-1}$ and 2.0 $m^3\ h^{-1}$ (which corresponded respectively to 130 s, 65 s and 30 s of empty bed residence time). Air and nutrient solution flowed counter currently inside the BTF.

2.2.5. Washing of biotrickling filter bed.

The procedure used to wash the bed was a sequence of three partial washings. Each partial washing was carried out in the following manner: 2/3 of BTF was filled with tap water (16 L), and then air was bubbled at a flow rate of 6 $m^3\ h^{-1}$ during 15 minutes.

2.2.6. Biomass determination.

The biomass as total solids in the bed was determined by taking samples of 150 mL of suspension formed during bed washing, as described above. Two samples were taken per washing, while air was bubbling. Samples were weighed before and after drying to constant weight in an oven at 110°C.

Total solids in the lixiviate were determined by sampling the lixiviate contained in the storage tank. The lixiviate was agitated manually and two samples of 150 mL were taken. Samples were weighed before and after drying to constant weight in an oven at 110°C. Accumulated solids in the lixiviate were calculated by subtracting the total solids of lixiviate at time zero from total solids in the lixiviate 24 hours after. Biomass in the biofilm and accumulated solids in the lixiviate are reported as dry weight.

2.2.7. Parameters for analysing the biotrickling filter performance.

BTF performance is discussed in terms of inlet load, elimination capacity and removal efficiency. These parameters are evaluated according to the following equations:

$$IL = \frac{Q \; C_i}{V}$$

$$EC = \frac{Q \; (C_i - C_o)}{V}$$

$$X = \frac{C_i - C_o}{V}$$

$$PCO_2 = \frac{Q \; (CO_{2o} - CO_{2i})}{V}$$

where IL is the inlet load (g m^{-3} h^{-1}), EC is the elimination capacity (g m^{-3} h^{-1}), X is the removal efficiency (dimensionless), PCO_2 is the carbon dioxide production rate, Q is the total air flow rate (m^3 h^{-1}), V is the packing bed volume (m^3), C_i is the ethanol inlet concentration (g m^{-3}), C_o is the ethanol outlet concentration (g m^{-3}), CO_{2i} is the carbon dioxide inlet concentration (g m^{-3}), and CO_{2o} is the carbon dioxide outlet concentration (g m^{-3}). The ethanol elimination was evaluated by comparing the ethanol concentration for the outlet gas flow with the inlet gas flow.

2.2.8. Analytical Methods.

The concentrations of ethanol were measured continuously by using a total hydrocarbon analyzer (Horiba model FIA-510, Horiba Instruments Inc., Irvine, CA, USA), with hydrogen flame ionization detection. Concentrations of carbon dioxide in air were measured continuously by using a portable gas analyzer model (Ultramat 22P, Siemens AG, Munich, GE), based on a non-disperse infrared absorption principle.

2.3. Results and discussion.

2.3.1. Effect of ethanol inlet concentration on removal efficiency.

Figure 2.2 shows removal efficiency as a function of ethanol inlet concentration. From 0.2 g m^{-3} to 3.3 g m^{-3} of ethanol inlet concentration, the removal efficiency presented the highest variations. It decreased from 100 % to 85 % for a residence time of 130 s, from 100 % to 80 % for 65 s and from 95 % to 65 % for 30 s. For inlet concentrations greater than 3.3 g m^{-3}, the removal efficiency was nearly constant for all residence times, varying between 80 and 85 % for a residence time of 130 s, 75 and 80 % for 65 s, and 60 to 65 for 30 s. This was due to the physicochemical properties of ethanol and its intermediate metabolites, all of them high water soluble and easily absorbable by the mobile liquid phase into the BTF. The absorption of different compounds in the lixiviate at high ethanol inlet concentrations maintained the removal efficiency nearly constant.

Unlike biofiltration without percolation, BTF did not appear to be adversely affected by increasing ethanol inlet concentration. Specifically, biofiltration without percolation may acidify the bed when the BTF operates at high ethanol inlet concentrations. LESON and coll. (1995) observed this problem at concentrations greater than 4.0 g m^{-3}, and LE CLOIREC and coll. (2001) reported the same problem at only 1.3 g m^{-3}. In contrast, the studies of BTF for controlling ethanol emissions do not report the problem of acidification (COX and coll., 2001; CIOCI and coll., 1997).

In our study, the monitoring of pH in the lixiviate demonstrated that this parameter was maintained between 6.0 and 6.5 for all experiments, this is explained by the tampon effect of phosphate preparation added to the nutrient solution (Table 2.1). On the other hand, the carbon dioxide (CO_2) yield coefficient was in the range of 0.05 to 0.70 g of CO_2 g^{-1} of ethanol consumed, for the highest and smallest ethanol inlet loads respectively. In comparison to the

stoichiometric yield coefficient of 1.91 g of CO_2 g^{-1} of ethanol consumed reported by AURIA and coll. (1998), the yield values obtained in the present study suggest the production of intermediate metabolites formed during ethanol biotransformation, such as acetaldehyde, acetic acid or ethyl acetate(DEVINNY and coll., 1995; TERAN PEREZ and coll., 2002). The accumulation of some of these compounds could be the cause of qualitatively changes in the lixiviate. For example, when the ethanol inlet concentration was smaller than 3.3 g m^{-3}, the CO_2 yield coefficient was at least 0.48 g of CO_2 g^{-1} of ethanol consumed for all residence times and the lixiviate was colorless and odorless. When the ethanol inlet concentration was equal or greater than 3.3 g m^{-3}, the CO_2 yield coefficient decreased with ethanol inlet concentration: as low as 0.05 g of CO_2 g^{-1} of ethanol consumed. For small CO_2 yield coefficients the lixiviate took on a green or yellow coloration and it had an odor similar to fermented fruit that one might observe with citrous fruits and pineapple.

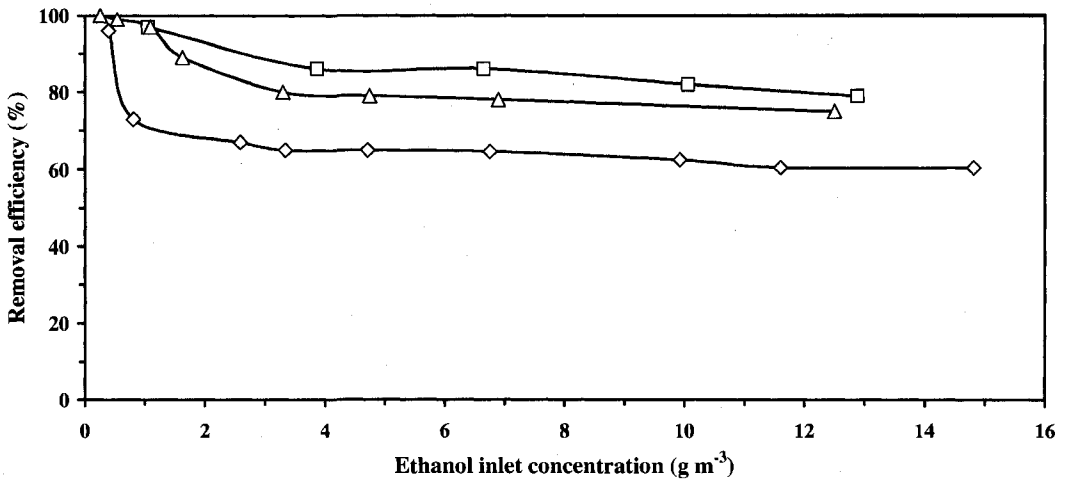

Figure 2.2. Effect of ethanol inlet concentration on removal efficiency at the following residence times: (-◊-) 30 s, (-Δ-) 65 s, (-□-) 130 s.

2.3.2. Effect of ethanol inlet load on elimination capacity.

Figure 2.3 shows the variation of elimination capacity with ethanol inlet load. In this Figure, two different behaviours of elimination capacity can be observed: a) up to 180 g m^{-3} h^{-1} of inlet load, BTF was able to completely transform ethanol, b) for values greater than 180 g m^{-3}

h^{-1} and up to 1610 g m^{-3} h^{-1}, elimination capacity was directly proportional to the ethanol inlet load. At the greatest load the BTF apparently began to be reaction limited, according to the definition used by OTTENGRAF (1986). Owing to equipment technical limitations, we did not test inlet loads greater than 1610 g m^{-3} h^{-1} for analyzing the BTF performance limited by reaction time. COX and coll. (2001) observed a similar tendency in a biotrickling filter treating ethanol: the elimination capacity varied proportionally with inlet load, in a range from 70 g m^{-3} h^{-1} to 320 g m^{-3} h^{-1}, and the reaction limitation region was also absent.

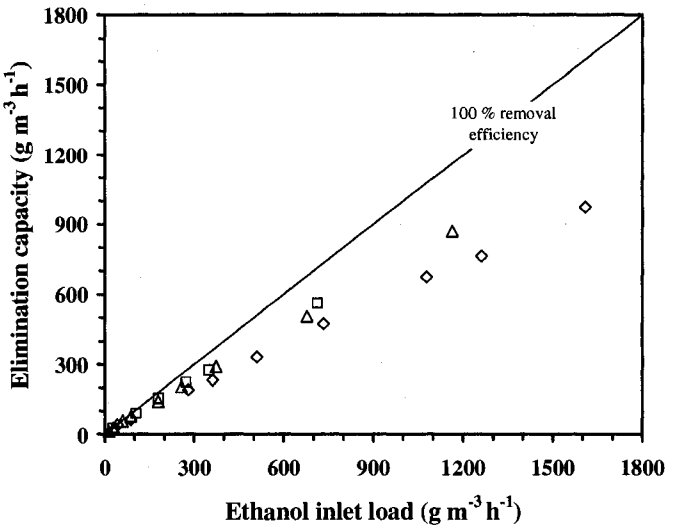

Figure 2.3. Effect of ethanol inlet load on elimination capacity at the following residence times: (◊) 30 s, (Δ) 65 s, (□) 130 s.

In this study, the maximal elimination capacity was 970 g m^{-3} h^{-1} and it was obtained at the greatest inlet load tested, which was 1610 g m^{-3} h^{-1}. To our knowledge no such high inlet loads have been evaluated before. The different studies of ethanol treatment by biofiltration with or without percolation report inlet loads and elimination capacities smaller than those tested in several of our experiments. The maximum ethanol inlet loads for biofiltration without percolation were reported by TERAN PEREZ and coll. (2002), they operated at an ethanol inlet load of 300 g m^{-3} h^{-1} and obtained a corresponding elimination capacity of 255 g m^{-3} h^{-1}. In the case of ethanol treatment by biotrickling filter, COX and coll. (2001) working with a

maximum inlet load of 320 g m^{-3} h^{-1} obtained an elimination capacity of 220 g m^{-3} h^{-1}. The removal efficiencies in these two studies were 85 % and 69 %, respectively. For equivalent operating conditions, the present study reports elimination capacities and removal efficiencies that are similar to those cited above, and occasionally better. For example, at an inlet load of 375 g m^{-3} h^{-1} and a residence time of 65 s, the elimination capacity was 290 g m^{-3} h^{-1}.

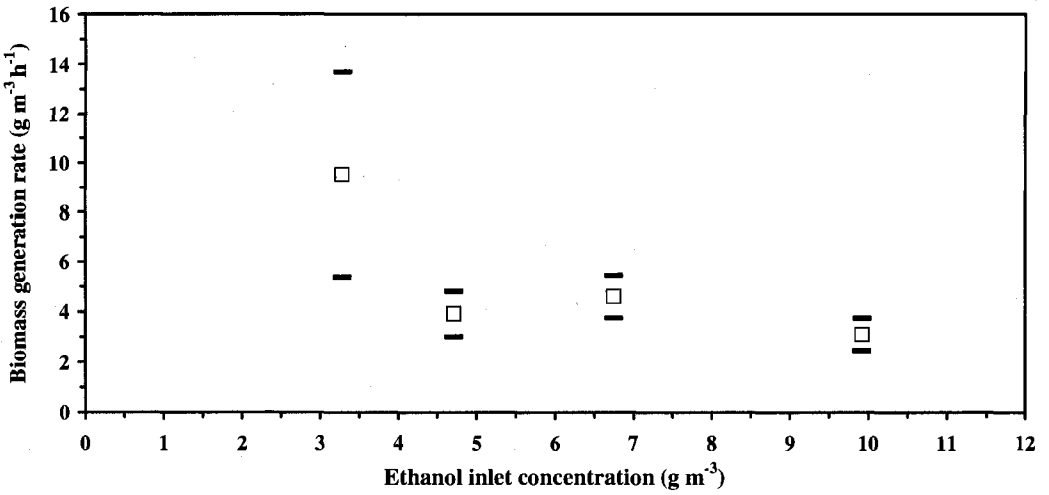

Figure 2.4. Effect of ethanol inlet concentration on biomass generation rate at an EBRT of 30 s. Average values (□) ± standard deviation (—).

2.3.3. Biomass generation rate in the biofilm.

Figure 2.4 presents the effect of ethanol inlet concentration on biomass generation rate in the biofilm for an air residence time of 30 s. Biomass generation rate decreased with increasing ethanol inlet concentration as follows: (1) at an ethanol inlet concentration of 3.3 g m^{-3} was obtained the greatest biomass generation rate of 9.5 g m^{-3} h^{-1}, (2) then the biomass generation rate decreased to 3.8 g m^{-3} h^{-1} when the ethanol inlet concentration increased to 4.7 g m^{-3}, (3) in the range of ethanol concentration of 4.7 g m^{-3} to 9.9 g m^{-3}, the biomass generation rate decreased slightly and presented its minimal value of 2.8 g m^{-3} h^{-1}. The greatest biomass generation rate in this paper was smaller than those obtained by COX and coll. (2001): 21.3 g m^{-3} h^{-1} at 22 °C and 16.6 g m^{-3} h^{-1} at 53 °C. For both temperatures, they operated the BTF at an ethanol inlet concentration of 2.0 g m^{-3} and obtained the same removal efficiency of 67 %. In our study, for a higher ethanol inlet concentration (3.3 g m^{-3}) and with a lower biomass

generation rate (9.5 g m^{-3} h^{-1}) we obtained a removal efficiency of 80 %. We think that these results are according to the theory exposed by ALONSO and coll. (1997). They supposed that the amount of biomass does not determine the elimination of pollutant; it is determined by the characteristics of biofilm: thickness, specific surface and biodegradability of the pollutant.

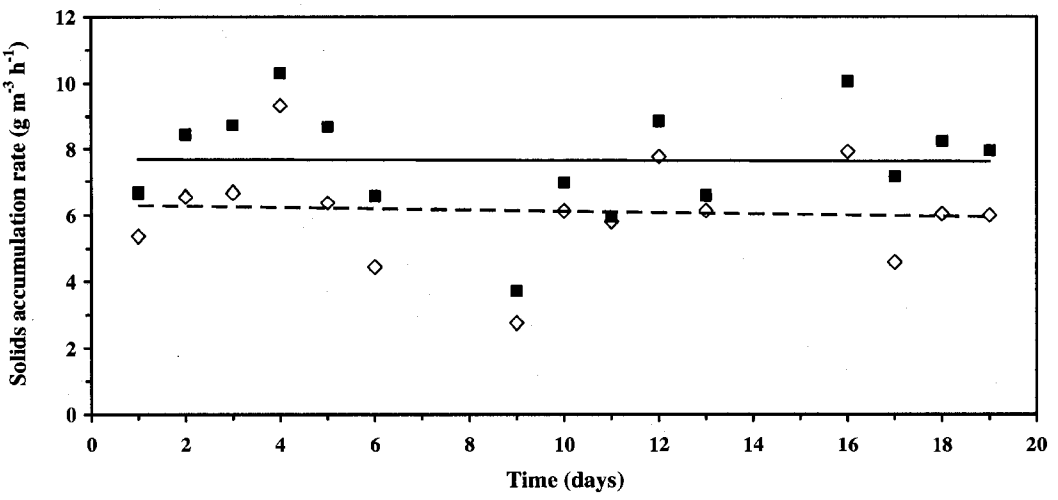

Figure 2.5. Evolution of solids accumulation rate during three weeks at an EBRT of 30 s and two ethanol inlet concentrations: (■) 4.7 g m^{-3} and (◊) 9.9 g m^{-3}. The average values are indicated as follows: (—) 4.7 g m^{-3} and (- - -) 9.9 g m^{-3}.

2.3.4. Accumulated solids in the lixiviate.

Total biomass produced in BTF can be divided into biomass which remains in the biofilm and suspended biomass in the lixiviate. In our study, we consider that accumulated solids in the lixiviate are the result of suspended biomass generation. Accumulated solids were determined in two experiments: at ethanol inlet concentrations of 4.7 g m^{-3} and 9.9 g m^{-3}. Both were done at a residence time of 30 s. Figure 2.5 shows the behaviour of solids accumulation rate in the lixiviate for these ethanol concentrations during three weeks of experimentation. The solids accumulation rate was approximately 8.0 g m^{-3} h^{-1} (± 1.8 g m^{-3} h^{-1}) at the ethanol inlet concentration of 4.7 g m^{-3} and 6.5 g m^{-3} h^{-1} (±1.6 g m^{-3} h^{-1}) at an ethanol inlet concentration of 9.9 g m^{-3}. These values show that solids generation rates decreased with increasing ethanol inlet concentration. We supposed that ethanol inhibits all microorganisms in biofilm and

lixiviate, but specially the nonspecific, by causing that cellular density of nonspecific microorganisms decreases faster than that one of ethanol degraders when ethanol concentration increases. The microbial activity in the lixiviate is important, for example COX and coll. (2001) observed that cellular density of ethanol specific microorganisms in the biofilm ($3.7x10^8$ number of colonies g^{-1} of total carbon) was similar to cellular density in the lixiviate ($1.7x10^8$ number of colonies g^{-1} of total carbon) at an ethanol inlet concentration of 2 g m^{-3}. The activity of suspended biomass was also analyzed by COX and coll. (2000b), they observed that suspended biomass was able to transform up to 21 % of the total amount of toluene degraded in their BTF. In our case, the oxidation of ethanol to CO_2 in the lixiviate is affected by high ethanol concentrations by causing the physical changes described above.

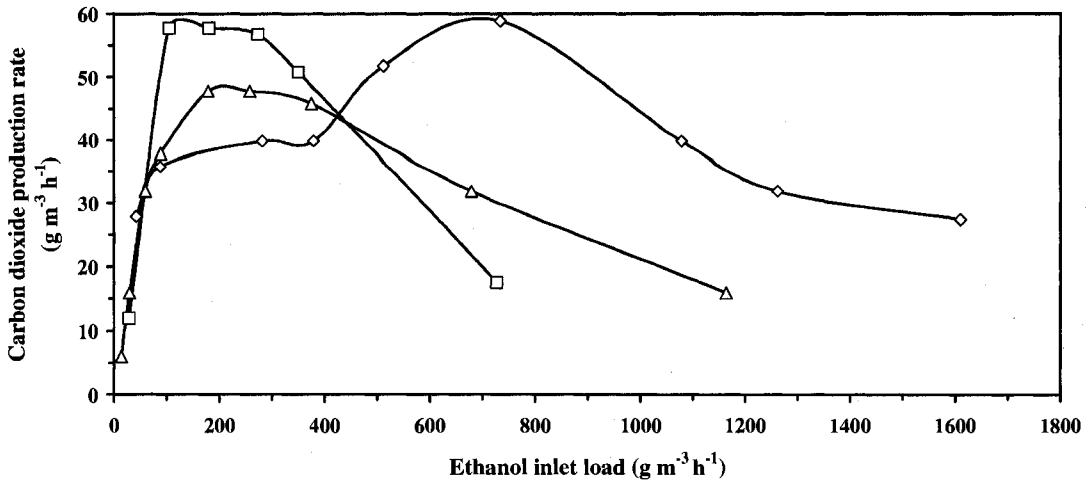

Figure 2.6. Effect of ethanol inlet load on carbon dioxide production rate at three EBRTs: (◊) 30 s, (Δ) 65 s, (□) 130 s.

2.3.5. Effect of ethanol inlet load on carbon dioxide production rate.

Figure 2.6 shows the variation of carbon dioxide (CO_2) production rate with ethanol inlet load. The CO_2 production rate varied similarly for three residence times. Initially, it increased with ethanol inlet load and reached a maximum, which was 58 g m^{-3} h^{-1} for residence times of 130 s and 30 s, and it was 48 g m^{-3} h^{-1} for 65 s. Afterwards, it decreased with increasing ethanol

inlet load. In our study, as ethanol inlet load increased, biomass and CO_2 generation decreased, but removal efficiency was nearly constant.

In the BTF, the CO_2 is produced by a consortium of microorganisms formed by: ethanol specific microorganisms, which are able to degrade ethanol, and by nonspecific microorganisms. As ethanol inlet load increases, the microorganisms are inhibited in a different degree, so the production rates of biomass and CO_2 decrease.

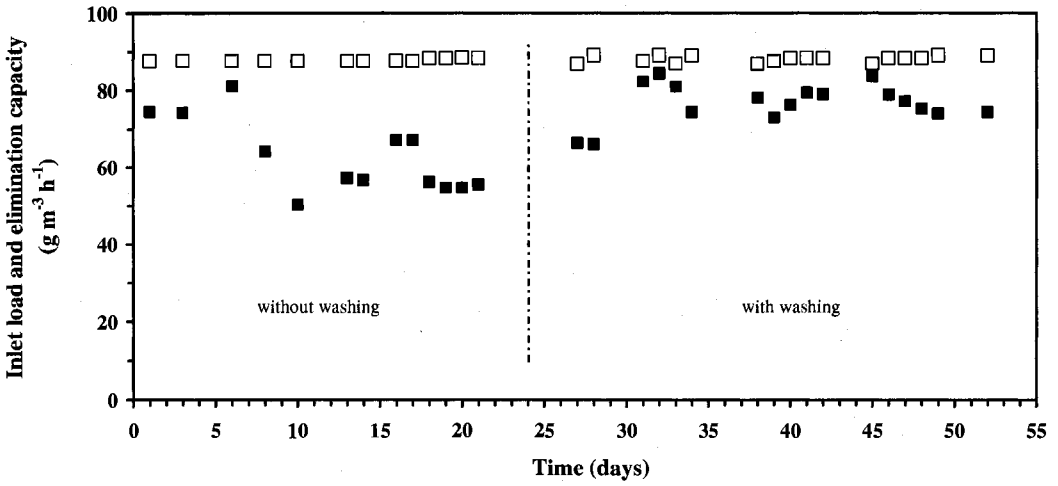

Figure 2.7. BTF performance at an EBRT of 65 s and an inlet load of 90 g m^{-3} h^{-1}. On the left are plotted the results of BTF without washing; on the right are the results of BTF with a weekly washing. (□) IL, (■) EC.

2.3.6. Effect of periodic washing on biotrickling filter performance.

Figure 2.7 presents the influence of periodic washing on BTF performance operating at an air flow rate of 1.0 m^3 h^{-1} and at an ethanol inlet load of 90 g m^{-3} h^{-1}. Figure 2.7 shows the results of two experiments, first without washing the bed and then with washing it with water and air bubbles. The benefits of using air bubbles to wash the bed, in comparison with backwashing, are shorter backwashing cycles and lower water and energy consumption. In the first experiment, the BTF was operated for three weeks without washing the bed. For this case, EC oscillated between 81 g m^{-3} h^{-1} and 50 g m^{-3} h^{-1}, with an average value of 63 g m^{-3} h^{-1} and a standard deviation of ± 9 g m^{-3} h^{-1}. In the second experiment, the BTF was operated for four

weeks with weekly washing. In this experiment, the EC oscillations were smaller with an average value of 78 g m^{-3} h^{-1} and a standard deviation of ± 5 g m^{-3} h^{-1}. One reason of the improvement in BTF performance is that the washing removes some of the inactive and the nonspecific biomass accumulated in the bed. After washing with air bubbles, the cells that remain attached to the packing conserve their biological activity. They are able to easily regenerate new biofilm which is active and pollutant specific, as was noted by SMITH (1999) and OKKERSE and coll. (1999a). Another reason of the improvement is the effect of washing the bed, it contributes to maintaining a high specific surface covered by a thin active biofilm (ALONSO and coll., 1997).

Another strategy for biomass control was also tested when the BTF was operated at a residence time of 30 seconds and an ethanol inlet concentration of 9.9 g m^{-3} during 6 weeks (these results are not shown). Instead of a weekly washing, the BTF was washed each 14th day. The nutrient solution was renewed daily, except each 7th day. This day the nutrient solution recirculated 48 hours in the BTF instead of 24 hours. With this strategy, we obtained removal efficiency similar to that obtained with the weekly washing strategy. The advantage of the last one is that it requires a lower washing frequency, which reduces the maintenance and the operating costs of the BTF.

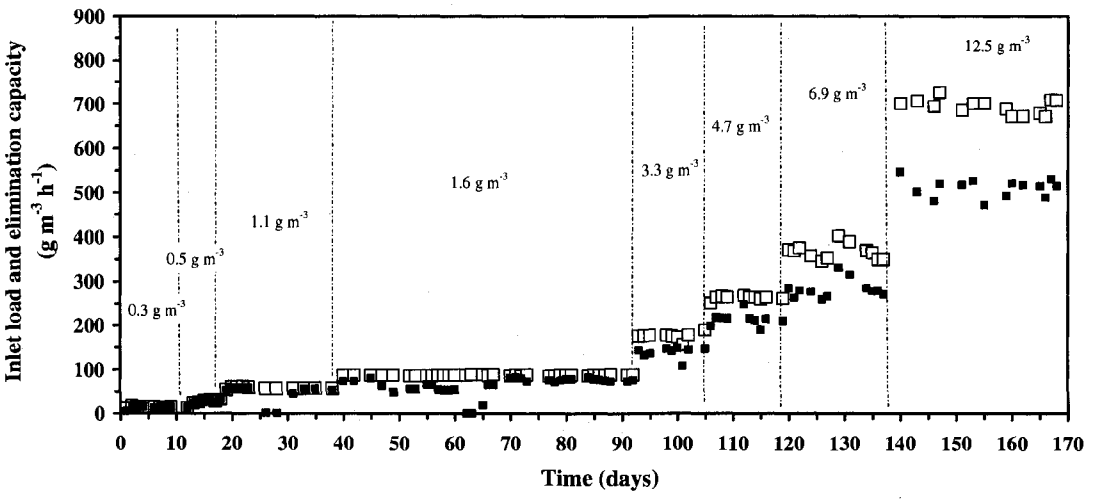

Figure 2.8. Performance of BTF at an EBRT of 65 s and eight different ethanol inlet concentrations. (□) IL, (■) EC.

2.3.7. Adaptability and stability of biotrickling filter.

Figure 2.8 presents the performance of the BTF over 170 days at a residence time of 65 s and different inlet loads. Figure 2.8 shows that the BTF presented a quick response and good adaptation to disturbances of ethanol inlet concentration or air flow rate, which were observed as inlet load disturbances. The BTF maintained its removal efficiency with only a small range of variation when these disturbances occurred. For example, the BTF responded quickly by reaching stability two or three days after the ethanol inlet concentration was changed for a different inlet load. The BTF was very stable for all experiments. One reason was the beneficial effect of bed washing, which was applied systematically to all experiments.

2.3.8. Reproducibility.

Most of the experiments were done twice to verify the reproducibility of the removal efficiencies of the BTF. The reproducibility was verified as follows: in one BTF operated at the same conditions but at a later date, in both BTFs operated simultaneously at the same conditions, and in both BTFs operated at different times under the same conditions. Figure 2.9 shows the removal efficiency of these experiments, which were done in a range of ethanol inlet concentration from 1.1 to 6.9 g m^{-3} h. The BTF had very good reproducibility for all cases.

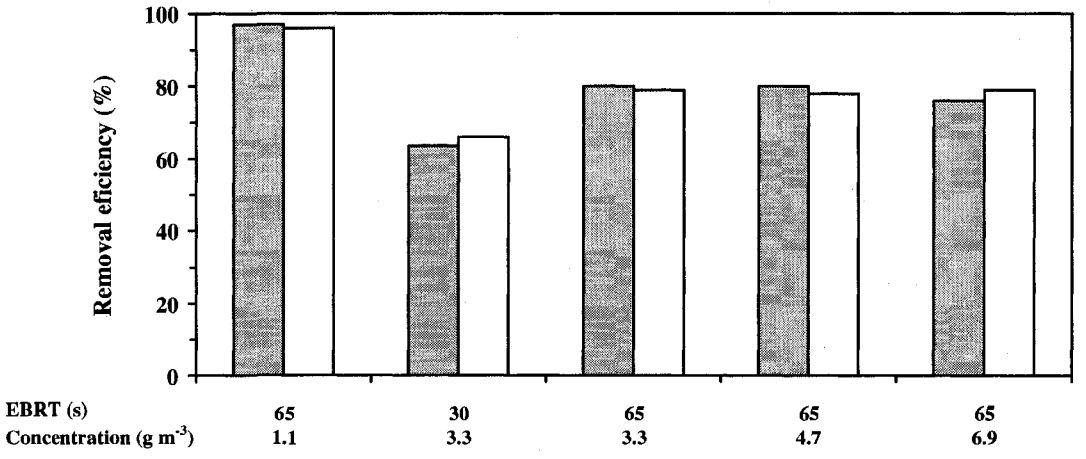

Figure 2.9. Removal efficiency of five experiments, duplicated to check the reproducibility of BTF performance. The residence time and the ethanol inlet concentration are given below the histogram.

2.4. Conclusion.

This paper presents the study of biotrickling filtration of air polluted with ethanol vapours. The effects of ethanol inlet concentration and air residence time on biotrickling filter performance, as indicated by elimination capacity and removal efficiency, were analyzed. In the range of ethanol inlet concentrations of 0.2 to 15.0 g m^{-3} the BTF provided a very stable system for controlling ethanol emissions. Removal efficiency varied from 60 % to 80 % in the range of residence time of 30 s to 130 s and for an inlet concentration of at least 15.0 g/m^{-3}. In this study the BTF was successfully operated at ethanol inlet loads greater than those reported in literature for biofiltration with and without percolation. The BTF performed well for high ethanol loads as compared to biofiltration without percolation. The maximal inlet load tested was 1610 g m^{-3} h^{-1} which provided a corresponding elimination capacity of 970 g m^{-3} h^{-1}, higher than results reported in literature. Biomass generation rate in the biofilm and in the lixiviate decreased with increasing ethanol inlet concentration, but removal efficiency was constant. Two strategies for controlling biomass accumulation were tested. One consisted on washing the BTF weekly with water and air bubbles, and the other one was a combination of washing the BTF each two weeks with nutrient starvation. Biomass accumulation and BTF performance were satisfactory controlled with these two different strategies. The effect of washing was analyzed and we observed that the BTF adapted and stabilized quickly to variations in inlet load when it was washed. Finally, the BTF presented high reproducibility, which is convenient for scaling up and validating results.

Acknowledgements

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SECTION II. EFFETS DES CONDITIONS D'OPERATION SUR LE BIOFILM ET LA PERFORMANCE DES BIOFILTRES AVEC ET SANS PERCOLATION.

Chapitre 3. Effet de l'azote, le matériel du garnissage et la charge de méthanol sur le biofilm et la performance des biofiltres garnis avec matériels inertes.

Article « *Treatment of methanol vapours in biofilters packed with inert materials* », qui est en presse dans le « Journal of Chemical Technology and Biotechnology », DOI : 10.1002/jctb.1944.

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Résumé

Cette étude porte sur la biofiltration du méthanol dans des biofiltres garnis avec des matériaux inertes : argile et polypropylène. L'étude analyse les effets des conditions d'opération sur la population microbienne, spécifiquement la dynamique des microorganismes spécifiques (méthylotrophes) et non spécifiques au méthanol. D'autres facteurs contribuant à l'activité microbienne ont été étudiés, tels l'accumulation de biomasse et le contenu d'eau dans le lit garni. Afin de caractériser adéquatement le lit filtrant du biofiltre, des méthodes expérimentales ont été développées, telles celle relative au calcul de la biomasse présente dans le lit filtrant.

Le biofiltre garni avec l'argile poreux a donné des taux de conversion avoisinant 95 %, par contre le polypropylène (garnissage non poreux) a présenté des taux de conversion autour de 35 %. Pour les deux garnissages, la performance des biofiltres a augmenté avec la concentration d'azote présent dans la solution nutritive. Cependant, pour la concentration maximale d'azote utilisée, soit 2.4 gN L^{-1}, la production de biomasse et la densité cellulaire des méthylotrophes ont présenté de l'inhibition. Le contenu d'eau dans le lit filtrant a été fonction du contenu de biomasse présent dans le matériel non poreux. La capacité d'élimination a été associée à la densité cellulaire des microorganismes méthylotrophes. La charge critique de méthanol a été de 80 g m^{-3} h^{-1} et a pu être corrélée avec la densité cellulaire des méthylotrophes la plus élevée.

Les résultats démontrent que la biofiltration peut être appliquée pour contrôler des émissions de méthanol et peut permettre d'obtenir des taux de conversion élevés. L'étude a permis d'éclaircir la relation entre les microorganismes spécifiques et la performance du biofiltre.

3. Treatment of methanol vapours in biofilters packed with inert materials.

Abstract

Methanol is a major pollutant emitted in Canada. Methanol is toxic to humans and it is associated with environmental problems such as smog generation. Biofiltration is a treatment method of considerable interest for controlling methanol emissions, because of its characteristics: no production of hazardous wastes, low energy consumption and low operating costs. The present study analyzed the effects of porous and non-porous packing materials, the nitrogen concentration in nutrient solution and the methanol inlet load on biofilter performance and biofilm characteristics.

The biofilter packed with porous material presented a removal efficiency up to 95%, which was higher than the 35% removal efficiency with the non-porous material. IL influenced the biomass and carbon dioxide production rates. The critical inlet load (IL_{crit}) occurred at 80 g m^{-3} h^{-1}. The cellular densities of methylotrophs and non-methylotrophs were affected by all operating variables examined.

Results show that biofiltration can be applied for controlling methanol emissions with high removal efficiency. The cellular density of methylotrophs is correlated with the performance of the biofilter.

3.1. Introduction

Methanol is a volatile organic compound (VOC) which is highly soluble in water. It has a wide variety of applications; for example, it is used for producing formaldehyde, acetic acid and methyl methacrylate (OPPT, 2007). In 2005, industrial activities released 71.6 and 17.7 ktons of methanol to the atmosphere in the United States and Canada respectively. In both countries, the pulp and paper industry and especially kraft mills contributed at least 65 % of these emissions (TRI-EXPLORER, 2007; NPRI, 2007).

Methanol is a toxic compound whose emissions are regulated in several countries, including Canada and the United States (COMMUNICATION CANADA, 2003; EPA, 1990). The exposure to methanol vapours produces several effects on human health; including headaches,

sleep disorders, gastrointestinal problems and optic nerve damage (OPPT, 2007). Methanol can also contribute to the formation of photochemical smog when it enters in contact with some radicals generated by other more reactive VOCs (MONOD and coll., 1998).

VOC emissions have been successfully controlled by applying biofiltration with or without percolation (JORIO and coll., 1999). This bioprocess is economically attractive for treating effluents with VOC inlet loads resulting from a combination of concentrations smaller than 10.0 g m^{-3} and air flow rates up to 100000 m^3 h^{-1} (COOPER and coll., 2002). In this bioprocess, the polluted gas passes through a packing material covered by a biofilm containing microorganisms which transform the VOCs into carbon dioxide, water, biomass and salts (DELHOMÉNIE and coll., 2005b).

Since methanol is high biodegradable and water soluble, emissions are successfully controlled by biofiltration. However, some studies on methanol biofiltration report that the critical inlet load (IL_{crit}) may be in the range from 100 to 280 g m^{-3} h^{-1} (KRAILAS and coll., 2000b; PRADO and coll., 2005). Methanol vapours have been also treated by biotrickling filtration. This biotechnology had shown higher performance than biofiltration. At similar operating conditions of IL from 20 to 250 g m^{-3} h^{-1} and Carbon:Nitrogen mass ratios from 3:1 to 800:1 of C:N, a biotrickling filter (BTF) presented a nearly stable removal efficiency of 80% while that of a biofilter decreased from 90 to 40%. In this comparative study, the bioconversion of methanol to carbon dioxide (CO_2) and biomass was smaller in the BTF than in the biofilter (AVALOS RAMIREZ and coll., 2007a). In a BTF, the nutrient solution apparently reduces the inhibition caused by methanol on microorganisms and microbial activity has been observed at methanol inlet concentrations as high as 20 g m^{-3}. At these concentrations, an important percent of methanol (up to 95%) was removed by absorption into the nutrient solution (AVALOS RAMIREZ and coll., 2005; AVALOS RAMIREZ and coll., 2007c).

The performance of a biofilter is affected by different operating parameters, such as the nitrogen availability, which can be controlled by means of periodic bed irrigation (DELHOMÉNIE and coll., 2001). The effect of nitrogen on biofilter performance has been widely studied (DELHOMÉNIE and coll., 2001; GRIBBINS and coll., 1998; JORIO and coll., 2000; MORGENROTH and coll., 1996; SONG and coll., 2003; YANG and coll., 2002). Literature results show that the biofilter has a maximal elimination capacity (EC_{max}) at a specific nitrogen concentration and that the form of nitrogen in nutrient solution affects the

biofilter performance. For example, in a biofilter treating methanol, the EC_{max} was 100 g m^{-3} h^{-1} with ammonium chloride as the source of nitrogen at a concentration of 14.5 gN L^{-1}. The same biofilter presented an EC_{max} of 60 g m^{-3} h^{-1} when sodium nitrate was added at a concentration of 4.9 gN L^{-1} (YANG and coll., 2002). The operating conditions influence the effect of nitrogen. For example, in biofilters treating toluene different nitrogen concentrations and diameters of packing material, from 5 to 20 mm, were tested. Urea was used as nitrogen source. At nitrogen concentrations around 4 gN L^{-1} the EC_{max} for all diameters occurred in a range from 30 to 170 g m^{-3} h^{-1} (DELHOMÉNIE and coll., 2002). In another study treating toluene in a biofilter packed with perlite and compost, EC was 25 g m^{-3} h^{-1} when nitrogen was not added. EC increased up to 100 g m^{-3} h^{-1} when ammonium nitrate was added at a nitrogen concentration of 4.4 gN L^{-1} (GRIBBINS and coll., 1998).

In the present study of methanol biofiltration, the objectives are to analyze the effects of the nature of packing (porous or non-porous), the nitrogen concentration in nutrient solution and the methanol inlet load on biofilter performance and biofilm characteristics.

3.2. Materials and methods

The research was divided into two experimental phases. The first phase studied the influence on methanol biofiltration of a) nitrogen concentration in nutrient solution and b) packing bed material. In the second phase, the influence of methanol inlet load (IL), methanol inlet concentration and EBRT on biofilter performance was analyzed. The packing material and the nitrogen concentration that had provided the highest removal efficiencies in the first phase were selected for operating the biofilters in the second phase.

3.2.1. Biofilters

The biofilters were constructed from Plexiglas cylinders with an internal diameter of 0.15 m and a total bed height of 1 m divided into three sections of 0.33 m (Figure 3.1). For the first phase, two different inert materials were used to pack two biofilters. One biofilter was packed with a porous packing of ceramic spheres (Hydroton®, Ökotau GmbH, Germany) of 0.012 m diameter, 310 m^2 m^{-3} specific surface and 40 % void space, another with a non-porous packing of polypropylene spheres (Jaeger Tri-Packs®, Fabco Plastics, Toronto, Canada) of 0.025 m

diameter, 280 m^2 m^{-3} specific surface and 90% void space. For the second phase, four identical biofilters were packed with the material selected in the first phase.

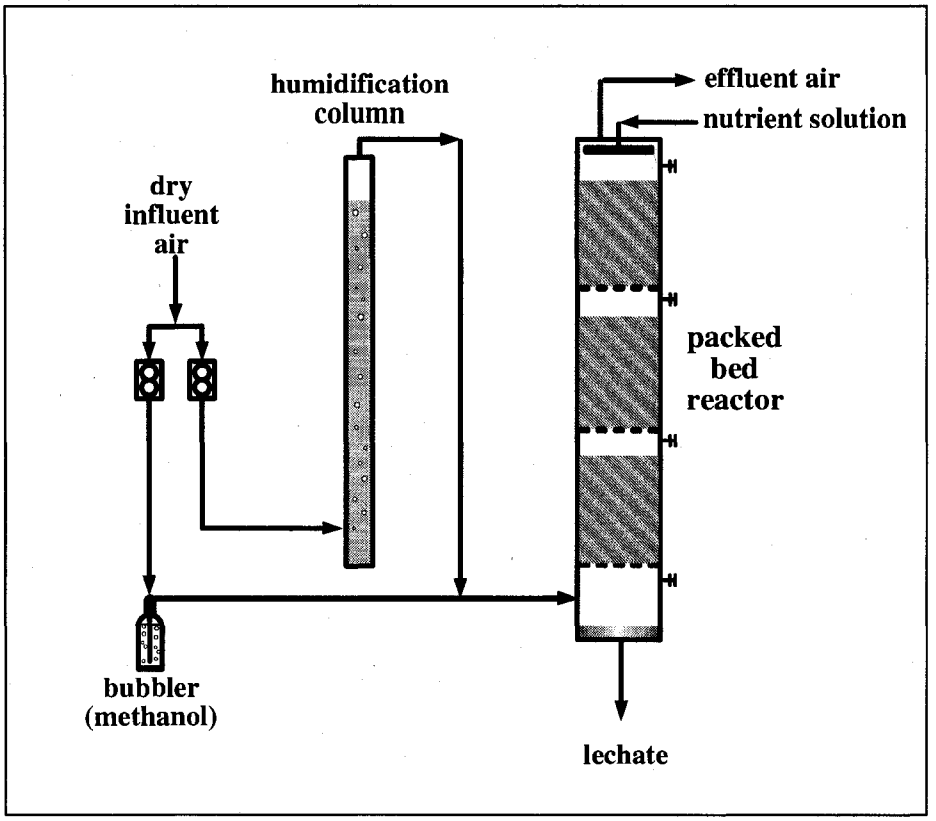

Figure 3.1. Schematic representation of experimental setup.

Inlet air, dry and particle free, was separated into two streams; one was bubbled in a humidification column, the other one was passed through a bubbler containing liquid methanol at 20°C in order to evaporate the methanol (98 % w/w, Anachemia, Canada). The two air streams were combined before entering the base of the biofilter. The biofilters were irrigated once per day with 2.7 L of nutrient solution using a centrifugal pump at a flow rate of 2.0 L min^{-1}. The nutrient solution had a constant nitrogen-phosphorus-potassium mass ratio of 3:3:1 throughout the experiments. The nutrients were urea, phosphoric acid neutralized with sodium hydroxide and potassium sulphate. No other nutrient was added.

The biofilter packed with non-porous material was inoculated with a lixiviate from a biotrickling filter which had been treating methanol vapors (AVALOS RAMIREZ and coll., 2005). When methanol and carbon dioxide (CO_2) concentrations of outlet gas of biofilter packed with non-porous packing were stabilized (during at least one week), the lixiviate of biofilter was used to start up the biofilter packed with porous packing.

3.2.2. Operating conditions

For the first phase of the study, the biofilters packed with porous and non-porous material were operated at four nitrogen concentrations (0.03, 0.1, 0.6 and 2.4 gN L^{-1}). The inlet air temperature was 24°C, the empty bed residence time (EBRT) was 65 s and the methanol inlet concentration was 1.5 g m^{-3}, for a constant IL of 80 g m^{-3} h^{-1}.

For the second phase, different ILs were tested. When EBRT was kept constant at 65 s, biofilters operated at four methanol inlet concentrations of 0.7, 1.5, 2.7 and 4.0 g m^{-3}, which corresponded to ILs of 40, 80, 150 and 220 g m^{-3} h^{-1} respectively. When methanol inlet concentration was kept constant at 1.5 g m^{-3}, biofilters operated at four EBRTs of 20, 35, 65 and 130 s, which corresponded to ILs of 235, 155, 80 and 40 respectively.

3.2.3. Biofilter performance

Biofilter performance was analyzed in terms of inlet load (IL), elimination capacity (EC), removal efficiency (X) and carbon dioxide production rate (PCO_2) defined as follows:

$$IL = \frac{Q\ C_i}{V}$$

$$EC = \frac{Q\ (C_i - C_o)}{V}$$

$$X = \frac{C_i - C_o}{C_i}$$

$$PCO_2 = \frac{Q\ (CO_{2o} - CO_{2i})}{V}$$

where IL, EC and PCO_2 have units of g m^{-3} h^{-1} and X is dimensionless. Q is the total air flow rate (m^3 h^{-1}), V is the empty bed volume (m^3), C is the methanol concentration (g of methanol m^{-3}), CO_2 is the carbon dioxide concentration (g of CO_2 m^{-3}), subscript *i* indicates inlet and subscript *o* indicates outlet. The concentrations of methanol and carbon dioxide in air were measured with a total hydrocarbon analyzer Horiba FIA-510 (Horiba, USA) and a portable CO_2 analyzer Ultramat 22P (Siemens AG, Germany), respectively. The pressure drop in the packing bed (ΔP, cm H_2O m^{-1} of packing bed) was measured with a differential manometer (Air Flow Developments, Canada).

3.2.4. Biomass and liquid content in the packing bed

Samples of biofilm and packing material were taken from each section one hour after adding the nutrient solution. Then the total volatile solids in the biofilm and packing material were determined using the method reported by SLUITER and coll. (2005). The liquid content in the biofilm was calculated by subtracting the mass of volatile solids from the mass of wet biomass. The liquid content per volume of packing bed expressed as kg H_2O m^{-3} of packing bed, was calculated by subtracting the mass of the sample of packing material before and after drying in an oven at 105 °C, and dividing by the empty volume of the sample. The empty bed volume of the sample was measured by means of the increase of the level of water contained in a graduate cylinder at 20°C.

The method developed for calculating the accumulation of wet biomass was derived from the method developed by COX and coll. (2001). The accumulation of wet biomass was calculated by periodically measuring the total mass of biofilter. The difference between two measures was the accumulation of wet biomass for the corresponding period of time. The accumulation of dry biomass was calculated by multiplying the wet biomass accumulation by the weighted arithmetic average of dry solids. The procedure for calculating the weighted arithmetic average of the content of dry volatile solids in biofilm is explained below in the section "carbon balances".

The dry biomass production rate was calculated by following the dry biomass accumulation during 14 days. The dry biomass accumulation was divided by the 14-day period expressed in hours (336 h) and by the empty bed volume (0.0184 m^{-3}).

3.2.5. Characterization of lixiviate

The lixiviate was recovered in a graduate cylinder each day after bed irrigation. The following parameters were determined: a) the volume of lixiviate and the liquid retained by the packing bed, which was calculated by subtracting the volume of lixiviate from the 2.7 L of nutrient solution added, b) the suspended biomass, which was calculated by differentiating the total solids of nutrient solution from those of the lixiviate (Standard Method 2540 B) (APHA, 1999), and c) the methanol absorbed in the lixiviate by means of a gas chromatograph coupled with a mass spectrometer (GC/MS, HP G1800A, Hewlett Packard, USA).

3.2.6. Microbial counting

The microbial counting was generally performed with samples of biofilm ten days after starting each experiment; because at that time, the biofilter had stabilized and the biofilm developed could easily detach from the packing surface. Occasionally, for the study of nitrogen effect, a second and a third microbial counting was performed one and/or two weeks later if the performance parameters of biofilter (EC and PCO_2) had not stabilized. For each section of biofilter, three samples of 0.15 g of biofilm were taken from the surface of packing material with a spatula as follows: 0.15 g of biofilm from the top, 0.15 g from the middle and 0.15 g from the bottom. The three samples of each section were mixed in sterile media and the suspension was homogenized by shaking. Each combined sample of 0.45 g of biofilm per section, was used for determining the microbial counting under methylotrophic and non-methylotrophic conditions.

The nomenclature of microorganisms hereinafter used is based on literature about methylotrophic microorganisms (ANTHONY, 1982; GREEN, 1992; SMITH and coll., 1977), where methylotrophs or methanol utilizers are defined as those microorganisms that use C_1 compounds as substrate. According to this definition, in the present paper the term non-methylotrophs or non-methanol utilizers is used for indicating those microorganisms that grow in multicarbon substrates and are not able to consume C_1 compounds.

The Most Probable Number method for three-essays per dilution (OBLINGER and coll., 1975) was adapted in 96-well plates (Corning Inc., NY). The culture media for the non-methylotrophic growth was Büshnell Haas broth (BHb, Difco) enriched with (per litre) 20 g NaCl, 2.5 g tryptone, 1.25 g yeast extract, and 0.5 g glucose. For the methylotrophic growth,

BHb (Difco) added with 1% V/V of sterilized methanol as the sole carbon source was used. The plates were incubated for 72h at 30°C and the microbial growth was detected by UV-visible spectrophotometry at 600 nm (Bio-Tek Instruments Inc, VT).

3.2.7. Carbon balances

A simple carbon balance was used in order to estimate the outlet carbon rate ($C_{out\text{-}calc}$) by means of Eq. 3-1.

$$C_{out\text{-}calc} = C_{in\text{-}exp} - C_{acc\text{-}exp} \qquad (3\text{-}1)$$

where $C_{in\text{-}exp}$ and $C_{acc\text{-}exp}$ are the inlet and accumulation carbon rates obtained by means of experimental measures. All carbon rates have units of g m^{-3} h^{-1}. They represent the total mass of carbon that entered in ($C_{in\text{-}exp}$), left from ($C_{out\text{-}calc}$, $C_{out\text{-}exp}$) and accumulated ($C_{acc\text{-}exp}$) in the empty bed volume during a period of 14 days.

The compounds considered for $C_{in\text{-}exp}$ were the methanol of the inlet air and the urea of the nutrient solution. In order to determine the $C_{acc\text{-}exp}$ a new methodology was developed. The total mass of three packed sections of biofilter was measured three times per week. At the same time, three samples of biofilm from each section were taken for determining the average solids content in each section: one from the top, one from the middle and one from the bottom of each section. A weighted arithmetic average of dry solids accumulation rate for the whole biofilter was calculated. With the assumption that dry solids accumulated in the packing bed had the empirical formula $CH_{1.8}O_{0.5}N_{0.2}$, reported by BAILEY and coll. (1986) as an average composition for bacterial biomass, the dry solids accumulation rate was converted to carbon accumulation rate.

The calculated $C_{out\text{-}calc}$ was compared with the experimental $C_{out\text{-}exp}$ in order to determine the error of the calculated value. The $C_{out\text{-}exp}$ was obtained with: 1) the carbon dioxide produced by the microorganisms (PCO_2) and the unconverted methanol present in the outlet air stream, 2) the absorbed methanol (measured with GC/MS) and the suspended biomass present in the lixiviate.

3.3. Results and discussion

3.3.1. Effects of nitrogen concentration and packing bed material

3.3.1.a) Biofilter performance

The experiments described in this section were carried out at a fixed IL of 80 g m^{-3} h^{-1}. Figure 3.2 shows the effect of the nitrogen concentration in nutrient solution on EC and carbon dioxide production rate (PCO_2) for the biofilters packed with porous and non-porous packing materials. The values of EC and PCO_2 are the average of daily data during at least two weeks of stable operation in terms of outlet concentrations of methanol and CO_2. For the biofilter with porous packing, the EC increased from 30 g m^{-3} h^{-1} (at a nitrogen concentration of 0.03 gN L^{-1}) to 75 g m^{-3} h^{-1} (at 2.4 gN L^{-1}). In contrast, in the biofilter of non-porous packing the EC varied from 20 to 30 g m^{-3} h^{-1}. For both packing materials when biofilters were operated at nitrogen concentration higher than 0.6 gN L^{-1} the EC leveled off. An increase of nitrogen concentration from 0.6 to 2.4 gN L^{-1} did not produced any improvement of the biofilter performance. For this reason, the concentration of 0.6 gN L^{-1} was selected for studying the effect of methanol IL on biofilter performance.

As shown in Figure 3.2 and Table 3.1, the PCO_2 and the biomass production rate (PB), respectively, presented trends similar to that of EC for each packing material. In the case of porous packing, the PB increased with nitrogen concentration from 3.8 to 20.6 g m^{-3} h^{-1} and the PCO_2 from 25 to 100 g m^{-3} h^{-1}. In the case of non-porous packing, the PB and the PCO_2 varied in a small range of values.

The kind of packing material affected the liquid content in the packing bed and consequently the biofilter performance. As shown in Table 3.1, the porous packing maintained a liquid content around 350 kg of liquid m^{-3} of packing bed independently of PB. The liquid content of non-porous packing bed varied from 21 to 132 kg m^{-3} proportionally to PB, which increased from 1.1 to 10 kg m^{-3} h^{-1}, respectively. This confirms that the liquid content variation in the packing bed was due to the liquid retained by the biomass accumulated in the packing bed (HART and coll., 1999).

Results of EC, PB and PCO_2 show that the non-porous packing limited the biofilm activity, by presenting a low rate of methanol biodegradation for all nitrogen concentrations. On the other hand, liquids could be retained inside the pores of porous material. In this manner, the pores play the role of reservoirs for nutrients and methanol. For these reasons, the biofilm of the

porous packing would be subjected to less stress than the non-porous when the nitrogen concentration or other operating condition changed. This led to the selection of the porous packing material for studying the effect of methanol IL on biofilter performance.

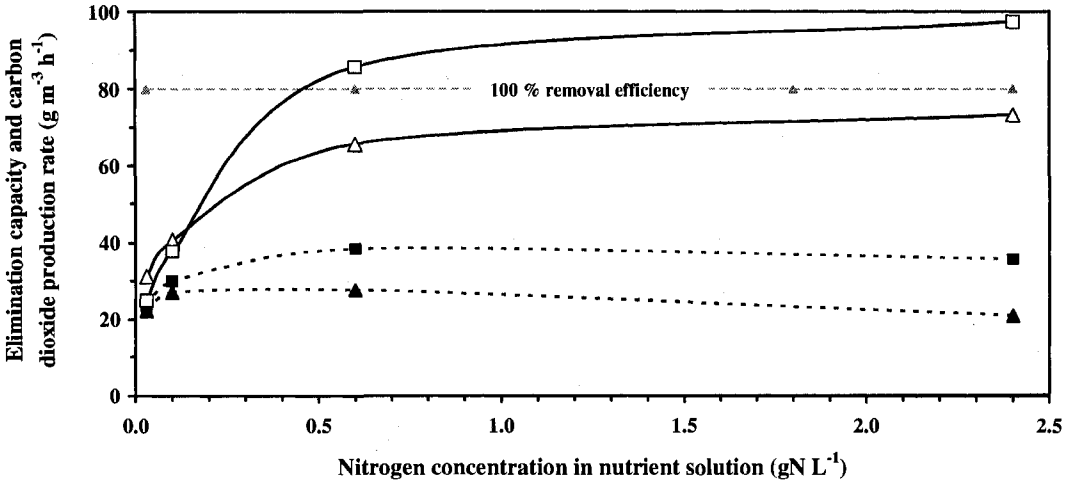

Figure 3.2. Effect of nitrogen concentration on elimination capacity and carbon dioxide production rate for both packing materials. The variables are identified as follow: (–Δ–) EC for porous packing, (–□–) PCO_2 for porous packing, (--▲--) EC for non-porous packing, (--■--) PCO_2 for non-porous packing.

3.3.1.b) Pressure drop

The pressure drop (ΔP) was measured daily in both biofilters. Table 3.1 shows the ΔP for both packing materials. The non-porous material with a void space of 90% presented a ΔP near zero for all experiments. The porous material with a void space of 40% presented a ΔP in the range from 0.05 to 0.8 cm H_2O m^{-1} packing bed for a period of time of two weeks. This was according to ΔP observed by DELHOMÉNIE and col. (2002) in biofilters treating toluene, in which the ΔP increased as the void space decreased.

Table 3.1 shows that ΔP was associated with PB in the biofilter packed with porous material. In the range of nitrogen concentration from 0.03 to 0.6 gN L^{-1}, the ΔP increased from 0.03 to 0.8 cm H_2O m^{-1} of packing bed and PB from 3.8 to 8.2 g m^{-3} h^{-1}. A similar behavior of ΔP as a function of biomass content was observed by MORGAN-SAGASTUME and coll. (2001) in

biofilters treating methanol vapours. In the present study, when nitrogen concentration increased from 0.6 to 2.4 gN L^{-1}, PB increased to 20.6 g m^{-3} h^{-1} but ΔP decreased from 0.8 to 0.25 cm H_2O m^{-1} of packing bed. At 2.4 gN L^{-1}, the biofilter presented the lowest content of liquid in the biofilm, 94.5% ± 0.9% s.d. (data not published) which could cause a more compact biofilm with a smaller specific volume.

3.3.1.c) Biofilm

Figures 3.3a and 3.3b show the evolution of EC and cellular densities for methylotrophs and non-methylotrophs in the biofilm of both packing materials, for approximately 150 days at different nitrogen concentrations (0.03, 0.1, 0.6 and 2.4 gN L^{-1}) and at a fixed IL of 80 g m^{-3} h^{-1}. Figures 3.3a and 3.3b show that the cellular densities of methylotrophs and non-methylotrophs were function of the nitrogen concentration.

Figure 3.3a shows that in the range of nitrogen concentration from 0.03 to 0.6 gN L^{-1}, the microbial counts of methylotrophs (M) were higher than non-methylotrophs (N-M) in a M:N-M ratio of 2 and up to 8 for the porous packing. On day 120, the biofilter started up at 2.4 gN L^{-1} and ten days after operating at this concentration the cellular density of non-methylotrophs had become greater than that of methylotrophs. As shown in Figure 3.3a, on day 130 the non-methylotrophs presented their highest cellular density, which was $6.6x10^{+10}$ cfu g^{-1} of dry biomass. At this nitrogen concentration the highest PB of 20.6 g m^{-3} h^{-1} (Table 3.1) occurred. It is assumed that the mass transfer of oxygen through the biofilm is by diffusion and its concentration depends on the thickness of biofilm and/or the oxygen consumption (OKKERSE and coll., 1999a). In this manner, the oxygen availability in the deepest layers should drop as biofilm thickness increased because of biomass accumulation. This favoured the formation of anaerobic zones, which were visually identifiable on day 135, similar to the anaerobic colonies observed by OKKERSE and coll. (1999b). When the biofilter was started up at 2.4 gN L^{-1} on day 120, the cellular density of methylotrophs was $8.7x10^{+10}$ cfu g^{-1} of dry biomass, then it was apparently inhibited by nitrogen concentration and decreased to $1.1x10^{+10}$ cfu g^{-1} of dry biomass on day 130 and finally to $2x10^{+9}$ cfu g^{-1} on day 150. Since the growth of non-methylotrophs is supported by the consumption of storage compounds produced by methylotrophs, the drop of cellular density of methylotrophs affected

the non-methylotrophic population. The cellular density of non-methylotrophs decreased from $6.6x10^{+10}$ cfu g^{-1} of dry biomass on day 130 to $1.1x10^{+10}$ cfu g^{-1} of dry biomass on day 150.

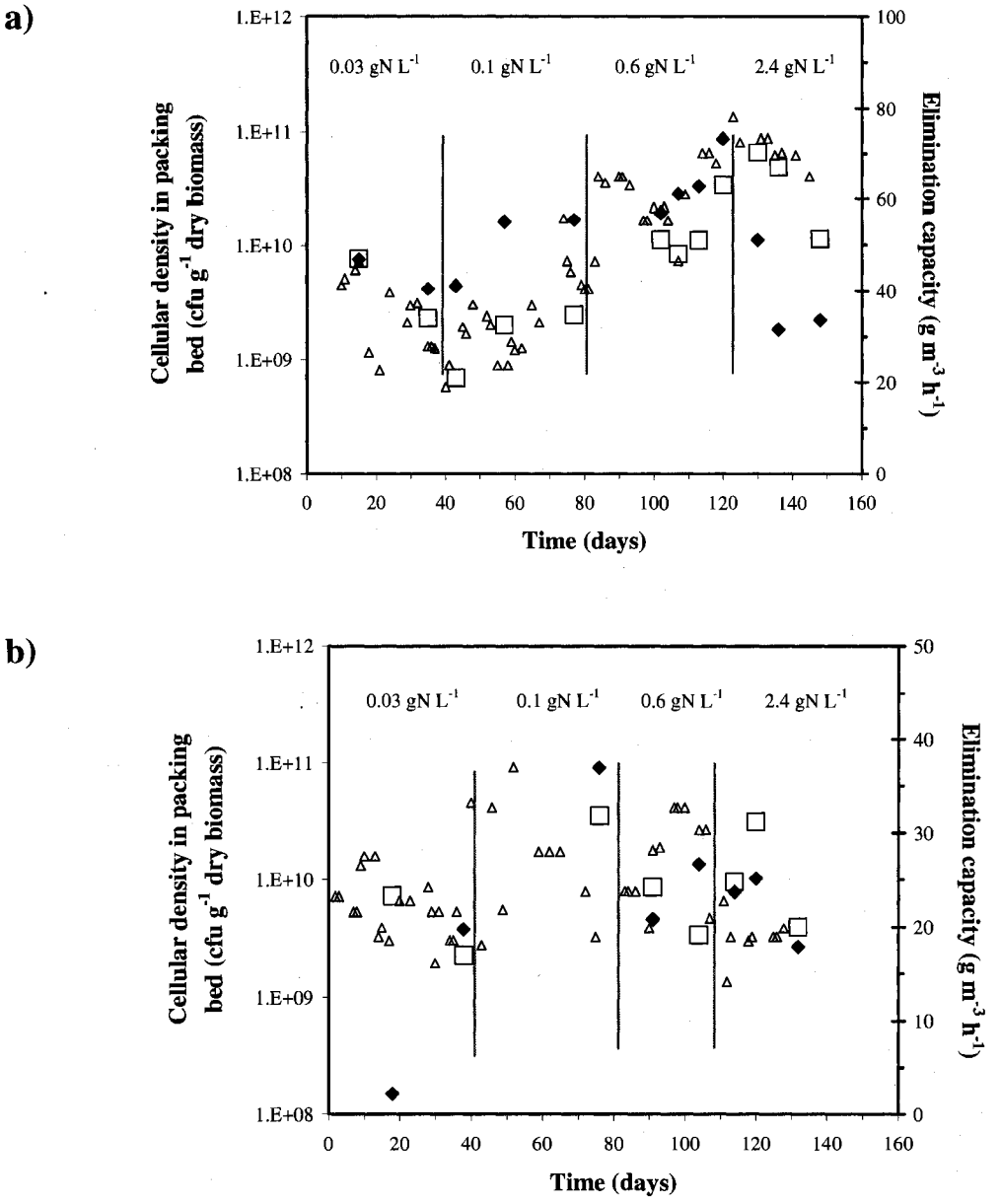

Figure 3.3. Evolution of elimination capacity (Δ), cellular density of methylotrophs (♦) and non-methylotrophs (□) in biofilters packed with: a) porous packing material, and b) non-porous packing material.

When the biofilter was packed with non-porous material, both populations coexisted without either dominating the other, as shown in Figure 3.3b. The highest cellular densities occurred at a nitrogen concentration of 0.1 gN L^{-1}: for methylotrophs $9x10^{+10}$ cfu g^{-1} of dry biomass and for non-methylotrophs $4x10^{+10}$ cfu g^{-1} of dry biomass. The trends of cellular densities were similar to those of the porous packing: the number of methylotrophs dropped with nitrogen concentration while that of non-methylotrophs increased.

In both packing materials, nitrogen became inhibitory for methylotrophic microorganisms at high nitrogen concentrations: for the non-porous material at concentrations higher than 0.1 gN L^{-1} and for the porous material at concentrations higher than 0.6 gN L^{-1}. These results agree with other studies of methane and methanol biofiltration. These studies report that the biofilter performance increased with nitrogen concentration in nutrient solution up to an optimal value and then the nitrogen concentration began to inhibit the methylotrophic microorganisms (NIKIEMA and coll., 2005; YANG and coll., 2002).

Figures 3.3a and 3.3b also show that EC was highly associated with cellular density of methylotrophs; especially in the case of porous packing material (Figure 3.3a). These results suggest that the EC is a good indicator of the metabolic state of specialized microorganisms in biofilters.

3.3.1.d) Carbon balances

Table 3.2 shows the carbon balances for biofilters packed with porous and non-porous material when it was operated at a fixed IL of 80 g m^{-3} h^{-1} (methanol inlet concentration of 1.5 g m^{-3} and EBRT of 65 s) and four different nitrogen concentrations. Balances were calculated with results shown in Figure 3.2 (EC and PCO_2) and Table 3.1 (PB and methanol and solids content in lixiviate). Other compounds different than methanol were not considered because they were not detected by GC/MS in lixiviate samples.

Since the biomass contains around 50% carbon (BAILEY and coll., 1986), the determination of biomass in the packing bed and lixiviate is essential for carbon balances. As opposed to the present study, other studies which report carbon balances did not determine the experimental biomass accumulation (KRAILAS and coll., 2000b; COX and coll., 2001; MORALES and coll., 1998; DESHUSSES, 1997).

For porous packing, the calculated $C_{out\text{-}calc}$ presented an error from -17 to +15% with respect to the experimental $C_{out\text{-}exp}$, while the error for the non-porous packing was from -1 to +3%. For both packing materials, the absolute value of error for the carbon balances is smaller than -18% reported by DESHUSSES (1997). The error obtained in the present research is acceptable, since the carbon balances were calculated from experimental data. As shown in Table 3.2, the average error and its respective standard deviation was generally higher for the porous packing than for the non-porous. The difference between both materials might be due to the pores, which could retain nutrients, biomass and water when the packing bed was manually washed, before changing the operating conditions. For example, when the biofilters started up at 0.6 and 2.4 gN L^{-1} the PCO_2 presented a maximum the first week. This caused the $C_{out\text{-}exp}$ to be higher than $C_{out\text{-}calc}$ by around 20 and 30%, respectively. In this way, the overproduction of CO_2 caused the average error to increase up to -17 and -15 for these nitrogen concentrations.

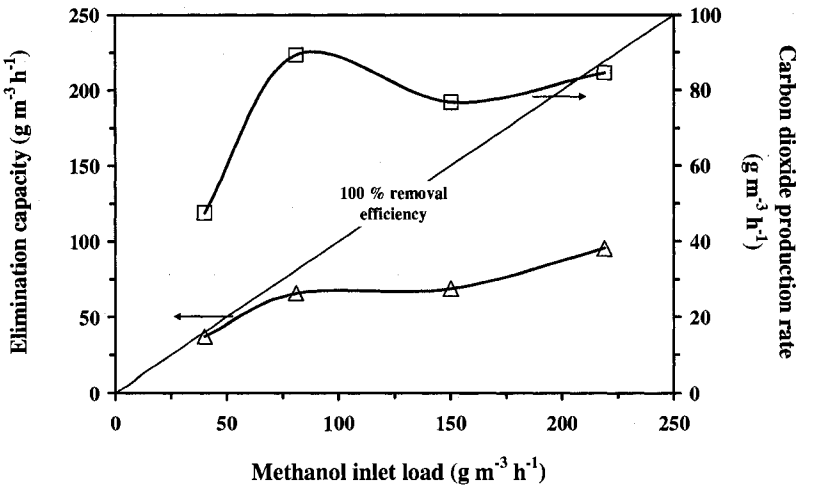

Figure 3.4. Effect of methanol inlet load on elimination capacity (–Δ–) and carbon dioxide production rate (–□–) for the biofilter packed with the porous material. EBRT was fixed at 65 s and four methanol inlet concentrations were tested.

3.3.2. Effects of methanol inlet load

3.3.2.a) Biofilter performance

The biofilter packed with porous material was selected to study the effect of methanol IL on biofilter performance at a fixed nitrogen concentration of 0.6 gN L^{-1}. Methanol IL was fixed by means of EBRT and methanol inlet concentration. Figure 3.4 shows EC and PCO_2 for the biofilter operated at a fixed EBRT of 65 s and four methanol inlet concentrations in order to test different ILs in the range from 40 to 220 g m^{-3} h^{-1}. Figure 3.5 shows EC and PCO_2 for the biofilter operated at a fixed methanol inlet concentration of 1.5 g m^{-3} and four EBRT in order to test different ILs in the range from 20 to 235 g m^{-3} h^{-1}.

According to Figures 3.4 and 3.5, EC and PCO_2 had a similar behaviour when IL was smaller than 80 g m^{-3} h^{-1}, whatever the combination of EBRT and methanol inlet concentration used for fixing IL. On the other hand, for methanol ILs higher than 80 g m^{-3} h^{-1}, the trends of EC and PCO_2 were function of the source of IL variations.

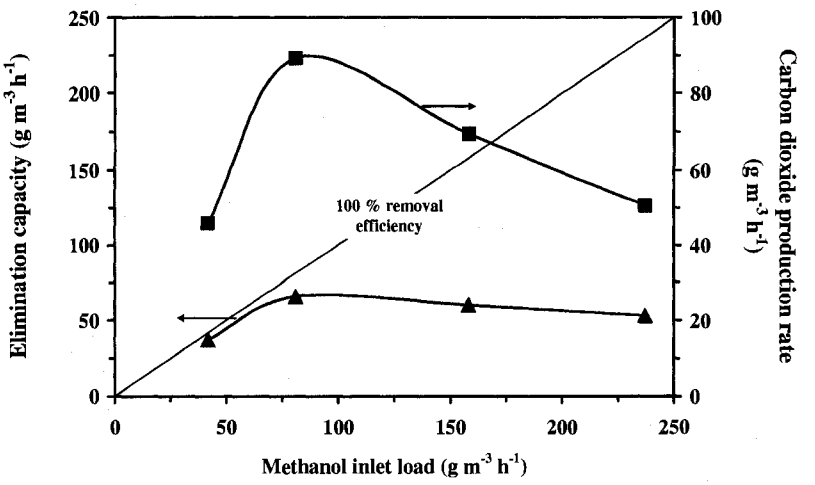

Figure 3.5. Effect of methanol inlet load on elimination capacity (–▲–) and carbon dioxide production rate (–■–) for the biofilter packed with the porous material. Methanol inlet load was fixed at 1.5 g m^{-3} and four EBRT were tested.

Figure 3.4 shows that in the range of IL from 80 to 220 g m^{-3} h^{-1}, EC increased from 70 to 95 g m^{-3} h^{-1} while PCO_2 oscillated around 80 g m^{-3} h^{-1}. The oscillatory behaviour of PCO_2 could be due to inhibition-acclimation processes occurring in the biofilm exposed to increments of methanol concentration.

Figure 3.5 shows that in the range of IL from 80 to 235 g m^{-3} h^{-1}, EC was nearly stable at around 60 g m^{-3} h^{-1}, which means that removal efficiency dropped from 80 to 20%. The limitation of EBRT on biofilter performance was also observed in PCO_2, which decreased from 90 to 50 g m^{-3} h^{-1}.

A special phenomenon was observed when the biofilter operated at the smallest EBRT of 20 s (the highest air flow rate of 3 m^3 h^{-1}). When the air stream passed through the packing bed, the external biofilm layer dehydrated and a dry layer of storage compounds was formed. It was observed visually that the dry layer covering the biofilm and packing bed was semi-permeable to nutrient solution. The dry layer caused that the absorption of nutrient solution by the packing bed decreased from 0.60 L day^{-1} at an EBRT of 35 s to 0.45 L day^{-1} at 20 s. This was reflected in the liquid content of packing bed, which was 300 kg m^{-3} at 20 s while it was higher than 370 kg m^{-3} at any other EBRTs. As a consequence, the smallest removal efficiency of 20% occurred at the smallest EBRT of 20 s, because the low liquid content diminished the microbial activity (KRAILAS and coll., 2000b). These results show that the biofilter was more sensitive to changes of EBRT than methanol inlet concentration in the same range of IL.

Table 3.3 shows that PB increased with IL when EBRT decreased. According to LEAK (1992), when methylotrophs are subject to nitrogen or oxygen limitation, the production of storage compounds may increase. In the present study, the biofilter could be limited by both compounds. For example, nitrogen concentration was fixed at 0.6 gN L^{-1} and the C:N mass ratio increased from 10:1 to 65:1 when IL increased from 40 to 235 g m^{-3} h^{-1}. The whole range of C:N is smaller than the value for C:N of 4:1 calculated with the empirical formula for biomass $CH_{1.8}O_{0.5}N_{0.2}$ reported in the literature (BAILEY and coll., 1986). In this way, the nitrogen limitation increased with IL and for the EBRT of 20 s which corresponded to the highest IL of 235 g m^{-3} h^{-1}, nitrogen limitation was combined with the phenomena of permeability mentioned above. The low permeability of biofilm at 20 s could decrease the mass transfer of oxygen and cause the limitation of this compound.

It should be noted that the oscillatory behavior of EC and PCO_2 observed in this study are similar to other studies for methanol treatment with biofilters. For example, PRADO and coll. (2005) and CHETPATTANANONDH and coll. (2005) observed that EC presented a maximum and a minimum with oscillatory trends in a range of IL from 100 to 600 g m^{-3} h^{-1}. PRADO and coll. (2005) also showed that the concentration of CO_2 followed a linear correlation with methanol concentration, which signifies that PCO_2 presented oscillatory trends similar to those of EC.

3.3.2.b) Biofilm

When the biofilter operated at a fixed EBRT of 65 s and a nitrogen concentration of 0.6 gN L^{-1}, the IL was fixed by means of methanol inlet concentration. Table 3.3 shows that methylotrophs and non-methylotrophs were apparently inhibited at methanol concentrations higher than 1.5 g m^{-3}. When the methanol concentration was increased from 1.5 to 4.0 g m^{-3}, cellular densities dropped from $6.4x10^{10}$ to $0.5x10^{10}$ cfu g^{-1} dry biomass for non-methylotrophs and from $17.0x10^{10}$ to $4.2x10^{10}$ cfu g^{-1} dry biomass for methylotrophs. As indicated above, when the methanol concentration increased, nitrogen could limit the growth of microorganisms and induce an overproduction of storage compounds. This would produce a nearly constant PB around 8.5 g m^{-3} h^{-1}, although the cellular densities decreased. In order to satisfy the energy requirements to support the overproduction of storage compounds, the microorganisms increased the consumption of methanol. This was observed in the trends of EC and PCO_2, which increased when methanol inlet concentration increased from 2.7 to 4.0 g m^{-3}.

On the other hand, when biofilter operated at a methanol inlet concentration of 1.5 g m^{-3} and a nitrogen concentration of 0.6 gN L^{-1}, IL was fixed by modifying the EBRT. This signifies that the mass of inlet methanol increased at a fixed methanol concentration and the inhibitory effect of methanol on microorganisms was smaller than in the previous case, when methanol concentration increased. These operating conditions favoured the acclimation of the methylotrophs (M) whose cellular density (Table 3.3) was always higher than that of the non-methylotrophs (N-M). The ratio of cellular densities M:N-M increased successively from 1.5 to 11 with IL.

Table 3.3 shows that the cellular density of the biofilm was higher than the cellular density of suspended biomass in the lixiviate most of the time. The biofilm presented cellular densities from 2 and up to 50 fold higher than suspended biomass in the lixiviate. These results show that the detached biofilm contained fewer active cells than the biofilm which remains on the packing bed. This observation agrees with other studies, which proposed that aging and death of cells are involved in the detachment of biofilm (DIKS and coll., 1994; KIM and coll., 2007).

3.3.2.c) Critical inlet load

Figures 3.4 and 3.5 and Table 3.3 show that the IL of 80 g m^{-3} h^{-1} (methanol inlet concentration of 1.5 g m^{-3} and EBRT of 65 s) was an inflexion point for EC, PCO_2, PB and cellular densities. Critical IL (IL_{crit}), defined as the IL at which EC begins to level out (COOPER and coll., 2002), occurred at 80 g m^{-3} h^{-1} whatever was the source of IL variation. The highest cellular densities for methylotrophs ($17.0x10^{+10}$ cfu g^{-1} of dry biomass) and non-methylotrophs ($6.4x10^{+10}$ cfu g^{-1} of dry biomass) were also observed at IL_{crit} (Table 3.3). These results led to the hypothesis that removal efficiency dropped off because IL caused an inhibition of methylotrophs and non-methylotrophs, observed as decreases of their cellular densities.

The IL_{crit} for methanol biofiltration was observed in the range from 100 to 280 g m^{-3} h^{-1} (KRAILAS and coll., 2000b; PRADO and coll., 2005), which is higher than the IL_{crit} of 80 g m^{-3} h^{-1} obtained here. However, the nutrient solution used in the present study was made up of only 3 compounds and no micronutrients. This could be one of the reasons for obtaining a lower value of IL_{crit} compared to other studies. In the case of IL_{crit} of 100 g m^{-3} h^{-1} (KRAILAS and coll., 2000b), the packing bed material was compost, which supplies indigenous microorganisms and nutrients. This favors the start up and operation of biofilters. For the study in which was obtained an IL_{crit} of 280 g m^{-3} h^{-1} (PRADO and coll., 2005), the EBRT was kept at 90 s and different IL were tested in the range from 50 to 330 g m^{-3} h^{-1}. In comparison, when EBRT was kept at 65 s in the present study, IL increased from 40 to 235 g m^{-3} h^{-1}. The EBRT at which operated the biofilters in both studies might be an important parameter in the difference of IL_{crit} observed in each case.

3.4. Conclusion

Biofiltration was applied to treat methanol vapours. Two kinds of inert packing materials were tested, porous and non-porous, in the range of nitrogen concentration from 0.03 to 2.4 gN L^{-1} at a fixed IL of 80 g m^{-3} h^{-1}. The porous packing performed better than the non-porous in the whole range of nitrogen concentration in the nutrient solution. For the porous packing biofilter, EC and PCO_2 increased with nitrogen concentration, from 30 to 75 g m^{-3} h^{-1} for EC and from 25 to 100 g m^{-3} h^{-1} for PCO_2. In contrast, these parameters presented slight variations for the biofilter packed with the non-porous material, which had an EC around 25 g m^{-3} h^{-1} and a PCO_2 around 30 g m^{-3} h^{-1}. The biofilter with porous packing provided a nearly constant liquid content (around 350 kg m^{-3}), which led the biofilter to reach high removal efficiencies at low nitrogen concentration.

The variations on IL were made by changing the EBRT or the methanol inlet concentration in the biofilter packed with the porous material. For IL up to 80 g m^{-3} h^{-1} both operating conditions produced similar variations on EC or PCO_2. For IL higher than 80 g m^{-3} h^{-1}, the value of EC and PCO_2 depended on the source of IL variations. For all operating conditions, biofilm and lixiviate were characterized in terms of biomass production rate, cellular density and liquid content in the packing bed. All these parameters were affected by nitrogen concentration, nature of packing material and methanol IL.

The highest cellular densities of methylotrophs and non-methylotrophs occurred at low nitrogen concentrations, between 0.1 and 0.6 gN L^{-1}. The ratio methylotrophs:non-methylotrophs was used as an indicator in order to understand the trends of performance parameters, such as biomass production rate which increased if the ratio increased. The variations of IL also affected the cellular densities and in consequence the performance of the biofilter. In both cases, when methanol inlet concentration and EBRT caused that IL varied, the biofilter presented a critical IL of 80 g m^{-3} h^{-1}, which was observed at the highest cellular density of methylotrophs.

Acknowledgements

The authors express their sincerely acknowledgements to Natural Sciences and Engineering Research Council of Canada for the financial support. One of the co-authors, Sandrine Bénard, Ph. D., would like to thank the Région Rhône-Alpes for her doctoral scholarship.

Table 3.1. Effects of operating conditions on some characteristic parameters of biofilm, packing bed and lixiviate. The biofilter operated at an EBRT of 65 s and a methanol inlet concentration of 1.5 g m^{-3}.

	Porous packing				**Non-porous packing**			
Nitrogen concentration (gN L^{-1})	0.03	0.1	0.6	2.4	0.03	0.1	0.6	2.4
Biofilm								
• biomass production rate (PB) (g m^{-3} h^{-1}) ± sd [a]	3.8 ± 0.9	5.7 ± 0.8	8.2 ± 2.0	20.6 ± 6.5	4.2 ± 1.5	10.0 ± 4.6	3.4 ± 0.8	1.1 ± 0.3
Packing bed								
• liquid content (kg m^{-3}) [b]	365	305	385	365	61	132	39	21
• pressure drop (cm H_2O m^{-1} bed) [a]	0.05	0.08	0.8	0.25	≈ 0	≈ 0	≈ 0	≈ 0
Lixiviate								
• methanol (g L^{-1}) ± sd	0.8 ± 0.5	1.3 ± 0.4	2.0 ± 0.7	0.7 ± 0.3	0.5 ± 0.2	2.6 ± 0.8	2.8 ± 0.9	2.2 ± 0.8
• solids (g L^{-1}) ± sd	0.6 ± 0.1	0.5 ± 0.2	3.0 ± 0.3	3.3 ± 0.8	3.4 ± 0.4	1.3 ± 0.8	2.9 ± 0.3	2.7 ± 0.9
• non-methylotrophs ucf g^{-1} [c] ($1x10^{+10}$)	0.2	0.6	6.1	3.1	0.1	n.d.	1.1	0.3
• methylotrophs ucf g^{-1} [b] ($1x10^{+10}$)	0.1	0.6	3.4	1.3	0.2	n.d.	0.9	0.2

a: the biomass production rate ist the average for a 15 day period and the pressure drop is the maximum value at the end of this period
b: values are referred to empty bed volume, they are a weighted arithmetic average of biofilter during the experiment
c: cellular density is referred to dry biomass in lixiviate
n.d.: non determined
sd: standard deviation

Table 3.2. Mass carbon balances for biofilters. Experiments for both packing materials were run at an EBRT of 65 s and a methanol inlet concentration of 1.5 g m^{-3}.

	Porous packing				**Non-porous packing**			
Nitrogen concentration (gN L^{-1})	0.03	0.1	0.6	2.4	0.03	0.1	0.6	2.4
Experimental $C_{in\text{-}exp}$ (g m^{-3} h^{-1}) ± sd	28.2 ± 2.9	29.7 ± 2.2	29.6 ± 0.6	34.6 ± 1.2	30.1 ± 2.5	31.6 ± 0.1	34.0 ± 1.0	36.5 ± 1.5
Experimental $C_{acc\text{-}exp}$ (g m^{-3} h^{-1}) ± sd	2.3 ± 1.4	4.7 ± 1.5	3.8 ± 1.4	7.5 ± 3.1	1.8 ± 0.9	4.0 ± 0.8	1.4 ± 0.3	0.6 ± 0.2
Experimental $C_{out\text{-}exp}$ (g m^{-3} h^{-1}) ± sd	22.7 ± 1.8	25.2 ± 2.2	31.6 ± 2.1	32.4 ± 6.2	27.8 ± 4.2	27.6 ± 0.8	32.8 ± 3.6	35.5 ± 4.2
Calculated $C_{out\text{-}calc}$ (g m^{-3} h^{-1}) ± sd	25.9 ± 2.5	25.1 ± 2.5	25.8 ± 2.0	27.0 ± 3.8	28.3 ± 3.2	27.5 ± 0.7	32.6 ± 0.8	35.9 ± 1.4
Error of $C_{out\text{-}calc}$ (%)± sd	15 ± 18	1 ± 14	-17 ± 11	-15 ± 15	3 ± 11	-1 ± 10	0 ± 9	3 ± 12

sd: standard deviation

Table 3.3. Effects of operating conditions on some characteristic parameters of biofilm, packing bed and lixiviate. Biofilters operated at a nitrogen concentration in nutrient solution of 0.6 gN L^{-1}. For the four methanol inlet concentrations the EBRT was constant at 65 s; for the four EBRTs the methanol inlet concentration was constant at 1.5 g m^{-3}.

	Methanol inlet concentration (g m^{-3})				**Empty bed residence time (s)**			
	0.7	1.5	2.7	4.0	130	65	35	20
Methanol inlet load (g m^{-3} h^{-1})	40	80	150	220	40	80	155	235
Biofilm								
• biomass production rate (PB) (g m^{-3} h^{-1}) ± sd	14.1 ± 3.7	8.2 ± 2.0	8.8 ± 1.7	9.1 ± 2.8	5.9 ± 1.9	8.2 ± 2.0	11.7 ± 4.0	16.5 ± 4.3
• non-methylotrophs ucf g^{-1} [a] ($1x10^{+10}$)	0.3	6.4	3.5	0.5	1.1	6.4	1.4	0.9
• methylotrophs ucf g^{-1} [a] ($1x10^{+10}$)	2.4	17.0	8.1	4.2	1.7	17.0	7.3	10.0
Packing bed								
• liquid content (kg m^{-3}) [b]	275	385	420	405	370	385	420	300
Lixiviate								
• non-methylotrophs ucf g^{-1} [c] ($1x10^{+10}$)	0.1	1.4	0.3	0.2	0.5	1.4	0.2	0.4
• methylotrophs ucf g^{-1} [c] ($1x10^{+10}$)	0.2	1.2	1.4	1.0	0.9	1.2	0.9	0.2

a: cellular density is refered to dry weight of biofilm
b: values are referred to empty bed volume, they are a weighted arithmetic average of biofilter during the experiment
c: cellular density is referred to dry biomass in lixiviate
sd: standard deviation

Chapitre 4. Biofiltration par percolation d'air pollué avec vapeurs de méthanol

Article « *Control of methanol vapours in a biotrickling filter: performance analysis and experimental determination of partition coefficient* », qui a été soumis le 25 février 2008 dans le journal « Bioresource Technology ».

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Résumé

Une étude relative au traitement du méthanol avec un biofiltre percolateur a été réalisée. Les effets des variables telles la concentration d'azote, le temps de résidence et la charge de méthanol sur la performance du biofiltre percolateur ont été étudiés. Le rôle de la solution nutritive dans l'enlèvement du méthanol à l'intérieur du biofiltre percolateur a été analysé. Dans cette étude a également été abordé le traitement du méthanol à de fortes concentrations et charges. Une nouvelle méthode pour la détermination du coefficient de partition du méthanol pour un biofiltre percolateur en opération a été développée.

La capacité d'élimination, les taux de production de biomasse et de dioxyde de carbone ont augmenté avec la concentration d'azote présent dans la solution nutritive et avec le temps de résidence. Le biofiltre percolateur a présenté une capacité d'élimination maximale de 2160 g m^{-3} h^{-1} pour une charge de méthanol à l'entrée de 3700 g m^{-3} h^{-1}. Le méthanol a été enlevé de la phase gazeuse par deux mécanismes : la biodégradation par les microorganismes présents dans le lit filtrant et l'absorption du méthanol par la solution nutritive. L'absorption peut représenter jusqu'à 80% d'élimination du méthanol enlevé de la phase gazeuse.

La solution nutritive a aussi le rôle de capter l'énergie émise par les microorganismes, ce qui a permis d'homogénéiser la température du lit filtrant autour de 32°C. Pour cette température, le coefficient de partition du méthanol vaut 2.64×10^{-4} $[\text{mole } L^{-1}]_{gaz}$ / $[\text{mole } L^{-1}]_{liquide}$.

Les résultats démontrent que la biofiltration par percolation permet de traiter de l'air pollué avec des vapeurs de méthanol. L'étude a permis de démontrer, pour la première fois, le rôle de la solution nutritive sur la performance d'un biofiltre percolateur traitant un composé très soluble dans l'eau.

4. Control of methanol vapours in a biotrickling filter: performance analysis and experimental determination of partition coefficient.

Abstract

Methanol vapours were treated in a biotrickling filter (BTF) packed with inert polypropylene spheres. The effects of nitrogen concentration in nutrient solution, empty bed residence time (EBRT) and methanol inlet concentration on BTF performance were studied. The elimination capacity (EC), biomass and carbon dioxide production rates increased with nitrogen concentration and EBRT. The EC also increased with methanol inlet load (IL) when methanol inlet concentration and the EBRT varied from 0.3 to 37.0 g m^{-3} and from 20 to 65 s, respectively. The BTF reached its maximum EC of 2160 g m^{-3} h^{-1} when it operated at an IL of 3700 g m^{-3} h^{-1}. Methanol was removed by two mechanisms: biodegradation and absorption in liquid phase. The partition coefficient of methanol in the BTF was determined at five EBRTs and along the packing bed. It followed the Henry model, with an average value of 2.64×10^{-4} $[mol\ L^{-1}]_{gas}/[mol\ L^{-1}]_{liquid}$.

4.1. Introduction

The biotrickling filter (BTF) is an efficient air treatment system at high inlet loads of volatile organic compounds (VOCs), specifically at concentrations smaller than 10.0 g m^{-3} and air flow rates between 1000 and 100 000 m^3 h^{-1} (COOPER and coll., 2002). The BTF is an aerobic bioreactor packed with inert materials in order to provide a support for the biofilm. In the biotrickling filter, a nutrient solution is trickled downwards through the filter while the gaseous effluent to be treated flows upward. The immobilized microorganisms transform the VOCs to carbon dioxide (CO_2), water, biomass and occasionally salts (DELHOMÉNIE and coll., 2005b).

Methanol emissions are regulated in Canada by the Canadian Environmental Protection Act (COMMUNICATION CANADA, 2003) and in United States by the Clean Air Act as amended in 1990 (EPA, 1990). In 2005, facilities required to report their releases emitted to the atmosphere 66 550 tons of methanol $year^{-1}$ in the United States and 22 240 tons $year^{-1}$ in

Canada. In these countries the pulp and paper industry, especially kraft mills, was the main source of methanol released to the atmosphere with at least 65 % of total emissions (NPRI, 2007; TRI PROGRAM, 2007).

Previous studies have shown that methanol emissions can be controlled by biofiltration with or without percolation (AVALOS RAMIREZ and coll., 2005; PRADO and coll., 2004). Since methanol is biodegradable, the elimination capacity (EC) in these bioprocesses is high. However, biofilters (BFs) and BTFs are limited by a critical inlet load (IL) after which the removal efficiency of bioprocesses decreases (COOPER and coll., 2002). In a BF treating methanol, the critical IL has been observed in the range from 100 to 280 g m^{-3} h^{-1} (KRAILAS and coll., 2000b; PRADO and coll., 2005), and in the case of BTF the critical IL has been observed up to 500 g m^{-3} h^{-1} (AVALOS RAMIREZ and coll., 2005).

Since nitrogen is a nutrient which is required in large quantities by the microrganisms, the studies on the BF and BTF performance have been focused on the effect of the form and concentration of nitrogen in the nutrient solution (HOLUBAR and coll., 1999; SMITH and coll., 1994; YANG and coll., 2002).

The present research is an experimental study of the BTF for controlling methanol vapour emissions. The research had as objective to analyse the effects of nitrogen, empty bed residence time and methanol inlet concentration on BTF performance. An experimental method was also developed in order to determine the partition coefficient (PC) of methanol (a water soluble VOC) inside a BTF operating at steady state. In fact, there are few studies about the determination of PC of VOCs in air-water biosystems, which are affected by dissolved salts, suspended biomass, temperature of BTF and biomass on the packing material (GUPTA and coll., 2000; HODGE and coll., 1994; LIN and coll., 2006; TEJA and coll., 2001).

4.2. Experimental methods

4.2.1. Biotrickling filter

Three identical BTFs, were constructed from Plexiglas cylinders with an internal diameter of 0.15 m and a total bed height of 1 m divided in three sections of 0.33 m. Figure 4.1 shows one of these experimental units. Each BTF was packed with inert polypropylene spheres (Jaeger Tri-Packs®, Fabco Plastics, Toronto, Canada). The humidity and the methanol concentration of the gaseous feed stream were controlled by separating the dry and particulate free air into

two streams and sending them to two bubblers containing water and methanol, respectively. The methanol (98 % w/w, Anachemia, Canada) used was kept at 20°C. The two air streams were mixed before entering at the base of BTF at an average temperature of 24°C.

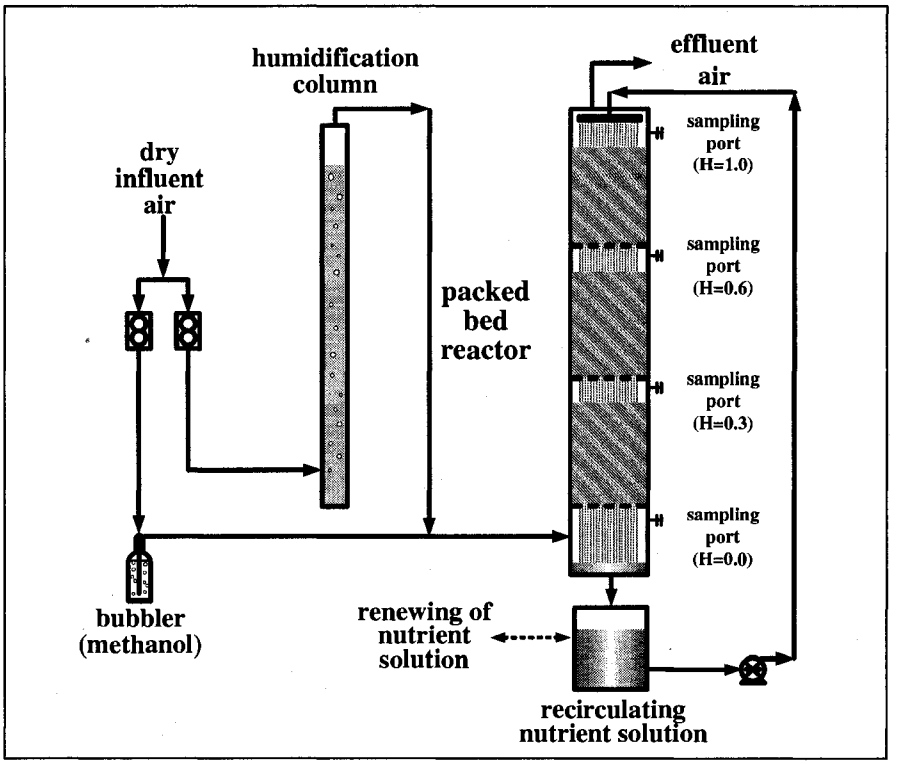


Figure 4.1. Schematic representation of biotrickling filter. H is the dimensionless height of the packing bed.

The nutrient solution had a fixed nitrogen-phosphorus-potassium mass ratio of 3:3:1 throughout the experimental programme (Table 4.1a). The filter bed was irrigated by means of a continuous recirculation of nutrient solution, which was stored in a holding tank. The total volume of nutrient solution (16 L) was renewed daily. For all experiments, air and nutrient solution flowed countercurrently. The operating conditions for all experiments are summarized in Table 4.1b and the performance parameters are defined in Table 4.2.

Table 4.1. Specifications of biotrickling filter and operating conditions.

a) Biotrickling filter

Packing bed material	polypropylene spheres (Jaeger Tri-Packs®)
Diameter	0.025 m
Specific surface	280 m^2 m^{-3}
Void space	90%
Empty bed volume	0.0184 m^{-3}
Packing bed height	1 m
Nutrient solution flow rate	2.7 L min^{-1}
N:P:K mass ratio	3:3:1

- urea[a] for nitrogen (N)
- phosphoric acid neutralized with sodium hydroxide[a] for phosphorus (P)
- potassium sulphate[a] for potassium (K)

[a] Compounds indicated are added to tap water.

b) Operating conditions

Effect of	Nitrogen concentration in nutrient solution (gN L^{-1})	Methanol inlet concentration (g m^{-3})	Empty bed residence time (s)
Nitrogen concentration in nutrient solution	from 0.0 to 0.5	fixed at 2.0	fixed at 65
Methanol inlet concentration	fixed at 0.005	from 0.3 to 37	from 20 to 65
Empty bed residence time	fixed at 0.005	fixed at 2.0	from 15 to 265

4.2.2. Start up of biotrickling filters

The first BTF was inoculated with lixiviate from a biofilter which had been treating methanol vapours (DASTOUS and coll., 2005). The operating conditions used for starting-up and stabilizing the first BTF were: 1.0 m^3 h^{-1} of air flow rate, 1.0 g m^{-3} of methanol inlet concentration and 0.005 gN L^{-1} during 9 weeks. Some packing spheres from the first BTF, with biofilm over the surface, were used as the inoculum for starting up the other two BTFs.

Table 4.2. Definition of biotrickling filter performance parameters. The BTF performance was analyzed in terms of the following parameters:

Parameter	Definition	Units
Inlet load	$IL = \frac{Q\ C_i}{V}$	g m^{-3} h^{-1}
Elimination capacity	$EC = \frac{Q\ (C_i - C_o)}{V}$	g m^{-3} h^{-1}
Removal efficiency	$X = \frac{C_i - C_o}{C_i}$	dimensionless
Biomass production rate	$PB = \frac{C_B}{\Theta\ V}$	g m^{-3} h^{-1}
Carbon dioxide production rate	$PCO_2 = \frac{Q\ (CO_{2o} - CO_{2i})}{V}$	g m^{-3} h^{-1}
Biomass yield coefficient	$YB = \frac{PB}{EC}$	g biomass produced g^{-1} of methanol consumed
Carbon dioxide yield coefficient	$YCO_2 = \frac{PCO_2}{EC}$	g CO_2 produced g^{-1} of methanol consumed

where Q is the total air flow rate (m^3 h^{-1}), V is the empty bed volume (m^3), Θ is the 20 h-recycling period (h), C is the methanol concentration, C_B is the dry biomass concentration in liquid phase and CO_2 is the carbon dioxide concentration, all concentrations in (g m^{-3}). The subscript *i* indicates that the compound is in an inlet stream and subscript *o* indicates that the compound is in an outlet stream.

4.2.3. Biomass production rate

In a previous study with a BTF treating methanol at similar operating conditions of the BTFs of the present study, the biomass content in the packing bed was nearly constant at steady state (AVALOS RAMIREZ and coll., 2005). The concentration of volatile suspended solids (VSS)

in lixiviate had increased when nutrient solution was completely renewed, after recycling 20 hours. In contrast, the biomass content in the packing bed rested nearly constant. This let to the utilization of VSS concentration to calculate the biomass produced by the BTF. The VSS concentration in lixiviate was assumed equal to the biomass concentration and it was calculated by means of the total solids (TS) concentration (Standard Method 2540-B; APHA, 1999). The TS concentration was determined in the nutrient solution before and after recirculating the nutrient solution during a period of 20 h. The TS concentration of fresh nutrient solution was subtracted from the TS concentration of recirculated nutrient solution. The difference of TS concentration represents the concentration of VSS accumulated in lixiviate during 20 h. The biomass production rate was calculated by multiplying the VSS concentration by the volume of nutrient solution (16 L) and dividing by the empty bed volume of BTF and the 20 h-recycling period.

4.2.4. Methanol and carbon dioxide concentrations in gas phase

The concentrations of methanol and carbon dioxide (CO_2) in gas phase were measured with a total hydrocarbon analyzer Horiba FIA-510 (Horiba, USA) and a portable CO_2 analyzer Ultramat 22P (Siemens AG, Germany), respectively. The methanol concentration profiles in gas phase were determined at the dimensionless heights (H) of 0.0, 0.33, 0.67 and 1.0. H was calculated as follows:

$$H = \frac{h_j}{Z} \qquad (4\text{-}1)$$

where h_j is the height of the packing bed at the j^{th} sampling port (m) and Z is the total height of the packing bed (m).

4.2.5. Fractional carbon load and carbon conversion

The fractional carbon load ($f_{C\text{-}Load}$) is the carbon load in gas phase at a specific height H with respect to the total inlet carbon (C-IL). The $f_{C\text{-}Load}$ is calculated by dividing the methanol load at the j^{th} sampling port by the methanol IL. The fractional conversion of inlet carbon to CO_2 ($f_{C\text{-}CO2}$) is the fraction of carbon contained in the C-IL which has been converted to CO_2 at a specific H. The $f_{C\text{-}CO2}$ is calculated by dividing C-PCO_2 at the sampling port j^{th} by the C-IL.

4.2.6. Partition coefficient of methanol

After the BTFs had stabilized and presented nearly constant concentrations of methanol and CO_2 in the outlet gas stream, the methanol concentrations in gas and liquid phases were measured simultaneously. These values were used to determine a partition coefficient. Methanol concentration in gas was measured as indicated above. The concentration of methanol in the liquid phase was measured by injecting 5 µL of filtered samples in a gas chromatograph coupled with a mass spectrometer (GC/MS, HP G1800A, Hewlett Packard, USA). The partition coefficient (PC_j) at each j^{th} sampling port was calculated with Eq. 4-2.

$$PC_j = \frac{[MetOH]_{gas-j}}{[MetOH]_{liquid-j}} \qquad (4\text{-}2)$$

where $[MetOH]_{gas\text{-}j}$ is the concentration of methanol in gas at the j^{th} sampling port and $[MetOH]_{liquid\text{-}j}$ is the corresponding methanol concentration in liquid. Units for both concentrations are mol L^{-1}.

4.3. Results and discussion

4.3.1. Nitrogen concentration in nutrient solution

Figure 4.2 shows the evolution of elimination capacity (EC), biomass production rate (PB) and CO_2 production rate (PCO_2) as a function of nitrogen concentration in nutrient solution. The nutrient solution was prepared with tap water which contained 0.00015 gN L^{-1} of ammoniacal nitrogen. Phosphorus and potassium were also present in tap water in a N:P:K mass ratio of 1:1:10. The content of these nutrients in tap water supported the biological activity in the BTF when any nutrient was not added. In this case the BTF presented a PB of 2.6 g m^{-3} h^{-1} and a PCO_2 of 7.1 g m^{-3} h^{-1}.

EC, PB and PCO_2 increased with nitrogen concentration. EC and PB presented similar trends. In the range of nitrogen concentration from 0 to 0.005 gN L^{-1}, EC increased from 75 to 85 g m^{-3} h^{-1} and PB from 2.6 to 6.7 g m^{-3} h^{-1}. When nitrogen concentration was higher than 0.005 gN L^{-1}, EC and PB tended to a plateau. Some authors report that at low nitrogen concentration the methanol oxidation with methylotrophs is induced by nitrogen, whereas at high nitrogen concentration the same compound becomes inhibitory (REAY and coll., 2004; SMITH and coll., 1977). For example, YANG and coll. (2002) show that the EC and PB decreased in a

biofilter treating methanol when operated at high nitrogen concentration corresponding to a nitrogen:carbon (C:N) mass ratio of 10:4. In the BTF of the present study, EC and PB were not inhibited but they tended to a plateau at the highest nitrogen concentration tested of 0.5 gN L^{-1} (not shown in Figure 4.2), which corresponded to a C:N mass ratio of 10:5.

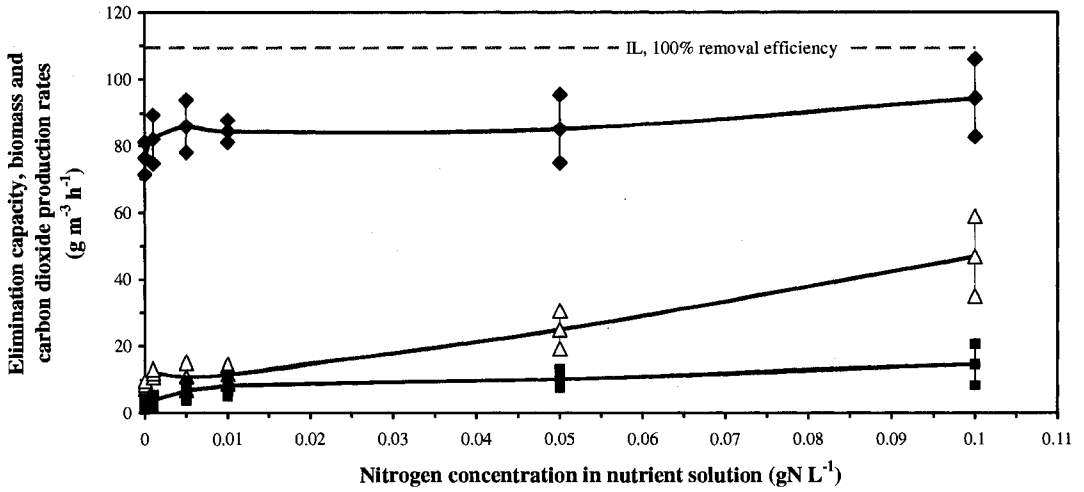


Figure 4.2. Effect of nitrogen concentration on elimination capacity (♦), biomass production rate (■) and carbon dioxide production rate (Δ) at fixed EBRT of 65 s and methanol inlet concentration of 2 g m^{-3}. In the Figure are presented the average values with their respective standard deviations.

Figure 4.2 shows also that PCO_2 increased with nitrogen concentration, but unlike EC and PB, PCO_2 had a small increase initially, from 7.1 to 11 g m^{-3} h^{-1} in the range of nitrogen concentration from 0 to 0.005 gN L^{-1}. Then, in the range from 0.005 to 0.1 gN L^{-1}, PCO_2 increased from 11 to 47 g m^{-3} h^{-1}. Some authors report also that PCO_2 increases with a different tendency that PB does (MOE and coll., 2001; ZHU and coll., 1996). Since nitrogen is essential for specific and non-specific microorganisms, the cellular densities of both populations are able to increase with increased nitrogen concentration. In the case of methanol biofiltration, the methylotrophs produce storage compounds, such as exo-polysaccharides, which are consumed by the non-methylotrophs (LEAK, 1992). If both populations increase

with nitrogen concentration, the production and consumption rates of storage compounds also increase. In this way, as shown in Figure 4.2, the PB increased slightly because the storage compounds are consumed. The increase of cellular densities caused an increase on the energy requirements of microbial population which have to oxidize methanol and storage compounds in order to satisfy these requirements. In this way, PCO_2 increased highly with nitrogen concentration.

As mentioned above, at nitrogen concentrations higher than 0.005 gN L^{-1}, the removal efficiency and the PB increased slightly. This let to the selection of a nitrogen concentration of 0.005 gN L^{-1} for analyzing the effects of other variables, such as empty bed residence time (EBRT), on performance parameters.

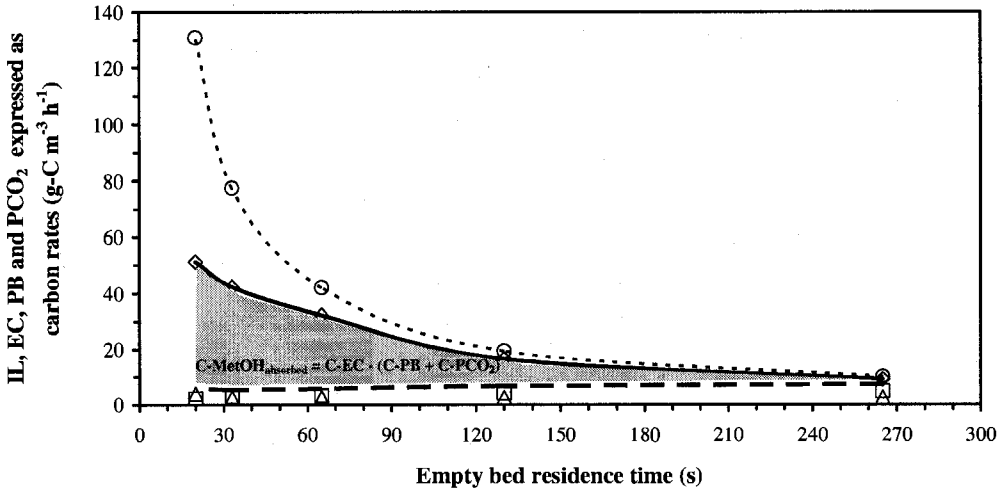
4.3.2. Empty bed residence time

Figure 4.3a shows IL, EC, PB and PCO_2 in terms of their carbon content (C-IL, C-EC, C-PB and C-PCO_2) as a function of EBRT. The C-IL (dotted line) is the total carbon which enters to the BTF and the C-EC (solid line) is the total carbon which is removed from the gas phase. For this experimental study, the BTF was operated at a methanol inlet concentration of 2 g m^{-3} and five EBRT in the range from 20 to 265 s were tested.

As shown in Figure 4.3a, the C-EC approached to C-IL as the EBRT increased. When the BTF operated at 20 s, C-IL was 131 g of C m^{-3} h^{-1} and C-EC was 51 g of C m^{-3} h^{-1}. At 265 s, C-IL was 10 g of C m^{-3} h^{-1} and C-EC was 9 g of C m^{-3} h^{-1}. In Figure 4.3a, C-PB and C-PCO_2 are the rates at which carbon is converted to biomass and CO_2. The addition of both rates (C-PB + C-PCO_2) is the total carbon removed by microbial activity (dashed line), which increased from 6.1 to 7.3 g of C m^{-3} h^{-1} for the range of EBRTs studied. Since methanol is water soluble, it can be removed by absorption into the liquid phase. The rate at which methanol was removed by absorption (C-$MetOH_{absorbed}$) was calculated by subtracting the value of methanol removed by microbial activity from the corresponding value of total removal of methanol from gas phase (C-EC) and expressed as follows:

$$(C\text{-}MetOH_{absorbed}) = (C\text{-}EC) - (C\text{-}PB + C\text{-}PCO_2) \quad (4\text{-}3)$$

a)



b)

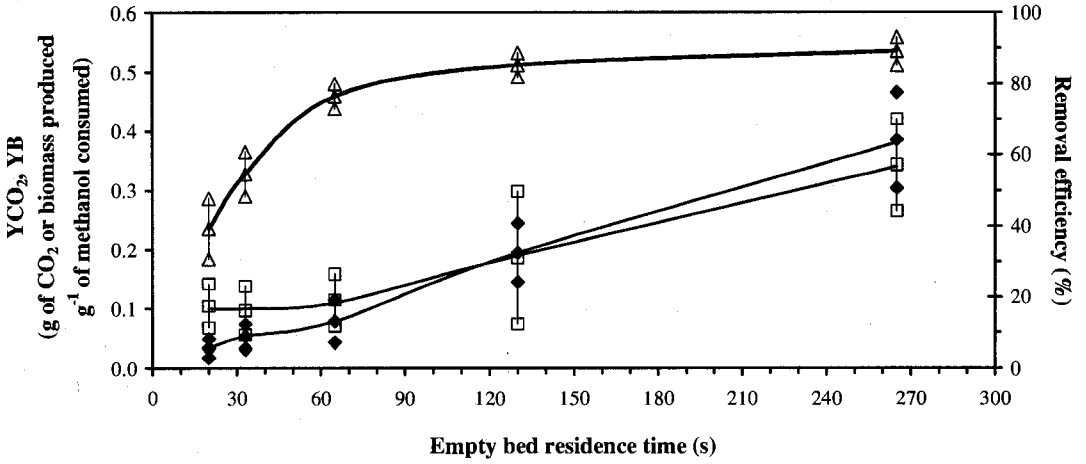


Figure 4.3. Effect of the empty bed residence time on removal and conversion of methanol at fixed nitrogen concentration in nutrient solution of 0.005 gN L^{-1} and methanol inlet concentration of 2 g m^{-3}. Figure 4.3a shows the equivalent carbon rates for inlet load C-IL (--○--), elimination capacity C-EC (—◊—), biomass production rate C-PB (Δ), carbon dioxide production rate C-PCO_2 (□) and the addition of (C-PB + C-PCO_2) (— —). Figure 4.3b shows the average values (± standard deviation) of removal efficiency (Δ), carbon dioxide yield coefficient YCO_2 (♦) and biomass yield coefficient YB (□).

According to Figure 4.3a, C-$MetOH_{absorbed}$ (gray area) was function of EBRT and decreased from 45 g of C m^{-3} h^{-1} at 20 s to 2 g of C m^{-3} h^{-1} at 265 s.

Figure 4.3b shows the effect of EBRT on removal efficiency (X) and methanol conversion to biomass (YB) and CO_2 (YCO_2). The BTF improved its performance with EBRT by increasing X from 20 to 90% in the range of EBRT from 20 to 265 s. In the same range of EBRT, YB and YCO_2 increased with similar tendencies and presented values from around 0.05 to 0.35 g of biomass or CO_2 g^{-1} methanol consumed. According to Figure 4.3b, as EBRT increased, the time for absorbing, transporting and degrading methanol in the biofilm also increased. The YB and YCO_2 increased with EBRT at a nearly constant rate. Since the nitrogen concentration in nutrient solution and the methanol inlet concentration were fixed, the microbial species in biofilm should not present changes. This means that the increase of YB and YCO_2 was due to the increase of time for occurring the phenomena mentioned above.

4.3.3. Methanol inlet concentration

Figure 4.4 shows the evolution of EC as a function of methanol IL at a fixed nitrogen concentration of 0.005 gN L^{-1}. The IL was varied by operating the BTF at three EBRTs (20, 30 and 65 s) in a range of methanol inlet concentration from 0.3 to 37 g m^{-3}. EC increased with IL and a tendency curve of first order kinetic fitted to the ECs of three EBRTs. The maximum EC was 2160 g m^{-3} h^{-1} and was observed at the highest IL of 3700 g m^{-3} h^{-1}. At this IL, the EC tended to the region where it becomes independent of IL, which means that the pollutant is removed by means of a zeroth order reaction (OTTENGRAF and coll., 1983). These results presented a similar behaviour of those reported by AVALOS RAMIREZ and coll. (2007b) for a BTF treating ethanol vapours. The authors observed that at an ethanol IL as high as 1610 g m^{-3} h^{-1}, the BTF did not reach the region at which the kinetic of pollutant degradation is of zeroth order. In a study performed by SOLOGAR and coll. (2003), a BTF treating methanol was tested at ILs up to 400 g m^{-3} h^{-1} and the behaviour of EC was similar to that observed in the present study. The EC followed a first order kinetic and not a zero order kinetic behavior.

Figures 4.5a and 4.5b show the evolution of YB and YCO_2 as functions of methanol inlet concentration. For the three EBRTs (20, 30 and 65 s), YB and YCO_2 dropped immediately. In the range of methanol inlet concentration from 0.3 to 2 g m^{-3}, YB decreased from 0.54 to 0.055 g of biomass produced g^{-1} of methanol consumed and YCO_2 from 0.57 to 0.1 g of CO_2 produced g^{-1} of methanol consumed. For concentrations higher than 2 g m^{-3}, YB and YCO_2

decreased slightly and tended to nearly constant values of 0.005 and 0.01 g of biomass or CO_2 produced g^{-1} of methanol consumed, respectively. The YB obtained at small methanol concentrations is comparable to the YB reported in literature for methylotrophs, which is in the range from 0.3 to 0.54 g of biomass produced g^{-1} of methanol consumed (CRUEGER and coll., 1990). A similar behaviour for YB and YCO_2 was observed in a BTF treating air polluted with ethanol, a very water soluble VOC (AVALOS RAMIREZ and coll., 2005).

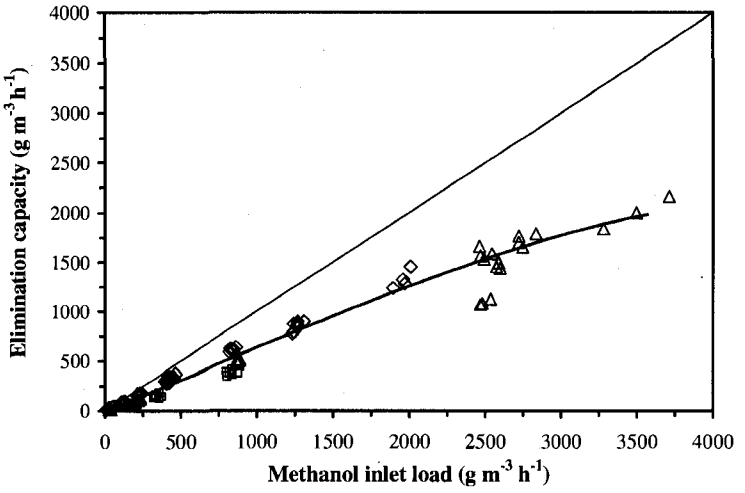


Figure 4.4. Elimination capacity as a function of methanol inlet load. The biotrickling filters operated at fixed nitrogen concentration of 0.005 gN L^{-1} and EBRTs of 20 s (□), 30 s (Δ) and 65 s (◊) in the range of methanol inlet concentration from 0.3 to 37 g m^{-3}.

In BTFs operating at steady state, the concentration of methanol in liquid increased proportionally with the concentration in the gaseous phase. The increase of methanol concentration in liquid caused the inhibition of specific and non-specific microorganisms. But, as shown in Figures 4.5a and 4.5b, the BTF presented microbial activity at a methanol inlet concentration as high as 37 g m^{-3}. For this concentration, the logarithmic average concentration (C_{ln}) in the BTF was 20 g m^{-3}. Assuming that methanol concentrations in gas and liquid phases were in equilibrium and using the partition coefficient of methanol in water at 32°C equal to 3.05×10^{-4} [mol L^{-1}]$_{gas}$/[mol L^{-1}]$_{liquid}$ (GUPTA and coll., 2000), the highest concentration of methanol in liquid was around 65 g L^{-1}. At this concentration methylotrophs

were able to biodegrade small quantities of methanol. But at high methanol concentrations or ILs, PB and PCO_2 were negligible in comparison to the values of EC observed. For example, for ILs higher than 800 g m^{-3} h^{-1}, PCO_2 was in the range from 15 to 22 g m^{-3} h^{-1} and PB was around 5 g m^{-3} h^{-1} while EC was higher than 500 g m^{-3} h^{-1}. This shows that the methanol removal at these operating conditions was mainly due to the methanol absorption by the nutrient solution.

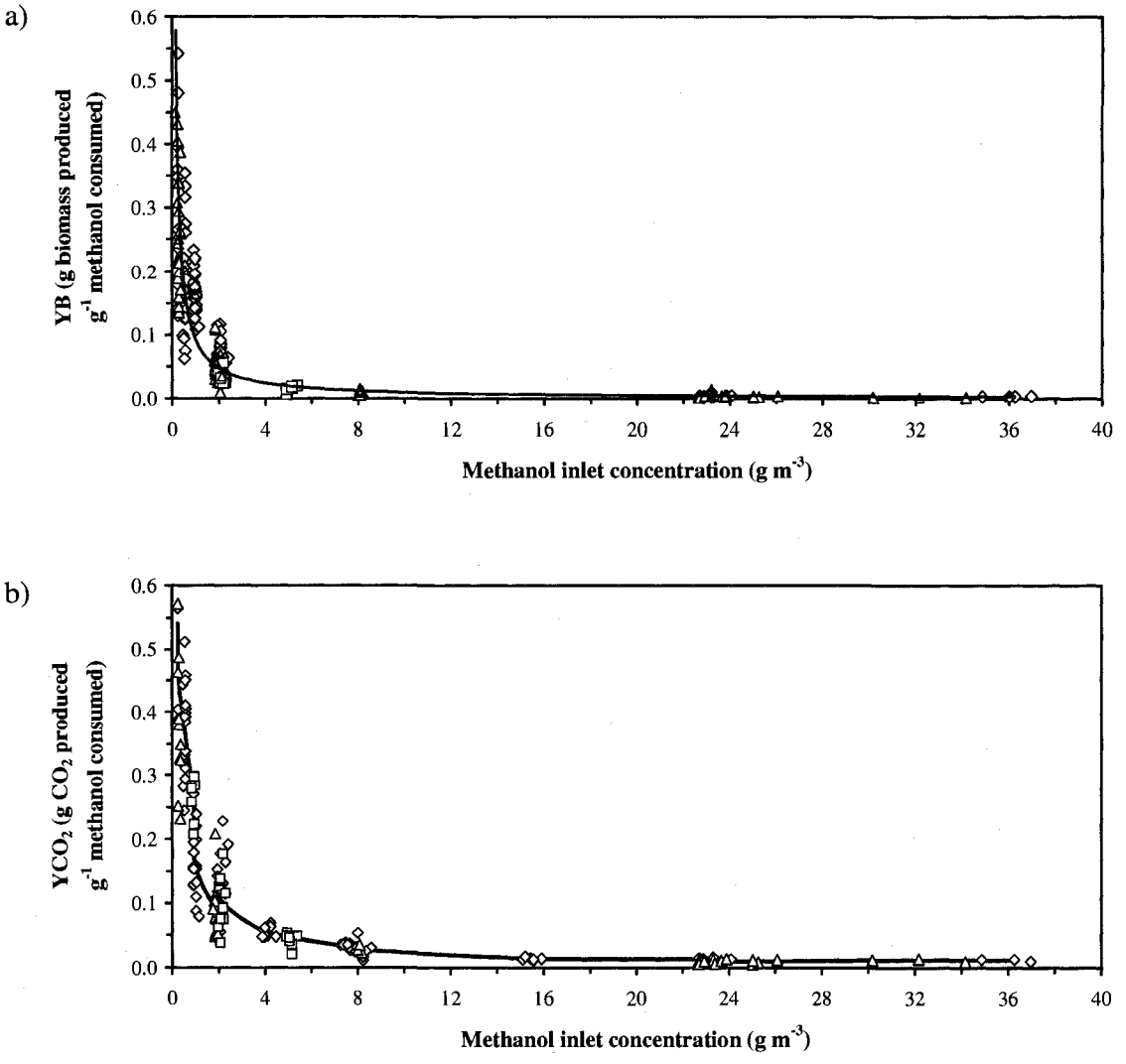


Figure 4.5. Effect of methanol inlet concentration on a) biomass yield coefficient (YB) and b) carbon dioxide yield coefficient (YCO_2). The biotrickling filters operated at fixed nitrogen concentration of 0.005 gN L^{-1} and 3 EBRTs: 20 s (□), 30 s (Δ) and 65 s (◊).

The range of methanol inlet concentration at which operates a BTF for treating methanol vapours in industrial facilities is smaller than the range tested in the present study. For example, the average concentration of methanol in gas effluents from pulp and paper industry is around 0.4 g m^{-3} (GARNER, 1996). This means that for industrial applications, the BTF should operate at methanol inlet concentrations which produce high performance and high yield coefficients of biomass and CO_2. According to Figures 4.4, 4.5a and 4.5b, at methanol inlet concentrations equal or smaller than 0.4 g m^{-3}, the BTF presented removal efficiencies higher than 90%. Similarly, YB and YCO_2 are higher than 0.2 and 0.3 g of biomass or CO_2 produced g^{-1} of methanol consumed, respectively.

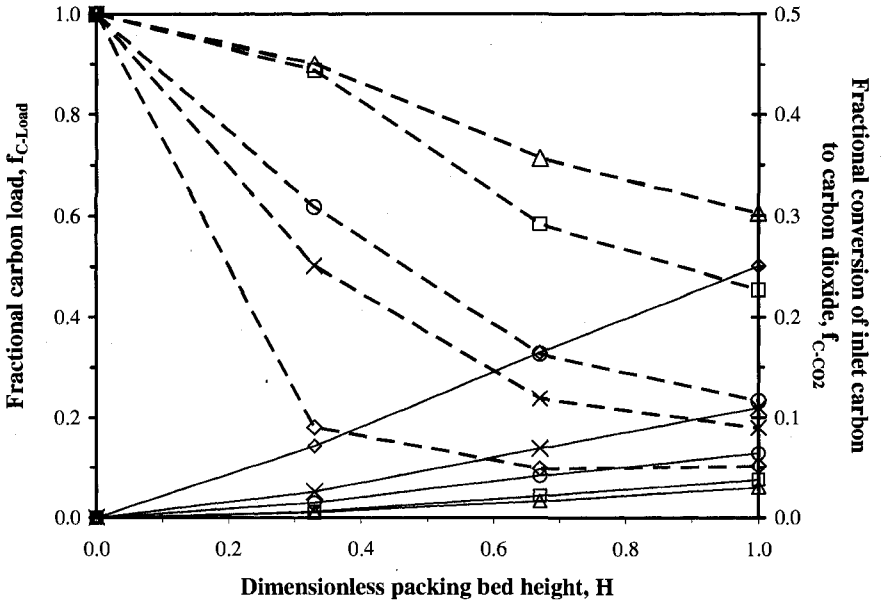


Figure 4.6. Profiles of fractional carbon load $f_{C\text{-}Load}$ (- -) and fractional conversion of carbon load to carbon dioxide $f_{C\text{-}CO2}$ (——) along the packing bed height. The EBRTs for $f_{C\text{-}Load}$ and $f_{C\text{-}CO2}$ are designed as follows: 20 s (Δ), 30 s (□), 65 s (○), 130 s (×) and 265 s (◊).

4.3.4. Methanol removal profiles

Figure 4.6 shows the evolution of the fractional carbon load ($f_{C\text{-}Load}$) and the fractional conversion of inlet carbon to CO_2 ($f_{C\text{-}CO2}$) as functions of the dimensionless height of packing

bed (H). The profiles of $f_{C\text{-}Load}$ and $f_{C\text{-}CO_2}$ were determined at a constant methanol inlet concentration of 2 g m^{-3} and five EBRTs: 20, 30, 65, 130 and 265 s. According to Figure 4.6, when the BTF operated at 265 s, the $f_{C\text{-}Load}$ was 0.2 at H=0.33, 0.1 at H=0.67 and 0.1 at H=1, which corresponded to X of 90%. In comparison, when the BTF operated at 20 s, the $f_{C\text{-}Load}$ was 0.9 at H=0.33, 0.7 at H=0.67 and 0.6 at H=1, which represented X of 40%. This confirms the observations discussed above, methanol removal increased with EBRT.

As opposed to $f_{C\text{-}Load}$, the $f_{C\text{-}CO_2}$ presented nearly constant slopes for the 5 EBRTs tested. As shown in Figures 4.5a and 4.5b PB and PCO_2 correlated highly through all the experiments. Since carbon contained in the methanol molecule is converted to biomass and CO_2, it is possible to use the CO_2 as an indicator of methanol elimination by microbial activity. In this way, the constant slopes of $f_{C\text{-}CO_2}$ suggest that the biodegradation rates of methanol were uniform along the packing bed. The comparison of the constant slopes of $f_{C\text{-}CO_2}$ to the slopes of $f_{C\text{-}Load}$ shows that methanol was removed by means of a constant biodegradation rate at each EBRT and a variable absorption rate which was function of EBRT and H. The methanol removal profiles observed in the present study are characteristic of water soluble VOCs. For example, similar removal profiles have been observed in the biotrickling filtration of water soluble VOCs, such as methylethylketone and methylacetate (CHOU and coll., 1997; LU and coll., 2001).

4.3.5. Temperature of packing bed and lixiviate

Figure 4.7 shows the difference of temperatures ΔT_{pb} between the temperature of the packing bed and the temperature of laboratory (T_e), around 24°C, along H and as a function of EBRT. Figure 4.7 shows also the difference of temperature ΔT_{ns} between the temperature of nutrient solution in the holding tank and T_e. ΔT_{ns} was smaller than ΔT_{pb} in the range of EBRT from 20 to 265 s. At an EBRT of 15 s it was observed that ΔT_{ns} was equal to ΔT_{pb} for the three sections of packing bed. When the BTF operated at 15 s, the production of biomass and CO_2 was not detectable. This suggests that the BTF did not present microbial activity at 15 s. In this way, ΔT_{ns} and ΔT_{pb} at 15 s were due to the heating effect of nutrient solution, which absorbed the heat diffused by the centrifugal pump when it was pumped to the BTF. In this way, when nutrient solution trickled through the BTF, it heated the packing material and maintained a constant temperature along the packing bed.

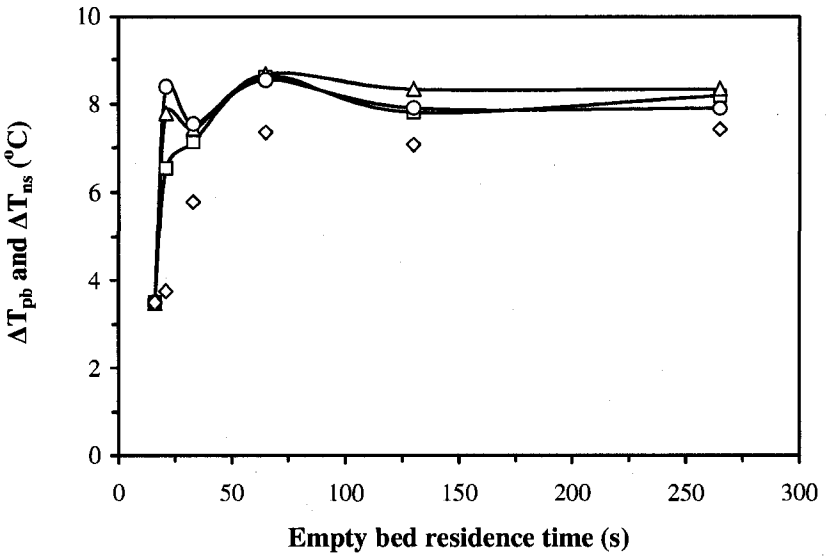


Figure 4.7. Evolution of the differences of temperature for the packing bed (ΔT_{pb}) and for the nutrient solution (ΔT_{ns}) with respect to the external temperature (24°C). The ΔT_{pb} at each dimensionless packing bed height is indicated as follows: H=0.33 (□), H=0.67 (Δ), H=1 (○). The ΔT_{ns} is indicated by (◊).

For EBRTs equal or higher than 65 s, ΔT_{ns} and ΔT_{pb} were nearly stable at around 7 °C and 8.5 °C, respectively. According to Figure 4.3a, the PB and PCO_2 increased slightly in the range from 65 to 265 s. This signifies that the rate at which the energy was released by the bioreaction to the environment was nearly constant. This energy should be also absorbed by the nutrient solution. In this way, the nutrient solution maintained a constant and uniform temperature in the packing bed by releasing or receiving energy. This favoured the methanol removal because the BTF operated at 32°C, near the optimal temperature of methylotrophic growth which is around 30°C (GREEN, 1992).

4.3.6. Partition coefficient

Figure 4.8a shows the evolution of average methanol concentrations in gas and liquid phases inside the BTF as a function of EBRT. The experiments were performed at a fixed methanol inlet concentration of 2 g m^{-3} and at nearly constant temperature around 32°C along the packing bed. The methanol concentrations in both phases decreased with EBRT from $1.7x10^{-4}$

to $0.01x10^{-4}$ mol L^{-1} in gas phase and from 0.1 to 0.02 mol L^{-1} in the liquid phase. The average concentrations for both phases in Figure 4.8a are well described by Eq. 2. This suggests that methanol concentration in both phases reached the thermodynamic equilibrium in the BTF.

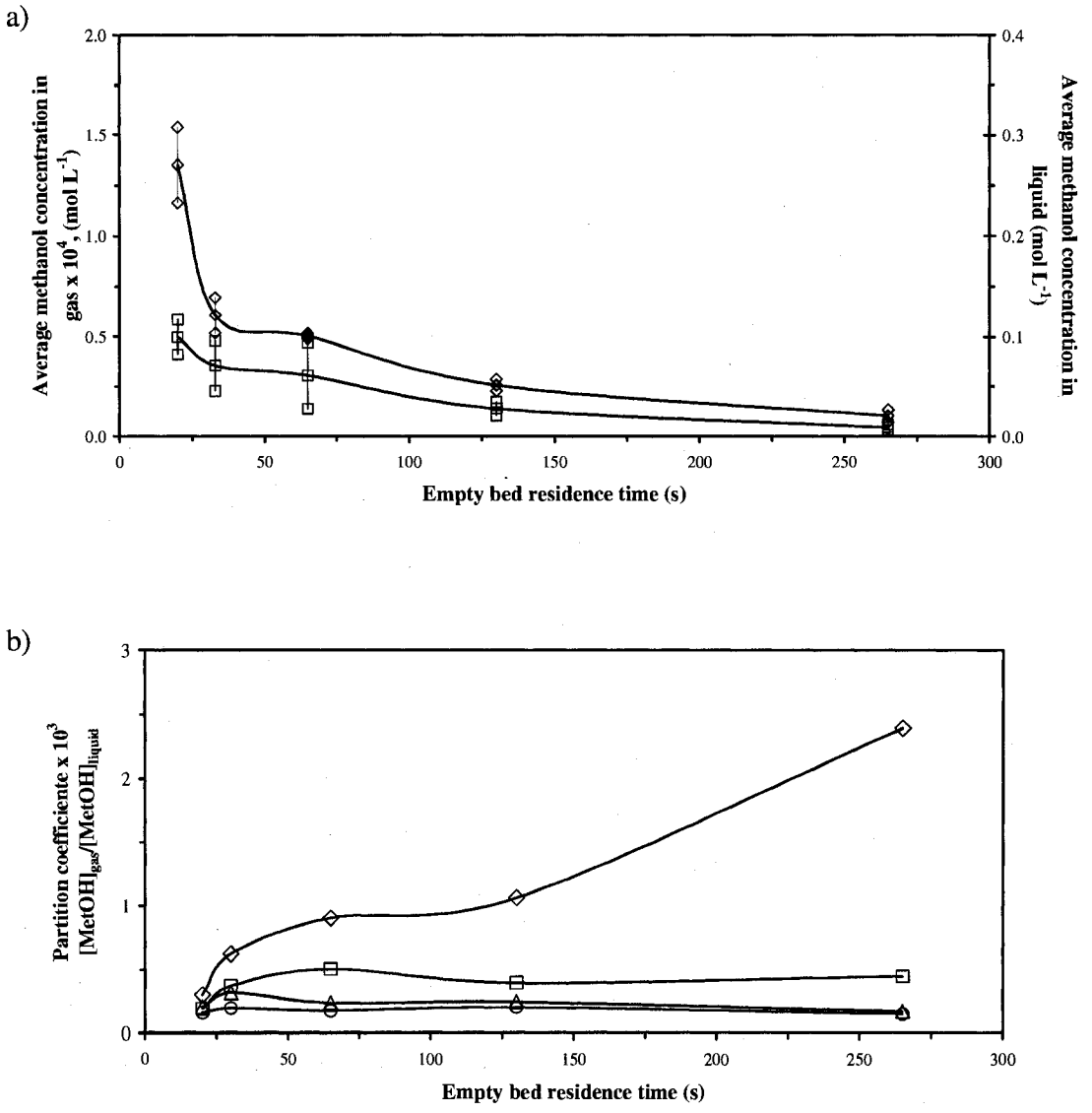


Figure 4.8. a) Average of methanol concentration in gas (□) and liquid (◊) phases as functions of empty bed residence time. b) Partition coefficient along the packing bed height: H=0.0 (◊), H=0.33 (Δ), H=0.66 (□), H=1.0 (○).

Figure 4.8b shows the partition coefficient (PC) at the j^{th} sampling port for the five EBRTs tested. The PC at H=0.0 was higher than the PC observed at H from 0.33 to 1. The H=0.0 corresponded to the inlet of air stream to the BTF, where the gas and the liquid come in contact. This suggests that the PC for H=0.0 was calculated with methanol concentrations in gas and liquid phases which were not in equilibrium, because both phases need to be in contact a certain time in order to transfer the VOC from gas to liquid and reach the equilibrium. For the H in the range from 0.33 to 1.0, the PC was not affected by EBRT and had an average value of 2.64×10^{-4} $[\text{mol } L^{-1}]_{gas}/[\text{mol } L^{-1}]_{liquid}$.

In the determinations of PC, the BTF was operated with a nutrient solution which had low concentration of salts. In this way, the PC obtained was compared to the PC for methanol in water at 32°C, which was calculated with data published by GUPTA and coll. (2000) and was equal to 3.05×10^{-4} $[\text{mol } L^{-1}]_{gas}/[\text{mol } L^{-1}]_{liquid}$. The PC calculated was 15% higher than the PC obtained in the present study. As shown in the literature (LIN and coll., 2006; TEJA and coll., 2001), the presence of compounds which modify the solubility of VOCs in water affects the PC. For example salts and suspended biomass generally reduce the solubility of VOCs in water and in consequence their concentration in the liquid phase. According to Eq. 2, when the concentration of VOC in the liquid decreases, the PC increases.

From 50 to 90% of the carbon contained in the biomass produced by microorganisms could be in the form of extracellular polymeric substances (EPS) (BAKKE and coll., 1984). The EPS are compounds rich in polar constituents (positive and negative charged residues) which are able to bind water (HART and coll., 1999). Additionally, FARRUGIA (1999) observed that the biofilm developed in biofilters treating methanol contained a high percentage of EPS. Since methanol is a polar molecule which could be also attracted by polar residues, the presence of EPS in the nutrient solution instead of decreasing the solubility of methanol might produce the opposite effect and cause PC to decrease, which was observed in the present study.

4.4. Conclusion

The treatment of methanol vapours in biotrickling filters packed with inert polypropylene spheres was studied. The elimination capacity, biomass and carbon dioxide production rates increased with nitrogen concentration in the range from 0.0 to 0.1 gN L^{-1}. The biotrickling

filter presented microbial activity when it operated with tap water without adding nutrients. A nitrogen concentration of 0.005 gN L^{-1} was selected for studying the effects of empty bed residence time (EBRT) on biotrickling filter performance. Removal efficiency and biomass and carbon dioxide yield coefficients increased with EBRT.

The biotrickling filter presented its maximum EC of 2160 g m^{-3} h^{-1} at an IL of 3700 g m^{-3} h^{-1}. Methanol was removed by two mechanisms: biodegradation and absorption in liquid. The continuous trickling of nutrient solution produced uniform degradation rates which were function of EBRT and a nearly constant temperature of 32°C along the packing bed. The biotrickling filter operating at the steady state at 32°C had an average value for the methanol partition coefficient of 2.64×10^{-04} $[\text{mol } L^{-1}]_{gas}/[\text{mol } L^{-1}]_{liquid}$.

Acknowledgements

The authors express their sincerely acknowledgements to Natural Sciences and Engineering Research Council of Canada for the financial support.

SECTION III. DETERMINATION DES PARAMETRES CINETIQUES DE LA CROISSANCE MICROBIENNE ET DE LA BIODEGRADATION DE COMPOSES ORGANIQUES VOLATILS DANS DES BIOFILTRES AVEC ET SANS PERCOLATION.

Chapitre 5. Méthode pour déterminer les paramètres microcinétiques d'un consortium microbien présent dans le biofilm développé dans un biofiltre traitant des vapeurs de méthanol garni avec un lit inerte

Article « *Experimental calculation of micro-kinetic parameters of a microbial consortium degrading methanol in an air treatment biofilter* », qui a été soumis dans le journal « Biodegradation ».

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Résumé

Une nouvelle méthode expérimentale pour calculer les paramètres cinétiques de croissance d'un biofilm développé dans un biofiltre traitant du méthanol a été développée. La méthode consiste en la détermination des paramètres cinétiques sous des conditions proches de celles auxquelles le biofilm est exposé dans un biofiltre opérant en régime quasi-permanent. Une procédure mathématique a été adaptée pour calculer les paramètres cinétiques à partir des concentrations de méthanol et de dioxyde de carbone présents dans la phase gazeuse d'un bioréacteur. La procédure mathématique utilisée établit une différence entre la quantité de méthanol absorbé et celle biodégradée.

Les paramètres microcinétiques ont été déterminés à une température de 25°C. Les résultats démontrent que la vitesse de croissance spécifique a répondu au modèle d'Haldane, étant donné que le méthanol inhibe les microorganismes. Les vitesses de croissance maximales expérimentales ont été de 0.049 h^{-1} pour un biofiltre garni avec des sphères d'argile et de 0.007 h^{-1} pour un biofiltre garni avec des boulettes de compost, tandis que les vitesses de croissance maximales calculées avec le modèle d'Haldane ont été respectivement de 0.044 et 0.007 h^{-1}.

Il a été observé que si les concentrations de méthanol dans le gaz et le biofilm s'approchent de l'équilibre thermodynamique, la diminution de la concentration de méthanol dans la phase gazeuse est contrôlée par le taux de biodégradation du méthanol dans le biofilm, lequel reste constant. La méthode développée peut être appliqué aux biofiltres traitant d'autres composés organiques volatils solubles dans l'eau.

5. Experimental calculation of micro-kinetic parameters of a microbial consortium degrading methanol in an air treatment biofilter

Abstract

An experimental method for calculating the microkinetic parameters of a microbial consortium which degrades methanol in an air treatment biofilter was developed. The kinetic parameters for microbial growth were calculated by taking biomass from biofilters packed with clay spheres or compost pellets. The micro-kinetic runs were carried out in batch bioreactors at a constant temperature of 25°C. The results obtained show that the growth rate of microorganisms was inhibited by methanol concentrations in biofilm higher than 13 kg m^{-3} for clay spheres and 40 kg m^{-3} for compost pellets. The Haldane model fitted to experimental specific growth rate μ in both cases. μ_{max} estimated with this model was 0.044 h^{-1} for clay spheres and 0.007 h^{-1} for compost pellets. The method developed in the present study could be easily applied to biofilters treating water soluble organic volatile compounds.

5.1. Introduction

The control of emissions of volatile organic compounds (VOCs) to the atmosphere by means of bioprocesses, such as biofiltration, has increased since the 1980s (JORIO and coll., 1999). VOC biodegradation inside biofilters occurs through a combination of biological, physical and chemical phenomena. The performance of biofilters depends on packing material and type of microorganisms present in the biofilters (DELHOMÉNIE and coll., 2005b). The understanding of these phenomena leads to an appropriate selection of operating conditions for the biofilter. In order to estimate the biofilter performance, mathematical models with macrokinetic or microkinetic approaches have been developed as reported by STREESE and coll. (2005) and IKEMOTO and coll. (2006).

In general, the mathematical models with a microkinetic approach include a cell growth model whose kinetic parameters must be determined experimentally. These kinetic parameters are function of the kind and concentration of microorganisms in the biofilm as well as the pollutant to be treated. Several methods developed to determine these parameters use pure or

isolated strains in suspended culture (JUTEAU, 1997; SHAREEFDEEN and coll., 1993; OTTENGRAF and coll., 1983) instead of the microbial consortium developed in the biofilters. In order to calculate the microkinetic parameters for the real conditions to which the biofilm is subjected in the biofilters, recent studies proposed the use of biofilm immobilized on the packing material (DELHOMÉNIE, 2002; GOVIND and coll., 1997). With this objective, DELHOMÉNIE (2002) developed a method for calculating the kinetics of microbial growth rate for a biofilter packed with compost pellets for treating toluene. The method consists of taking packing material covered with biofilm and putting it in a batch bioreactor in order to follow the biodegradation of toluene.

In a bioreactor for determining the kinetics of microbial growth, the concentration in gas phase of water soluble VOCs, such as methanol, presents a behaviour which is different than that of low water soluble VOCs, such as toluene. For high water soluble VOCs, a new experimental method and the appropriate mathematical procedure must be developed to account for the rapid absorption of water soluble VOC. The mathematical procedure must include steps which allow determining the amounts of VOC biodegraded and VOC absorbed. This leads to the estimation of actual kinetic parameters. The present study was focussed on developing a method for calculating the growth kinetic parameters of a microbial consortium present in a biofilter treating methanol, a high water soluble VOC.

5.2. Materials and methods

5.2.1. Biofilters

Two biofilters were constructed from Plexiglas cylinders with an internal diameter of 0.15 m and a total bed height of 1 m. One biofilter was packed with compost pellets and the other with clay spheres (Hydroton®, Ökotau GmbH, Germany). Biofilters were inoculated with a lixiviate issued from a biotrickling filter which had been treating methanol vapors (AVALOS RAMIREZ and coll., 2005). Both biofilters were operated at a methanol inlet concentration of 1.5 g m^{-3} and 130 s of empty bed residence time.

5.2.2. Kinetic bioreactors and handling of packing material

When the biofilter operated at steady state, samples of biofilm were taken. In the case of biofilter packed with clay spheres, the samples were clay spheres covered with biofilm. In the

case of biofilter packed with compost pellets, the samples were biofilm detached from the pellets. A sample was introduced for 1 hour in a sealed chamber and a clean and humidified air stream circulated inside in order to deplete the methanol contained in the biofilm. Hermetic and sterile Pyrex bottles with a total volume of 600 mL (model #1396, Corning, US) were used as batch bioreactors. The bioreactors were equipped with open top caps for fixing a septum of polytetrafluoroethylene (PTFE) faced silicone (model GL45, Kimble/Kontes, US). The sample was put into a bioreactor which was hermetically closed and maintained at constant temperature of 25°C in a controlled temperature bath (Julabo, model P, Germany). One hour after putting the bioreactor in the constant temperature bath, a known volume of liquid methanol was injected into the bioreactor by using liquid handling syringes from 5 to 100 µL (Hamilton, US). During each kinetic experiment, the methanol and carbon dioxide concentrations in the bioreactor headspace were followed by taking 100 µL samples of gas with a manual injection GC syringe (Gastight #1710, Hamilton Co., US). The gas samples were analyzed in a gas chromatograph coupled to a mass spectrometer (GC/MS, HP G1800A, Hewlett Packard, USA). The GC was periodically calibrated with known amounts of methanol (98 % w/w, Anachemia, Canada) taken from a calibration unit.

After finishing the kinetic experiment, the sample contained in the bioreactor was transferred to a porcelain crucible and dried at 105°C in order to determine the water content (SLUITER and coll., 2005). The crucibles were put into an oven for calcining the volatile solids and determining the final dry biomass according to the Standard Method 2540-E (APHA 1999).

The density of biofilm was determined periodically by taking approximately 1 g of biofilm in a 10 mL volumetric flask. The total volume (10 mL) was filled with distillated water at 20°C. The volume of water added let to the calculation of the volume of biofilm. The mass of biofilm was calculated by subtracting the masses of the flask with and without biofilm. The density of the biofilm was calculated by dividing the mass of biofilm by its volume.

The volume of biofilm in the sample was calculated by dividing the wet mass of biofilm contained in the sample by the density of biofilm calculated above. When the sample was the biofilm detached from compost pellets, the total volume of the sample was the volume of biofilm. When the sample was clay spheres, the total volume of the sample was the addition of biofilm and clay spheres volumes. The volume of clay spheres was measured by placing them

after calcining in a graduated cylinder containing a known volume of water. The increase of liquid level in the cylinder indicated the volume of clay spheres.

5.3. Results

Figure 5.1 shows the decrease of methanol concentration in the gas phase ($C_{MetOH\text{-}gas}$) of the bioreactor containing clay spheres covered with biofilm. For the experiment presented in Figure 1, 15 µL of liquid methanol were injected at 0 h. Methanol evaporated instantaneously and at 0.025 h the $C_{MetOH\text{-}gas}$ increased up to 11.5 g m^{-3}. Afterwards, the $C_{MetOH\text{-}gas}$ decreased with time and at the end of experiment, at 6.1 h, it was 0.85 g m^{-3}, which corresponded to a decrease of 85%.

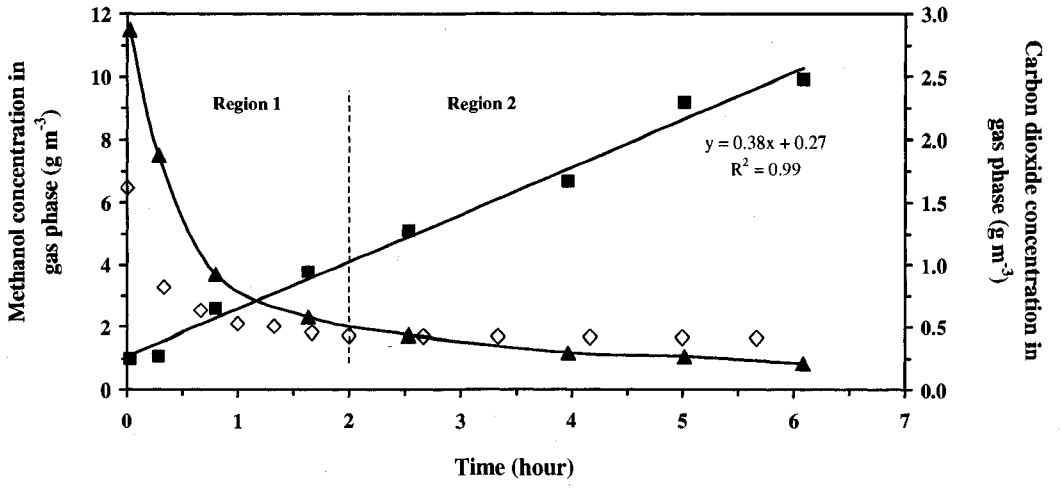

Figure 5.1. Evolution of methanol (—▲—) and carbon dioxide (—■—) concentrations in the gas phase of batch bioreactor. For the kinetic experiment, 15 µL of liquid methanol were injected in the bioreactor. Evolution of methanol concentration in the blank (◊) containing drops of water in the bioreactor.

In Figure 5.1, it is possible to identify two regions for the behavior of $C_{MetOH\text{-}gas}$. Region 1 occurred at the beginning of the experience and finished at around 2.5 h. This region was characterized by a quick decrease of $C_{MetOH\text{-}gas}$, from 11.5 g m^{-3} at 0.025 h to 2.5 g m^{-3} at 2.5 h. For all methanol concentrations tested, the region 1 presented the same behavior and varied

from 1 to 3 hours long. The duration of region 1 was a function of the volume of liquid methanol injected. In Figure 5.1, region 2 was characterized by a slow decrease of $C_{MetOH\text{-}gas}$, from 2.5 g m^{-3} at 2.5 h to 0.85 g m^{-3} at 6.1 h. Region 2 presented the same behavior for all methanol concentrations.

Figure 5.1 shows also the CO_2 concentration in gas ($C_{CO_2\text{-}gas}$) as a function of time. $C_{CO_2\text{-}gas}$ increased from 0.25 g m^{-3} at 0.025 h to 2.5 g m^{-3} at 6.1 h.

Figure 5.2 presents the evolution of methanol concentration in the biofilm ($C_{MetOH\text{-}biofilm}$) for the bioreactor presented in Figure 1. At 0h, $C_{MetOH\text{-}biofilm}$ was near zero and increased up to a maximum value of 6.4 kg m^{-3} at 0.8 h, afterwards it decreased with time and had a value of 4.1 kg m^{-3} at the end of the experiment, at 6.1 h.

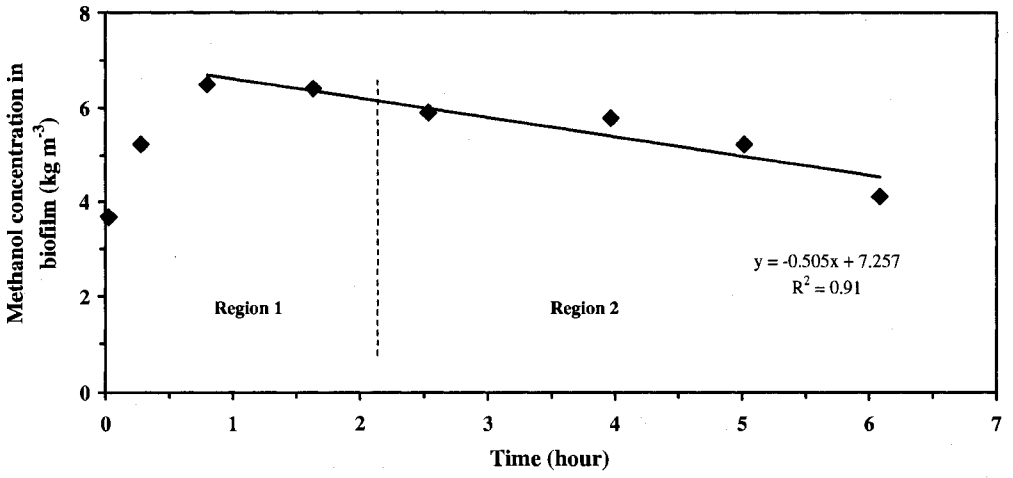

Figure 5.2. Evolution of methanol concentration in biofilm (♦) in the gas phase of batch bioreactor. The experiment corresponds to data presented in Figure 5.1.

Figure 5.3 shows the logarithm of biomass as a function of time for the experiment presented in Figure 5.1. Figure 5.3 shows that biomass increased with time at a specific growth rate (μ) of 0.017 h^{-1}.

Figure 5.4 shows μ as a function of $C_{MetOH\text{-}biofilm}$ for the biofilm developed in the biofilter packed with clay spheres. The experiments were performed at $C_{MetOH\text{-}biofilm}$ ranging from 0.5 to 48 kg m^{-3}. The maximal μ (μ_{max}) was 0.049 h^{-1} and occurred at a $C_{MetOH\text{-}biofilm}$ of 13.2 kg

m^{-3}. Figure 5.4 shows the experimental μ (lozenges) and μ estimated with the Monod model (dashed line) and the Haldane model (solid line).

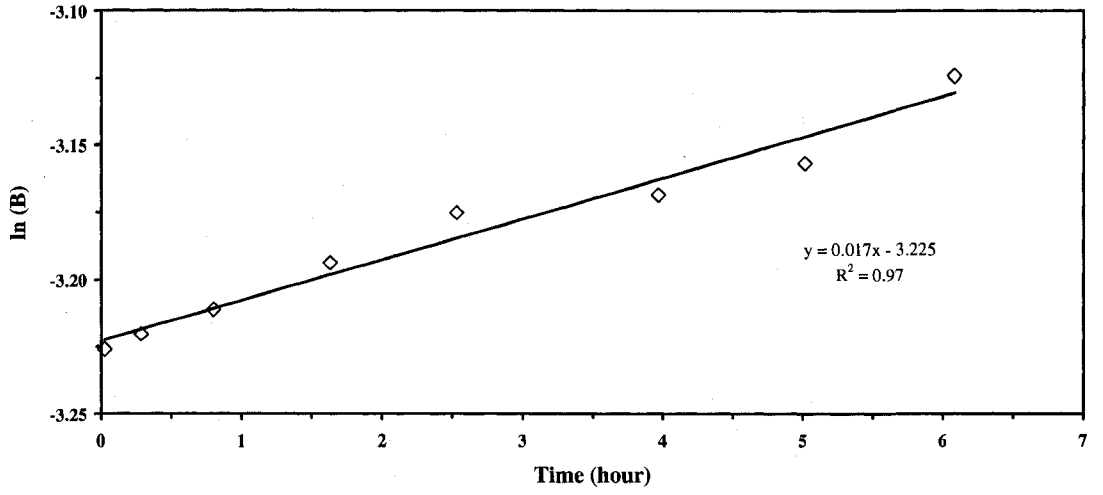

Figure 5.3. Ln (B) as a function of time for the experiment presented in Figure 1. The slope of 0.017 h^{-1} calculated by linear regression corresponds to the specific growth rate (μ) for a methanol concentration in biofilm of 6.4 kg m^{-3}.

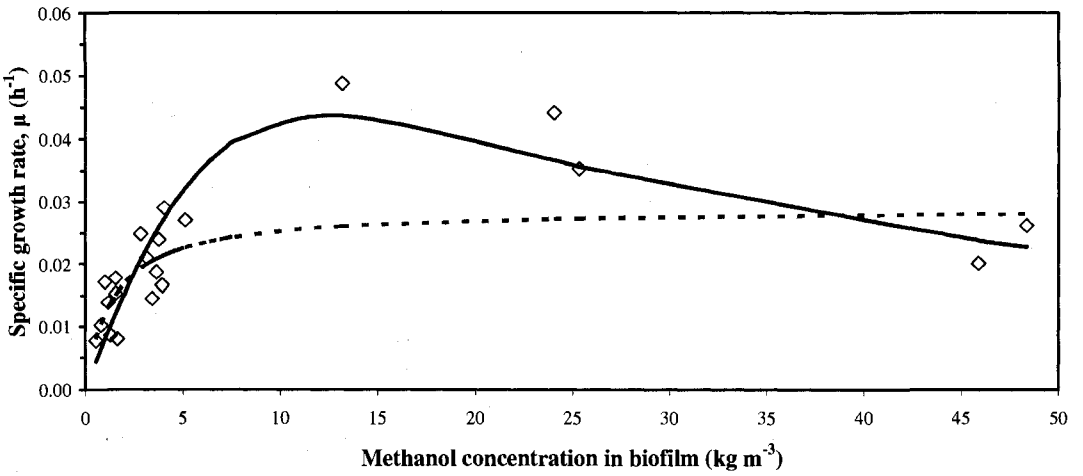

Figure 5.4. Specific growth rate of microbial consortium developed in a biofilter packed with clay spheres as a function of methanol concentration in biofilm. Experimental μ (◊), μ estimated with Monod model (- - -), μ estimated with Haldane model (——).

Figures 5.5 and 5.6 show Eqs. A-2 and A-5 fitted to experimental data of $C_{MetOH\text{-}biofilm}$ and μ. By means of linear regression of Eq. A-2 and quadratic regression of Eq. A-5, the kinetic parameters for Monod and Haldane models were obtained. For the Monod model the μ_{max} calculated was 0.029 h^{-1} and K_S 1.41 kg m^{-3}. For the Haldane model the μ^* was 0.295 h^{-1}, μ_{max} 0.044 h^{-1}, K_S 35.7 kg m^{-3} and K_I 4.32 kg m^{-3}.

For the biofilter packed with compost pellets was followed the same procedure. Figure 5.7 shows μ for the biofilter packed with compost pellets. The experiments were performed at $C_{MetOH\text{-}biofilm}$ ranging from 2.5 to 58 kg m^{-3}. The μ_{max} observed was 0.007 h^{-1}. The kinetic parameters were calculated by following the same procedure than for the biofilter packed with clay spheres. For the Monod model the μ_{max} calculated was 0.009 h^{-1} and K_S was 22.6 kg m^{-3}. For the Haldane model the μ^* was 0.041 h^{-1}, μ_{max} 0.007 h^{-1}, K_S 108 kg m^{-3} and K_I 17 kg m^{-3}.

5.4. Discussion

Figure 5.1 shows that $C_{MetOH\text{-}gas}$ in the bioreactor containing clay spheres decreased with time. The rate at which methanol was taken by the biofilm varied along the experiment and presented two regions. Region 1 was characterized by a quick decrease of $C_{MetOH\text{-}gas}$ and region 2 by a slight decrease.

Figure 5.1 shows a blank which was performed by injecting liquid methanol into a bioreactor containing some drops of water. In this blank, methanol was absorbed by water and caused that $C_{MetOH\text{-}gas}$ decreased similarly to the region 1. $C_{MetOH\text{-}gas}$ reached a plateau and stayed constant the rest of the time. In comparison to kinetic determinations, $C_{MetOH\text{-}gas}$ in region 2 decreased continuously without turning constant. It is believed that, the quick decrease of $C_{MetOH\text{-}gas}$ in region 1 was due to the absorption of methanol by the biofilm.

The $C_{CO_2\text{-}gas}$ shown in Figure 5.1, increased at a constant rate of 0.38 g of CO_2 m^{-3} h^{-1}. This indicates that the biodegradation rate of methanol in the biofilm ($R_{MetOH\text{-}biofilm}$) should be assumed constant throughout the experiment. This produced a continuous decrease of $C_{MetOH\text{-}biofilm}$, which means that methanol was adsorbed in order to readjust the equilibrium between $C_{MetOH\text{-}gas}$ and $C_{MetOH\text{-}biofilm}$. This observation and the blank show that the decrease of $C_{MetOH\text{-}gas}$ in region 2 was due to the constant $R_{MetOH\text{-}biofilm}$.

At 0.025 h, $C_{MetOH\text{-}gas}$ was 11.5 g m^{-3} (Figure 5.1) and $C_{MetOH\text{-}biofilm}$ was 3.68 kg m^{-3} (Figure 5.2). The ratio $C_{MetOH\text{-}gas}/C_{MetOH\text{-}biofilm}$ was 0.003, which was higher than the Henry constant

(K_h) of $2.05x10^{-04}$ (kg of methanol m^{-3} of gas)/(kg of methanol m^{-3} of liquid) calculated at 25°C with data published by GUPTA and coll. (2000). The ratio $C_{MetOH\text{-}gas}/C_{MetOH\text{-}biofilm}$ ten fold higher than K_h confirmed that the decrease of $C_{MetOH\text{-}gas}$ in region 1 was mainly due to the absorption of methanol by the biofilm.

Figure 5.2 shows that $C_{MetOH\text{-}biofilm}$, after reaching its maximum, decreased at a nearly constant rate of 0.5 kg m^{-3} h^{-1}. The rate at which decreased $C_{MetOH\text{-}biofilm}$ (mass of methanol removed from gas phase per unit of bioreactor volume and time) was the $R_{MetOH\text{-}biofilm}$ which was the same for both regions.

Figure 5.3 shows that ln B correlated highly to time as shown in Eq. A-7. This behavior was observed for each methanol concentration tested. The high coefficient of determination (R^2) of 0.97 observed in Figure 5.3 suggests that the mathematical procedure developed in the presented study let to the correct calculation of B along each experiment.

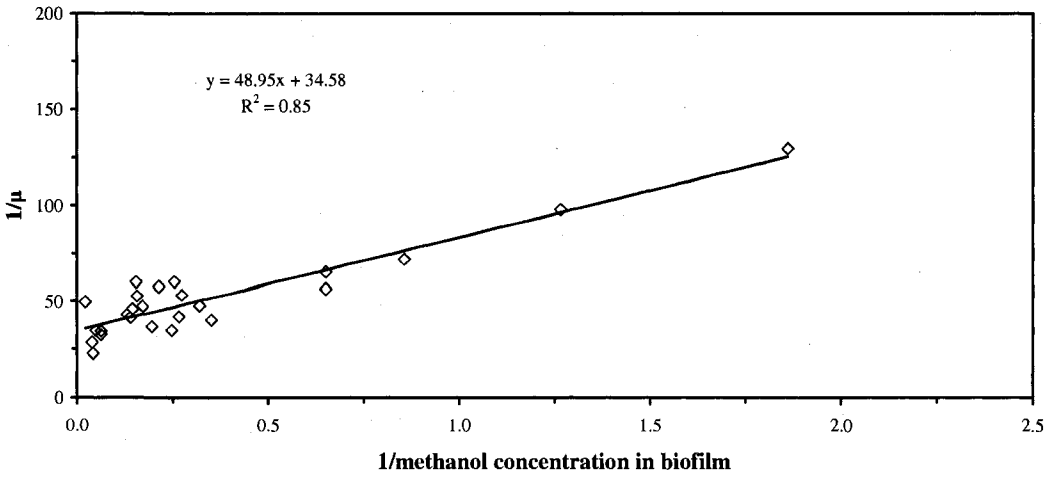

Figure 5.5: Monod model in the form of Lineweaver-Burk equation fitted to experimental data. The ordinate $1/\mu_{max}$ and the slope K_S/μ_{max} are calculated by linear regression.

Figure 5.4 shows that μ increased with $C_{MetOH\text{-}biofilm}$ up to a maximal value of 0.049 h^{-1}, which occurred at a $C_{MetOH\text{-}biofilm}$ of 13.2 kg m^{-3}. For $C_{MetOH\text{-}biofilm}$ higher than 13.2 kg m^{-3}, the microorganisms were inhibited and μ began to decrease. In the whole range of methanol

concentration tested, Figure 5.4 shows that the μ estimated with Haldane model (solid line) fitted better the experimental μ than the Monod model (dashed line).

Figures 5.5 and 5.6 show Eqs. A-2 and A-5 fitted to experimental data and the regressions of each equation is presented in the respective figure. Figure 5.6 confirms that Haldane model fitted better to experimental data with a R^2 of 0.96, while the R^2 for the Monod model was 0.85 (Figure 5.5).

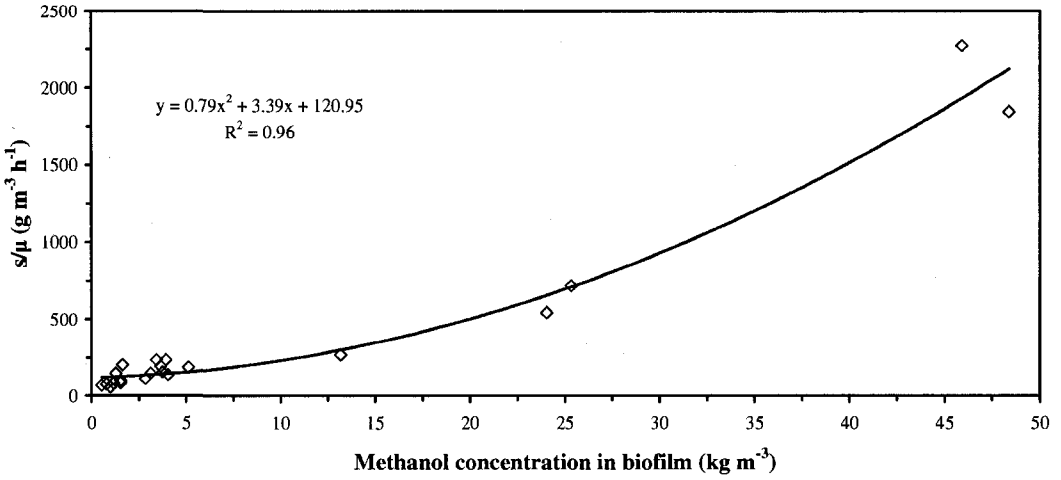

Figure 5.6. Experimental data fitted to the Haldane model rearranged in a form of a second order equation in terms of substrate concentration in biofilm. The kinetic parameters μ*, K_S and K_I are calculated by quadratic regression.

For the biofilter packed with compost pellets, Figure 5.7 shows that the Haldane model fitted the experimental μ better than the Monod model. This was also due to the inhibition of microorganisms at high methanol concentration. The experimental μ_{max} was 0.007 h^{-1} and occurred at a $C_{MetOH\text{-}biofilm}$ of 41 kg m^{-3}. The experimental μ_{max} observed for both packing materials was smaller than the μ_{max} of 0.162 h^{-1} reported by SHAREEFDEEN and coll. (1993), for microorganisms isolated from a biofilter treating methanol. It was also smaller than the range of μ_{max} from 0.075 to 0.5 h^{-1} reported by CRUEGER and coll. (1990) for methylotrophs. However, the values of μ_{max} reported in the literature (CRUEGER and coll., 1990; SHAREEFDEEN and coll., 1993) were calculated for pure strains or isolated bacteria

adapted to methanol as the carbon source. In these studies, the microorganisms were grown suspended in nutrient solution, in agitated flasks in order to homogenize the concentration of nutrients, oxygen and VOC. Agitation could increase the availability and the mass transfer of these compounds and the growth rates obtained were higher than the growth rates of immobilized microorganisms in the biofilm, such as the samples used in the present study.

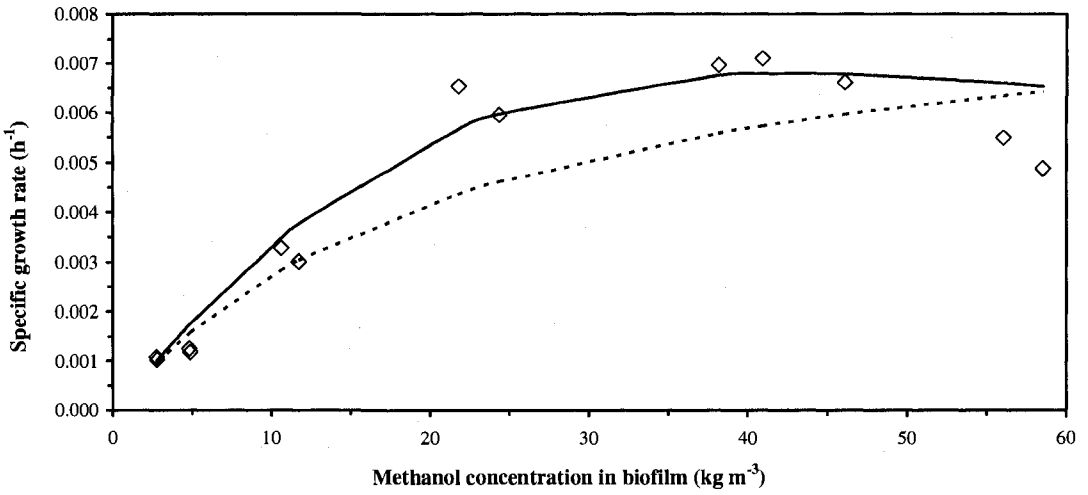

Figure 5.7. Specific growth rate of microbial consortium developed in a biofilter packed with compost pellets as a function of methanol concentration in biofilm. Experimental μ (◊), estimated μ with Monod model (- - -), estimated μ with Haldane model (——).

For the biofilter packed with compost pellets, the kinetic parameters were calculated with biofilm detached from its support. Probably the structure of biofilm was damaged, which could modify the mass transfer and the moisture regulation of the biofilm and reduce the activity of microorganisms. In this way, the biofilm from compost pellets presented a μ_{max} which was 15% of the value observed on clay spheres, although both biofilters had been inoculated with the same lixiviate and operated at similar conditions.

The present method, which takes into account the biodegradation and absorption of methanol, could be used for calculating the kinetics of other water soluble VOCs. It can be also applied in biofilters packed with other inert materials, such lava rock which can be calcinated or

polypropylene spheres which can be digested in acid solutions, in order to determined the real biomass which was tested in each kinetic experiment.

5.5. Conclusion

The microkinetic parameters of microbial consortiums which degrade methanol in air treatment biofilters packed with clay spheres and compost pellets were calculated. Both biofilters presented inhibition at high methanol concentration in biofilm. In the biofilter packed with clay spheres the inhibition occurred at concentrations higher than 13 kg m^{-3} and in the biofilter with compost pellets at concentrations higher than 40 kg m^{-3}. The μ_{max} observed at a temperature of 25°C was 0.049 h^{-1} for clay spheres and 0.007 h^{-1} for compost pellets. The Haldane model fitted experimental specific growth rates better than Monod. The μ_{max} estimated with Haldane model was 0.044 h^{-1} for clay spheres and 0.007 h^{-1} for compost pellets.

A mathematical procedure for calculating the microkinetic parameters of Monod and Haldane models was developed in the basis of mass balances of methanol transformation to biomass and carbon dioxide. The behaviour of methanol concentration in gas phase presented two tendencies. The first was characterized by a quick absorption of methanol by the biofilm. The second was characterized by a slow absorption of methanol and occurred when methanol concentrations in gas and biofilm reached the thermodynamic equilibrium. Both tendencies were considered in the mathematical procedure for calculating the methanol concentration in biofilm, which presented a constant biodegradation rate of methanol.

Acknowledgements

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Appendix A - Theoretical considerations and mathematical expressions

Most of the methods for determining the growth rate of microorganisms have been developed on the basis of the Monod model (LIU, 2007):

$$\mu = \frac{\mu_{max} \; S}{K_S + S} \tag{A-1}$$

where μ is the specific growth rate at which grow the microorganisms exposed at the substrate concentration S in the phase where the microorganisms are growing (biofilm or nutrient solution medium). The μ_{max} is the maximal specific growth rate of microorganisms and K_S is the constant of Monod model. Eq. A-1 is rearranged as the Lineweaver-Burk equation and fitted to experimental μ and S as follows the kinetic parameters for the Monod model are calculated:

$$\frac{1}{\mu} = \frac{1}{\mu_{max}} + \frac{K_S}{\mu_{max}} \frac{1}{S} \tag{A-2}$$

When microorganisms present inhibition by the substrate, the specific growth rate is better described by other models, such as the Haldane model (OKPOKWASILI and coll., 2005) which is written as follows:

$$\mu = \frac{\mu^* \; S}{K_S + S + \frac{S^2}{K_I}} \tag{A-3}$$

where μ, S and K_S are as defined for Monod model, μ* is the specific growth rate of Haldane model and K_I is the inhibition constant. With the assumption that the microorganisms inhibited by substrate are not subject to oxygen limitation, the μ_{max} can be calculated with the derivate of Eq. A-2 with respect to substrate concentration (SHAREEFDEEN and coll., 1993) as follows:

$$\mu_{max} = \frac{\mu^*}{1 + 2\left(\frac{K_s}{K_I}\right)^{0.5}} \tag{A-4}$$

Eq. A-2 can be rearranged as a second order equation in terms of substrate concentration (JORIO and coll., 2005) in order to calculate the kinetic parameters of the Haldane model by means of a quadratic regression:

$$\frac{S}{\mu} = \frac{K_S}{\mu^*} + \frac{S}{\mu^*} + \frac{S^2}{\mu^* \ K_I} \qquad \text{(A-5)}$$

The biomass variation with time can be expressed as a function of the specific growth rate and the biomass as follows:

$$\frac{dB}{dt} = \mu \ B \qquad \text{(A-6)}$$

where B is the biomass content in the phase where the microorganisms are growing and t is the time. Equation 6 can be integrated from t_0=0 to t and from B_0 (at t_0) to B (at t):

$$\ln (B) = \ln (B_0) + \mu \ t \qquad \text{(A-7)}$$

The calculation of μ is done with data of B at different times of the experiment. Since the experiments are carried out in hermetically closed bioreactors, it is not possible to measure B when the experiment is carried out. B is calculated by means of a mathematical procedure presented below and it is necessary a reference value, which could be the initial or the final B. In the present study the final B is used. The biomass production in a biofilm which degrades methanol can be calculated by means of the following global reaction:

$$CH_3OH + \alpha \ O_2 + \beta \ CO(NH_2)_2 \rightarrow \delta \ CH_2O_{0.65}N_{0.1} + \eta \ CO_2 + \kappa \ H_2O \qquad \text{(A-8)}$$

where α, β, δ, η and κ are the stoichiometric coefficients expressed on a mol basis and referred to one mole of methanol consumed. $CH_2O_{0.65}N_{0.1}$ is the average of elemental composition for the biofilm developed in biofilters degrading methanol, which was determined experimentally (data not published) and is similar to that proposed by BAILEY and coll. (1986).

The stoichiometric coefficients δ and η for biomass and CO_2 respectively are defined as follows:

$$\delta = \frac{mol \quad CH_2O_{0.65}N_{0.1} \quad produced}{mol \quad methanol \quad consumed} \tag{A-9}$$

$$\eta = \frac{mol \quad CO_2 \quad produced}{mol \quad methanol \quad consumed} \tag{A-10}$$

By means of an elemental mass balance using Eqs. A-8, A-9 and A-10, an expression for calculating the biomass yield coefficient ($Y_{B/MetOH}$) as a function of the molecular weight (MW) of methanol, CO_2 and biomass and the CO_2 yield coefficient ($Y_{CO_2/MetOH}$) can be obtained:

$$Y_{B/MetOH} = \frac{MW_{biomass}}{MW_{MetOH}} \; 1.05 \left(1 - Y_{CO_2/MetOH} \; \frac{MW_{MetOH}}{MW_{CO_2}} \right) \tag{A-11}$$

$Y_{CO_2/MetOH}$, defined as the mass of CO_2 produced per mass of methanol consumed, can be calculated at any time (t_i) if the masses of methanol and CO_2 in the bioreactor are known:

$$Y_{CO_2/MetOH}(t_i) = \frac{M_{CO_2}(t_i) - M_{CO_2}(t_{i-1})}{M_{MetOH}(t_{i-1}) - M_{MetOH}(t_i)} \tag{A-12}$$

where M is the mass of methanol or CO_2 at the i^{th} or $(i-1)^{th}$ gas sampling time. Throughout all the kinetic experiments the volume of biofilm ($V_{biofilm}$) in the reactor was always smaller than 0.5 mL. Considering that the Henry constant for CO_2 at 25°C is 1.21 $C_{CO_2\text{-gas}} / C_{CO_2\text{-liquid}}$ (calculated from COOPER and coll. 2002), the mass of CO_2 which accumulated in the biofilm during the kinetic experiments was neglected. In this way, the mass of CO_2 at any time was calculated by multiplying the CO_2 concentration in gas ($C_{CO_2\text{-gas}}$) by the volume of gas (V_{gas}). The variation of the total mass of methanol (M_{MetOH}) contained in the bioreactor can be expressed in terms of $Y_{B/MetOH}$, B and μ:

$$\frac{dM_{MetOH}}{dt} = -\frac{B}{Y_{B/MetOH}} \; \mu \tag{A-13}$$

Since the biofilm developed in biofilters treating methanol presented a water content higher than 90% (data not published), the biofilm was assumed as a static liquid phase and the Henry law was applied for calculating the concentration of methanol in the biofilm $C_{MetOH\text{-}biofilm}$. The Henry constant for methanol (K_h) at 25°C was calculated from GUPTA and coll. (2000) and was 2.05E-04 $C_{MetOH\text{-}gas}/C_{MetOH\text{-}liquid}$. The total mass of methanol (M_{MetOH}) was calculated as follows:

$$M_{MetOH} = M_{MetOH-biofilm} + M_{MetOH-gas} \quad \text{(A-14)}$$

and the masses of methanol in the gas phase ($M_{MetOH\text{-}gas}$) and in the biofilm ($M_{MetOH\text{-}biofilm}$) were calculated as follows:

$$M_{MetOH-gas} = V_{gas} \; C_{MetOH-gas} \quad \text{(A-15)}$$

$$M_{MetOH-biofilm} = V_{biofilm} \left(\frac{C_{MetOH-gas}}{K_h} \right) \quad \text{(A-16)}$$

By substituting Eqs. A-15 and A-16 in Eq. A-14, then in Eq. A-13 and this one in Eq. A-6 it is obtained the next expression for the variation of B as a function of $Y_{B/MetOH}$:

$$\frac{dB}{dt} = - Y_{B/MetOH} \left(\frac{V_{biofilm}}{K_h} + V_{gas} \right) \frac{dC_{MetOH-gas}}{dt} \quad \text{(A-17)}$$

The integration of equation A-17 for a period of time comprised between two gas samplings, one at t_{i-1} and the other one at t_i, with initial conditions of B and $C_{MetOH\text{-}gas}$ at t_{i-1} and final conditions at t_i, gives the equation A-18 which leads to the calculation of the biomass at each time of gas sampling t_i:

$$B_i = B_{i-1} + Y_{B/MetOH} \left(\frac{V_{biofilm}}{K_h} + V_{gas} \right) \left(C_{MetOH-gas}(t_{i-1}) - C_{MetOH-gas}(t_i) \right) \quad \text{(A-18)}$$

With the set of B calculated at each gas sampling it is possible to calculate μ at different $C_{MetOH\text{-}biofilm}$ by linear regression of Eq. A-7. With μ and the respective $C_{MetOH\text{-}biofilm}$ (S in Monod and Haldane models) are calculated the kinetic parameters of Eqs. A-1 and A-3.

For region 2, the methanol concentration in biofilm was calculated by using K_h with the assumption that methanol concentrations in gas and biofilm are in equilibrium. With the assumption that the methanol biodegradtion rate in biofilm ($R_{MetOH\text{-}biofilm}$) is constant in each experiment, the concentration of methanol in biofilm for region 1 can be calculated with the following equation:

$$C_{MetOH-biofilm}(t_i) = \frac{(\Delta C_{MetOH-gas} \quad V_{gas}) - (t \quad R_{MetOH-biofilm})}{V_{biofilm}} \qquad \text{(A-19)}$$

where $\Delta C_{MetOH\text{-}gas}$ is the variation of methanol concentration in gas for the interval of time from t=0 to t_i, t is the time elapsed from the starting up to t_i, $R_{MetOH\text{-}biofilm}$ is calculated with $C_{MetOH\text{-}biofilm}$ of region 2, by multiplying the rate at which $C_{MetOH\text{-}biofilm}$ decreases by $V_{biofilm}$.

Notation

B, biomass, kg

C, concentration of a compound, kg m^{-3}

d, derivative of a variable

K_h, partition coefficient of methanol (Henry constant), $C_{MetOH\text{-}gas}/C_{MetOH\text{-}liquid}$

K_I, inhibition constant for Haldane model, kg m^{-3}

K_S, saturation constant for Monod or Haldane model, kg m^{-3}

M, mass of a compound, kg

MW, molecular weight of a compound, kg $kgmol^{-1}$

$R_{MetOH\text{-}biofilm}$, biodegradation rate of methanol in the biofilm, kg h^{-1}

$R_{MetOH\text{-}gas}$, removal rate of methanol in the gas phase, kg h^{-1}

R^2, coefficient of determination, dimensionless

S, substrate concentration for Monod or Haldane models, kg m^{-3}

t, time, h

V, volume, m^{-3}

$Y_{B/MetOH}$, biomass yield coefficient, g biomass produced g^{-1} MetOH consumed

$Y_{CO2/MetOH}$, carbon dioxide yield coefficient, g CO_2 produced g^{-1} MetOH consumed

greeks

α, β, δ, η, κ, stoichiometric coefficients

μ, specific growth rate, h^{-1}

μ^*, specific growth rate for Haldane model, h^{-1}

μ_{max}, maximum value of the specific growth rate, h^{-1}

Δ, difference of a variable from final to initial conditions

subscripts

biofilm, in the biofilm or referent to the biofilm

biomass, referent to biomass

CO2, referent to carbon dioxide

f, final conditions

gas, in the gas phase or referent to the gas phase

i, at the i^{th} sampling time

i-1, at the $(i-1)^{th}$ sampling time

MetOH, referent to methanol

0, initial conditions

chemical species

$CH_2O_{0.65}N_{0.1}$, biomass

CH_3OH, methanol

CO_2, carbon dioxide

$CO(NH_2)_2$, urea

O_2, oxygen

H_2O, water

Chapitre 6. Détermination des paramètres cinétiques de la biodégradation des composés organiques volatils et de la croissance microbienne dans des biofiltres avec et sans percolation garnies avec des lits inertes

Article « *Kinetics of microbial growth and biodegradation of methanol and toluene in biofilters and analysis of energetic indicators* », qui a été soumis le 6 mars 2008 dans le « Journal of Biotechnology ».

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Résumé

Une étude sur la cinétique des biofiltres avec et sans percolation pour traiter le méthanol et lè toluène a été réalisée. Des modèles cinétiques pour calculer la croissance microbienne et la capacité d'élimination sous des conditions réelles d'opération ont été testées pour des biofiltres présentant de l'inhibition liée à la concentration élevée du polluant. Une brève analyse d'indicateurs énergétiques utiles lors du calcul de transfert de chaleur et de la température dans le lit garni a été faite.

La vitesse de croissance spécifique de la biomasse a été calculée pour les biofiltres avec et sans percolation sous des conditions réelles d'opération. La vitesse spécifique de croissance pour le biofiltre percolateur traitant le méthanol a été de 0.037 h^{-1}. Dans le cas du biofiltre traditionnel, la vitesse spécifique de croissance microbienne du méthanol et du toluène a été fonction des conditions d'opération, telles la concentration d'azote présent dans la solution nutritive, le garnissage, la concentration de toluène et de méthanol dans le biofilm.

Dans les cas des biofiltres percolateurs, la capacité d'élimination du méthanol s'est ajustée au modèle de type Michaelis-Menten, puisque les biofiltres percolateurs n'ont pas présenté d'inhibition. Dans le cas des biofiltres traditionnels, la capacité d'élimination pour le méthanol et le toluène s'est ajustée au modèle de type Haldane puisque les biofiltres ont présenté de l'inhibition à des concentrations élevées de polluants.

Le biofilm développé dans des biofiltres traditionnels a présenté une composition élémentaire moyenne de $CH_{1.99}O_{0.64}N_{0.11}$ pour le méthanol et de $CH_{1.98}O_{0.44}N_{0.18}$ pour le toluène. Les chaleurs de combustion varient entre 3440 à 4460 cal g^{-1} de biofilm. Ces donnés de composition élémentaire et de chaleur de combustion du biofilm sont utiles dans le développement de modèles mathématiques intégrant une approche énergétique.

6. Kinetics of microbial growth and biodegradation of methanol and toluene in biofilters and analysis of energetic indicators

Abstract

The kinetics of microbial growth and biodegradation of methanol and toluene in biofilters (BF) and biotrickling filters (BTF) packed with inert materials was analyzed. The specific growth rate μ for the BTF treating methanol was 0.037 h^{-1} for a wide range of operating conditions. In the BF, μ was a function of methanol and toluene concentration in the biofilm. In BFs treating methanol, μ was affected by the nitrogen concentration in the nutrient solution and the kind of packing material. The kinetics of methanol and toluene biodegradation were also analyzed with mixed order models. A Michaelis-Menten type model provided a good fit to elimination capacity (EC) of BTF treating methanol and a Haldane type model provided a good fit to EC of BF treating methanol and toluene. The carbon dioxide production rate was related to the packing bed temperature and the content of volatile solids in the biofilm. For BF, the ratio temperature/carbon dioxide production rate (PCO_2) was 0.024 °C per unit of PCO_2 and for BTF it was 0.15 °C per unit of PCO_2.

6.1. Introduction

6.1.1. Biofiltration of volatile organic compounds

Volatile organic compounds (VOCs) are widely used in industry where they are often released to the atmosphere. In Canada, among the ten most released Non-Criteria Air Contaminants in 2006, five of them were VOCs. Methanol was in 2nd place with emissions of around 16 ktons $year^{-1}$ and toluene in 6th place with more than 4 ktons $year^{-1}$ (NPRI, 2007). Most of the VOCs are toxic to humans and their emissions must be controlled in order to avoid health problems (MONOD, 1998). Several VOCs are biodegradable, this leads to the use of biotechnologies for controlling their releases (JORIO and coll., 1999). The biotechnologies have attracted the attention of environmental engineers because of their favourable operating conditions, such as atmospheric pressure and near ambient temperatures varying from 20 to 40°C (JORIO and coll., 1999).

Traditionally, biofilters (BF) and biotrickling filters (BTF) have treated effluents with low VOC concentrations (IRANPOUR and coll., 2001; POPOV and coll., 1999). In fact, industrial scale biofilters are recommended for VOC concentrations smaller than 10 g m^{-3} (COOPER and coll., 2002). Some recent studies have analyzed the operation of BF and BTF at high inlet concentrations or inlet loads, for example a BTF treating ethanol at an IL up to 1610 g m^{-3} h^{-1} (AVALOS RAMIREZ and coll., 2005; CHETPATTANANONDH and coll., 2005; DELHOMÉNIE and coll., 2005b; JORIO and coll., 1998; PRADO and coll., 2004). These studies supply information about the EC behaviour of BF and BTF at high VOC concentrations. These studies may be used to calculate macrokinetic parameters of BF and BTF at high VOC concentrations.

6.1.2. Kinetic approaches to microbial growth and VOC biodegradation in biofilters

There are several approaches for the kinetic analysis of BF and BTF. They can be classed in two main groups: the microkinetic approach related to the microbial growth rate (IKEMOTO and coll., 2006) and the macrokinetic approach related to the VOC biodegradation rate (STREESE and coll., 2005). In the case of microbial growth kinetics, the models are often based on the Monod model for population growth (LIU, 2007). In the case of VOC inhibition, a modification of the Monod model which includes an inhibition term is used, such as the Haldane model (OKPOKWASILI and coll., 2005). For BF and BTF, the kinetic parameters for Monod model are commonly determined by growing pure strains in batch culture and suspended in a liquid nutrient solution (OTTENGRAF and coll., 1983; SHAREEFDEEN and coll., 1993; TANG and coll., 1997). But it is to be noted that the mass transfer and the microkinetics of bioreactions in nutrient solution are different from those which occur in a biofilm (BISHOP, 1997). Particularly, some studies show that the microbial population and its growth are affected by the operating conditions, such as nutrients supplied and VOCs treated (ACUÑA and coll., 1999; FARRUGIA, 1999; KRAILAS and coll., 2000b).

In the case of VOC biodegradation, the macrokinetic models describe the behaviour of elimination capacity (EC) of the BF or BTF. The model based on a first order chemical reaction is the simplest model reported in literature (JONES and coll., 2004). The models based on Michaelis-Menten has been widely used in studies of BF and BTF macrokinetics

(HIRAI and coll., 1990; KRAILAS and coll., 2002; SOLOGAR and coll., 2003; STREESE and coll., 2005; WANI and coll., 1999). Results of these studies show that macrokinetic models fit well to experimental EC. But these models have not been tested on BF or BTF presenting inhibition due to high VOC concentration. Several VOCs might inhibit the microorganisms present in biofilm, such as methanol and toluene (DELHOMÉNIE and coll., 2005a; SHAREEFDEEN and coll., 1993).

6.1.3. Heat transfer and energy indicators

The mathematical models for simulating biofilter performance can include heat transfer calculations. This requires the determination of the heat which is transferred to the packing bed. The source of this heat is the VOC biodegradation reaction (MYSLIWIEC and coll., 2001). In order to calculate the energy produced and released during the bioreaction in the biofilm, it is necessary to determine some parameters. For example, the heat of combustion of biofilm which is associated with the energy stocked in the bonds of chemical species present in the biofilm (BATTLEY, 2003; SANDLER, 1991). During the bioreaction, the energy which is not captured by the microorganisms is released and dissipates through the packing bed. This causes the temperature in the BF or BTF to increase (GUTIÉRREZ-ROJAS and coll., 1996; PINETTE and coll., 1995). Some recent studies have also shown that there is a relationship between the temperature of the packing bed and the degradation rate of pollutant or the concentration of carbon dioxide (CO_2) in the outlet gas stream (DELHOMÉNIE and coll., 2003; DELHOMÉNIE and coll., 2005a; MORALES and coll., 1998).

The aim of the present study is to analyze the behaviour of microbial growth and VOC biodegradation kinetics in BF and BTF treating methanol and toluene, two VOCs which may cause inhibition. The identification and quantification of parameters which could be used to estimate the temperature and heat transfer in the packing bed were also performed in the study.

6.2. Materials and methods

The present research is divided into four phases. The 1st is a kinetic study of a biotrickling filter (BTF) treating methanol. The 2nd is a comparison of the effect of two pollutants with different chemical nature on biofilter (BF) kinetics: a) one polar and water soluble (methanol)

and b) one non-polar and not very water soluble (toluene). The 3rd is a study on the effect of nitrogen (N) concentration in the nutrient solution and packing material on the microkinetics of a BF treating methanol. The 4th is an analysis for identifying energetic indicators which could be used in the estimation of temperature and heat transfer in the packing bed of a BF or a BTF.

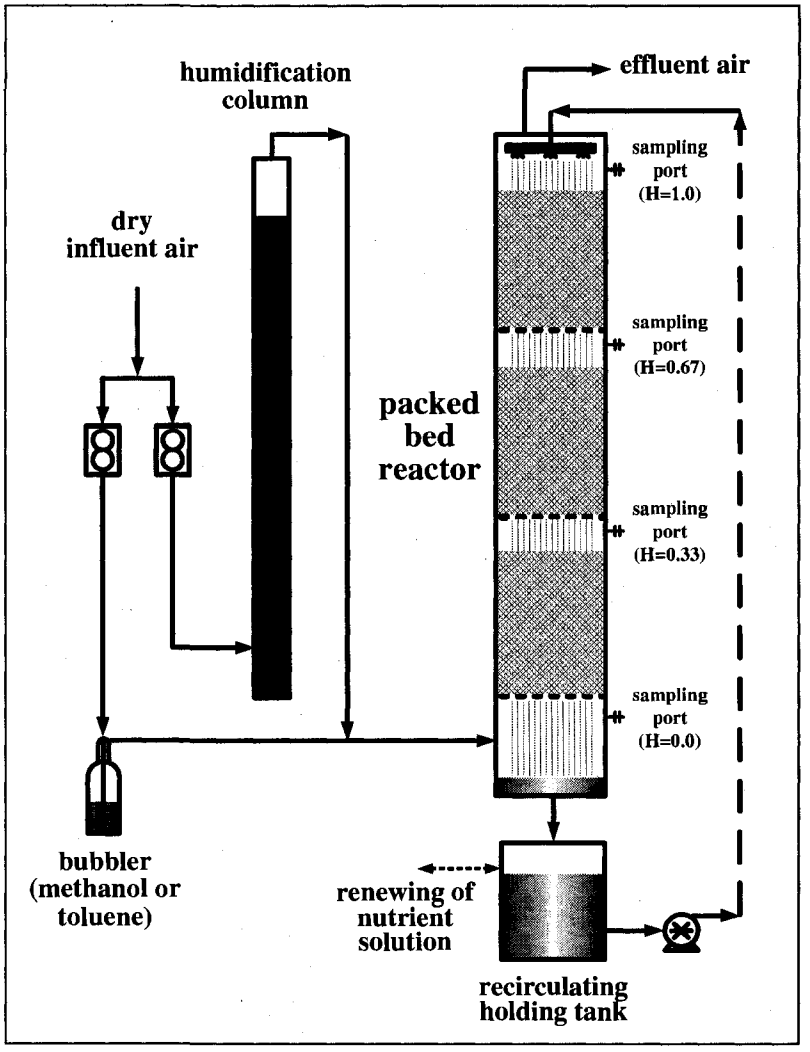


Figure 6.1. Schematic representation of bioreactors. When the bioreactor was operated as a biofilter the nutrient solution was not recirculated (— — —).

6.2.1. Bioreactors

The BTF and the BF were constructed from Plexiglas cylinders with an internal diameter of 0.15 m and a total bed height of 1 m divided in three sections of 0.33 m (Figure 6.1). The BTF was packed with polypropylene spheres (Jaeger Tri-Packs®, Fabco Plastics, Toronto, Canada). One BF treating methanol was packed with polypropylene spheres and another with clay spheres (Hydroton®, Ökotau GmbH, Germany). The BF for treating toluene was packed with clay spheres. The characteristics of the two packing materials are shown in Table 6.1-a.

Table 6.1. Operating conditions of biotrickling filters and biofilters and characteristics of packing bed materials.

a) Characteristics of packing bed materials

	Clay spheres*	Polypropylene spheres
Pores	Porous material	Non-porous material
Diameter (m)	0.012	0.025
Specific surface (m^2 m^{-3})	310	280
Void space (%)	40	90

* mean characteristics

b) Biotrickling filter treating methanol

Methanol inlet concentration (g m^{-3})	Air flow rate (m^{-3} h^{-1})	Empty bed residence time (s)	Nitrogen concentration in nutrient solution (gN L^{-1})
0.2 – 15.5	1, 2 and 3	20, 30 and 65	0.005

c) Biofilters treating methanol and toluene

Volatile organic compound (VOC)	Packing bed material	VOC inlet concentration (g m^{-3})	Air flow rate (m^{-3} h^{-1})	Empty bed residence time (s)	Nitrogen concentration in nutrient solution (gN L^{-1})
Methanol	Clay spheres	0.8 to 4.3	0.25 to 3	20 to 260	0.03 to 2.4
Methanol	Poly-propylene spheres	1.5	1	65	0.03 to 2.4
Toluene	Clay spheres	0.4 to 3.5	1	65	3

Table 6.2. Definition of equations used in this paper.

Parameter	Mathematical expression	Units
Elimination capacity	$EC = \frac{Q\ (C_i - C_o)}{V}$	g m^{-3} h^{-1}
Carbon dioxide production rate	$PCO_2 = \frac{Q\ (CO_{2o} - CO_{2i})}{V}$	g m^{-3} h^{-1}
Biomass production rate	$PB = \frac{C_B}{\Theta\ V}$	g m^{-3} h^{-1}
Biomass yield coefficient	$YB = \frac{PB}{EC}$	g biomass produced g^{-1} of methanol consumed
Logarithmic average concentration	$C_{ln} = \frac{C_i - C_o}{\ln\left(\frac{C_i}{C_o}\right)}$	g m^{-3}
Concentration of pollutant in biofilm	$C_{biofilm} = \frac{C_{gas}}{m}$	g L^{-1}
Difference of temperature between the packing bed and the environment.	$\Delta T = T_{bed} - T_{environment}$	°C

Q is the total air flow rate ($m^3 h^{-1}$)
V is the empty bed volume (m^3)
Θ is the 20 h-recycling period (h)
C is the concentration of VOC in gas phase (g m^{-3}) or biofilm (g dm^{-3})
C_B is the dry biomass concentration in liquid phase (g m^{-3})
CO_2 is the carbon dioxide concentration (g m^{-3})

m is the Henry coefficient (dimensionless):
2.05×10^{-4} for methanol (Gupta *et al.*, 2000)
0.27 for toluene (Lide, 1999).

Subscripts: *i* indicates an inlet stream
o indicates an outlet stream

Inlet air, dry and particle free, was separated in two air streams; one was bubbled in a humidification column and the other was passed through a bubbler in order to evaporate the methanol (98 % w/w) or the toluene (99 % w/w; both from Anachemia, Canada). The two air streams were mixed before entering the base of BF or BTF. The compositions of nutrient solution for BF and BTF treating methanol and toluene are based in previous studies

(AVALOS RAMIREZ and coll., 2007b; AVALOS RAMIREZ and coll., 2008; DION ST.-PIERRE and coll., 2006). For the BF or BTF treating methanol, the nutrient solution had a constant nitrogen-phosphorus-potassium (N:P:K) mass ratio of 3:3:1 throughout all the experiments. The sources of nutrients were urea, phosphoric acid neutralized with sodium hydroxide and potassium sulphate. The N concentration in the nutrient solution for the BF treating toluene was 3.0 gN L^{-1} (N:P:K = 18:6:1), the detailed composition is reported by DION ST.-PIERRE and coll. (2006). The BF was irrigated daily with 2.7 L of nutrient solution and the BTF was irrigated continuously at a nutrient solution rate of 2 L min^{-1} using a centrifugal pump which took the nutrient solution from a holding tank (16 L).

The BF and the BTF were inoculated with lixiviates from BFs which had been treated methanol and toluene vapors (DASTOUS and coll., 2007; DION ST.-PIERRE and coll., 2006). The operating conditions of experiments are shown in Tables 1b and 1c and the definitions of performance parameters used in kinetic models are presented in Table 6.2.

6.2.2. Calculation of biomass concentration in packing bed

For the BF, the biomass concentration in packing bed was calculated by dividing the dry biomass accumulated in the packing bed by the empty bed volume. The biomass accumulation was calculated with a method reported by AVALOS RAMIREZ and coll. (2008).

The biomass content in the packing bed of the BTF was controlled by means of nutrient starvation, as reported by AVALOS RAMIREZ and coll. (2007b). With this strategy, the biomass content in the packing bed was nearly constant and formed a biofilm with a homogeneous thickness of around 2.5 mm. This corresponded to a biofilm volume in the packing bed near 14 L. On the other hand, the biomass content in the lixiviate increased with time and at the end of the 20 hour recycling period tended to a stable value, which was function of the VOC inlet concentration. It was assumed that at this time the concentration of volatile solids in liquid phase was similar to that in the biofilm. According to this observation, the biomass accumulated in the 16 L of lixiviate was equivalent to the biomass contained in the packing bed. This let to the calculation of biomass concentration in packing bed, by dividing the total solids accumulated in lixiviate by the empty bed volume. The total solids accumulated in lixiviate were calculated by subtracting the total solids of lixiviate from those

of the fresh nutrient solution. The total solids were determined with the Standard Method 2540-B (APHA, 1999).

6.2.3. Analytical methods

The inlet and outlet concentrations of methanol and CO_2 in gas phase were measured by means of a total hydrocarbon analyzer Horiba FIA-510 (Horiba, USA) and a portable gas analyzer Ultramat 22P (Siemens AG, Germany), respectively. The elemental composition of the biofilm was determined with an EA1108 Elemental Analyzer (Fisons Instruments, Beverly, MA). The heat of combustion of the dry biofilm was determined in a 1341 Oxygen bomb calorimeter (Parr Instrument Company, Moline, IL).

6.2.3. Kinetic models for microbial growth

The growth rate of biomass (μ) can be expressed in terms of the specific VOC biodegradation rate (q) and the biomass yield coefficient (Y_B) as follows (LIU and coll., 2003):

$$\mu = q \quad Y_B \tag{6-1}$$

The term q can be calculated with a modified expression reported by ECKENFELDER (1989):

$$q = \frac{C_{in} - C_{out}}{B \quad EBRT} \tag{6-2}$$

where, C_{in} and C_{out} are the inlet and outlet concentrations of the VOC in the gas phase, B is the biomass concentration in the packing bed and EBRT is the empty bed residence time of VOC. Substituting Eq. 6-2 into Eq. 6-1, the following equation is obtained:

$$Y_B = \frac{\mu \quad (B \quad EBRT)}{(C_{in} - C_{out})} \tag{6-3}$$

Eq. 6-3 is expressed in terms of parameters which can be experimentally determined. In a BTF at steady state, B is a function of operating conditions but it is stable with respect to the time

elapsed. In this way, at different EBRTs or C_{in} can be obtained an specific value of B in order to calculate μ by means of regression of Eq. 6-3. In a BF, the biomass accumulates in the packing bed and can be expressed by the following equation:

$$\frac{dB}{dt} = \mu \quad B \tag{6-4}$$

Integrating Eq. 6-4 from $t_0 = 0$ to t and from $B(t_0) = B_0$ to $B(t) = B$, one obtains the following expression:

$$\ln(B) = \ln(B_0) + \mu \quad t \tag{6-5}$$

With Eq. 6-5, one can calculate μ for a BF at certain operating conditions by following the mass of BF.

6.2.4. Kinetic models for VOC biodegradation

In BF or BTF treating a biodegradable VOC, the elimination capacity (EC) follows commonly a behaviour which can be described by a Michaelis-Menten type model (HIRAI and coll., 1990):

$$EC = \frac{EC_{max} \quad C_{ln}}{K_s + C_{ln}} \tag{6-6}$$

Where EC_{max} is the maximal EC, K_s is the constant of saturation and C_{ln} is the logarithmic average of inlet and outlet concentrations of VOC in gas phase. EC_{max} and K_s can be calculated by rearranging Eq. (6-6) in the form of the Lineweaver-Burk equation:

$$\frac{1}{EC} = \frac{K_s}{EC_{max}} + \frac{EC_{max}}{C_{ln}} \tag{6-7}$$

When BF and BTF present inhibition, EC follows a behaviour described by a mixed order equation which contains an inhibition term (OKPOKWASILI and coll., 2005), such as the following equation proposed in the basis of the Haldane model:

$$EC = \frac{EC^* \; C_{ln}}{K'_S + C_{ln} + \frac{C_{ln}^2}{K_I}} \qquad (6\text{-}8)$$

Where EC* is the maximal EC in the absence of inhibition, K'_S is the saturation constant and K_I is the inhibition constant for the Haldane type model. Constants can be calculated by means of a regression of Eq. 8 rearranged as follows:

$$\frac{C_{ln}}{EC} = \frac{K'_S}{EC^*} + \frac{C_{ln}}{EC^*} + \frac{C_{ln}^2}{EC^* \; K_I} \qquad (6\text{-}9)$$

By assuming that there is not limitation of oxygen in the biofilter, the EC_{max} can be calculated by analogy to the equation for μ_{max} derived from Haldane model by SHAREEFDEEN and coll. (1993):

$$EC_{max} = \frac{EC^*}{1 + 2\left(\frac{K'_s}{K_I}\right)^{0.5}} \qquad (6\text{-}10)$$

6.3. Results and discussion

6.3.1. First phase: Kinetics of a biotrickling filter treating methanol

Figure 6.2 shows the evolution of YB in the BTF treating methanol as a function of the inverse of the specific VOC biodegradation rate ($1/q = B\ EBRT/C_{in}\text{-}C_{out}$). The model proposed in Eq. 6-3 fitted to experimental results in a wide range of operating conditions with a high coefficient of determination (R^2) of 0.997. The specific growth rate (μ) in a BTF was 0.037 h^{-1}, which was near the range of μ for a consortium isolated from a biofilter treating methanol from 0.05 to 0.16 h^{-1} observed by SHAREEFDEEN and coll. (1993). The microkinetic study of SHAREEFDEEN and coll. (1993) was performed in batch culture, with isolated microorganisms growing in a nutrient solution contained in agitated bioreactors. The most important differences between the cited and the present studies are the elimination of microorganisms which are not able to consume methanol during the isolation and the effect of agitation on mass transfer. For example, the isolation let to the elimination of microorganisms

which could compete with methanol utilizers for up taking nutrients during the microkinetic study. This favors the growth of methanol utilizers.

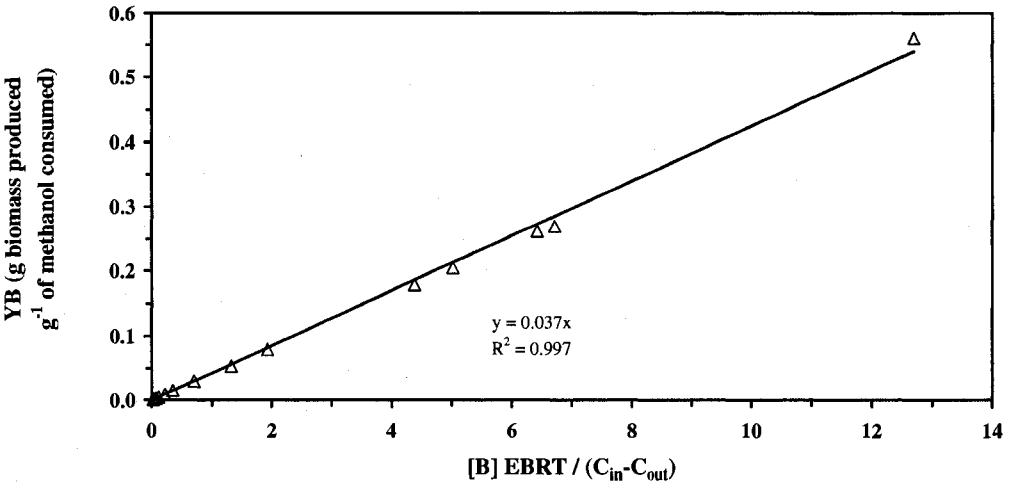


Figure 6.2. Biomass yield coefficient (YB) as a function of the inverse of the specific methanol biodegradation rate: experimental YB (Δ), tendency of YB (- -).

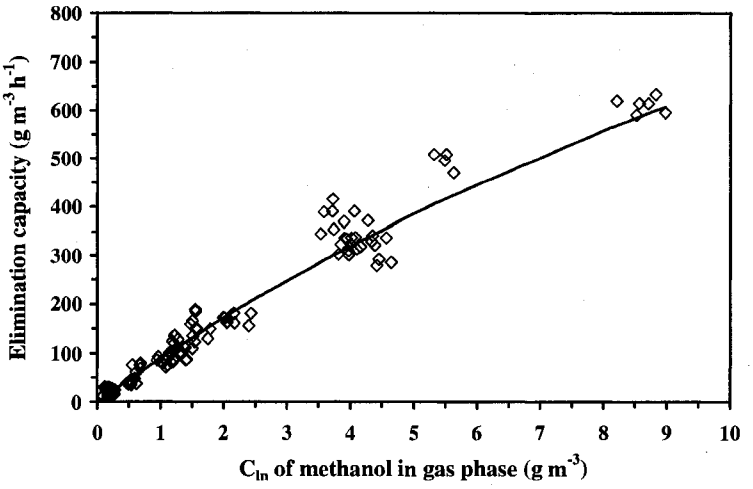


Figure 6.3. Elimination capacity in function of methanol concentration in a BTF. Experimental elimination capacity (◊) and the estimated elimination capacity by using the kinetic parameters in the Michaelis-Menten type model (—).

Figure 6.3 shows the EC of BTF as a function of the logarithmic average concentration of methanol in the gas phase. The experimental data is represented by the lozenges and the EC estimated with Eq. 6-6 based on Michaelis-Menten model is represented by the solid line. The EC_{max} estimated was 2230 g m^{-3} h^{-1}, which was near the EC_{max} observed in a previous study in a similar BTF with a value of 2160 g m^{-3} h^{-1} at an IL of 3700 g m^{-3} h^{-1} (data not published). Figure 6.3 shows also that the Michaelis-Menten type model fitted to the experimental EC because the BTF was not inhibited in the whole range of methanol concentration, up to 10 g m^{-3} of logarithmic average concentration (C_{ln}). The absence of inhibition may be due to the effect of the mobile liquid phase on methanol removal. According to the literature, water soluble VOCs such as methanol and ethanol can be treated in a BTF without presenting inhibition at inlet concentrations which commonly affects the performance of a BF (AVALOS RAMIREZ and coll., 2005; DEVINNY and coll., 1995; LESON and coll., 1995; PRADO and coll., 2005).

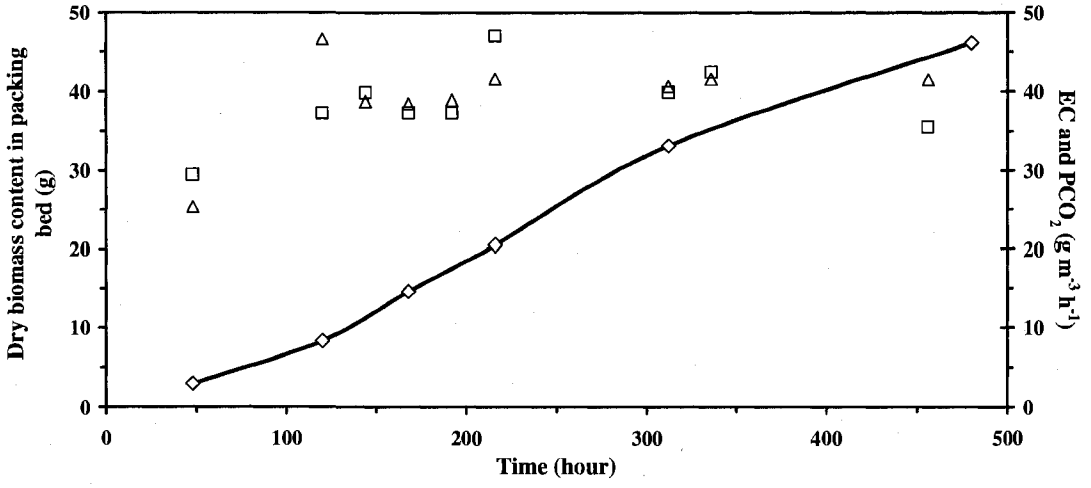


Figure 6.4. Evolution with time of dry biomass content in the packing bed for a biofilter treating methanol at an inlet concentration of 1.5 g m^{-3} and an empty bed residence time of 130 s. Dry biomass content in the packing bed (—◊—), elimination capacity EC (□), carbon dioxide production rate PCO_2 (Δ).

6.3.2. Second phase: Effect of nitrogen concentration and packing material on microbial growth kinetics

Figure 6.4 shows the evolution with time of dry biomass content in the packing bed of a BF treating methanol at an inlet concentration of 1.5 g m^{-3} and an EBRT of 130s. Figure 6.4 presents also the evolution of EC and PCO_2 for this BF. Figure 6.4 shows that the BF operated at steady state in terms of EC and PCO_2, but the biomass content in the packing bed increased with time without reached a plateau. This shows that the VOC biodegradation in BF is not associated with the biomass concentration in the packing bed, as shown in Eq. 6-3. For all the experiments performed in BF for treating methanol and toluene, the same behavior was observed.

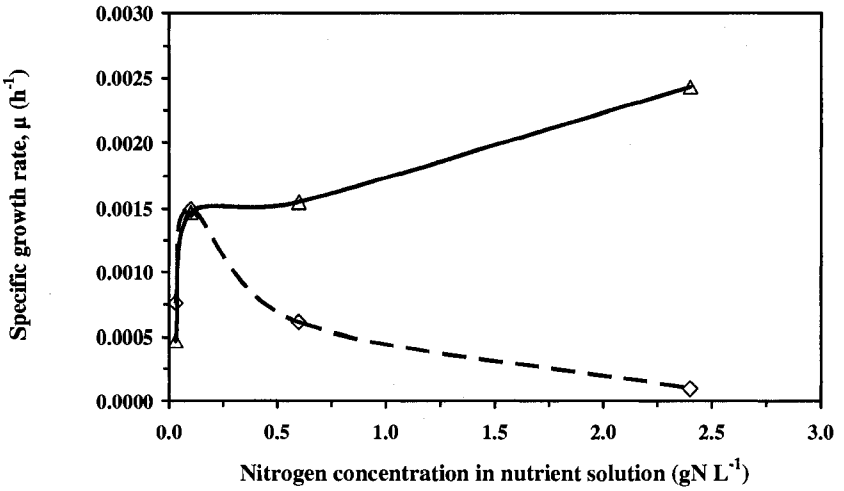


Figure 6.5. Specific growth rate for a biofilter treating methanol as a function of nitrogen concentration in nutrient solution and packing bed material. Biofilter packed with clay spheres (—Δ—), biofilter packed with polypropylene spheres (- - ◊ - -).

Figure 6.5 shows the effect of N concentration and packing material on μ for BF treating methanol. One BF was packed with polypropylene spheres and the other with clay spheres. Both BF were operated at N concentrations in nutrient solution ranging from 0.03 to 2.4 gN L^{-1}. For both packing materials, μ increased quickly from 0.0005 to 0.0015 h^{-1} in the range of N concentration from 0.03 to 0.1 gN L^{-1}. Then, in the range of N concentration from 0.1 to 2.4

gN L^{-1}, μ for the BF packed with polypropylene spheres decayed to 0.0001 h^{-1} while μ for clay spheres increased to 0.0025 h^{-1}. A previous study (AVALOS RAMIREZ and coll., 2008) shows that the porous material (clay spheres) maintained a nearly constant moisture in the packing bed because the nutrient solution retention in the pores of the clay spheres. This favored the microbial activity and the microorganisms were able to grow at a higher μ than on the polypropylene spheres, which were not able to retain liquid. When nutrient solution at high N concentrations was absorbed by a biofilm which was growing over a non porous material, the high salts content of the nutrient solution stocked inside the biofilm might increase the osmotic pressure. It is known that high osmotic pressure affects the microbial activity (MILLE and coll., 2005). This tendency was observed in the non porous material when μ decreased for N concentration higher than 0.1 gN L^{-1}. The biofilm over the clay packing could regulate the osmotic pressure by taking liquid from the porous and μ increased with N concentration.

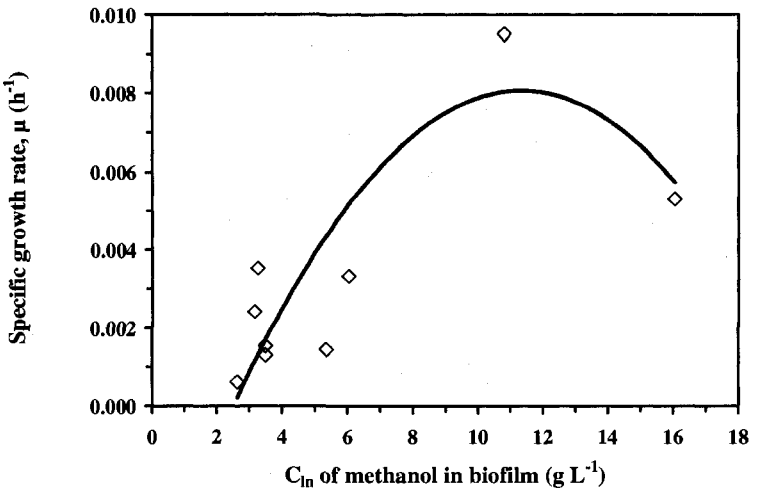
Comparing the results of experiments of methanol treatment in a BTF and in BF, the BTF presented a uniform μ of 0.037 h^{-1}, contrary to the μ of the BF which varied from 0.0001 to 0.0025 h^{-1}. This shows that the mobile liquid phase in the BTF had a beneficial effect on the stability of μ.

6.3.3. Third phase: Kinetic comparison between methanol and toluene biofiltration

Figures 6.6-a and 6.6-b show μ in biofilters packed with clay spheres treating methanol and toluene. Both BFs operated at N concentrations which produce the best performance of biofilters treating methanol and toluene with the same packing material (AVALOS RAMIREZ and coll., 2008; DION ST.-PIERRE and coll., 2006). For methanol, the BF operated at 0.6 gN L^{-1} and for toluene at 3.0 gN L^{-1}. Figure 6.6-a shows μ as a function of the average methanol concentration in the biofilm in a range from 2 to 16 g m^{-3}. Figure 6.6-b shows μ as a function of the average toluene concentration in the biofilm in a range from 0.5 to 12 g m^{-3}. Figures 6.6-a and 6.6-b show that the microorganisms were inhibited at concentrations in biofilm higher than 11 g m^{-3} for methanol and 8 g m^{-3} for toluene. For methanol, μ_{max} was 0.0095 h^{-1} and for toluene 0.007 h^{-1}. For methylotrophs, μ_{max} has been observed in the range from 0.075 to 0.5 h^{-1} (CRUEGER and coll., 1990), and for microorganisms which degrade toluene, μ_{max}

has been observed in the range from 0.025 h^{-1} to 0.54 h^{-1} (OTTENGRAF and coll., 1983; CHANG and coll., 1993). The values of μ_{max} in the present study were smaller than those reported in literature, which were obtained with pure strains of methylotrophs or toluene utilizers.

a)



b)

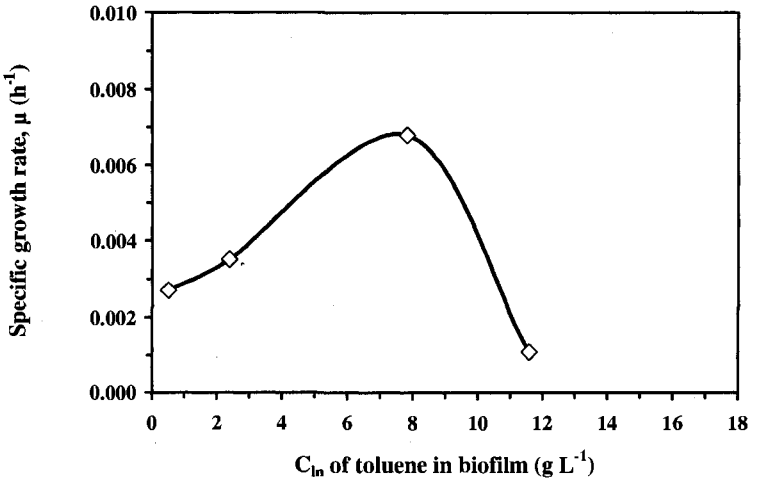
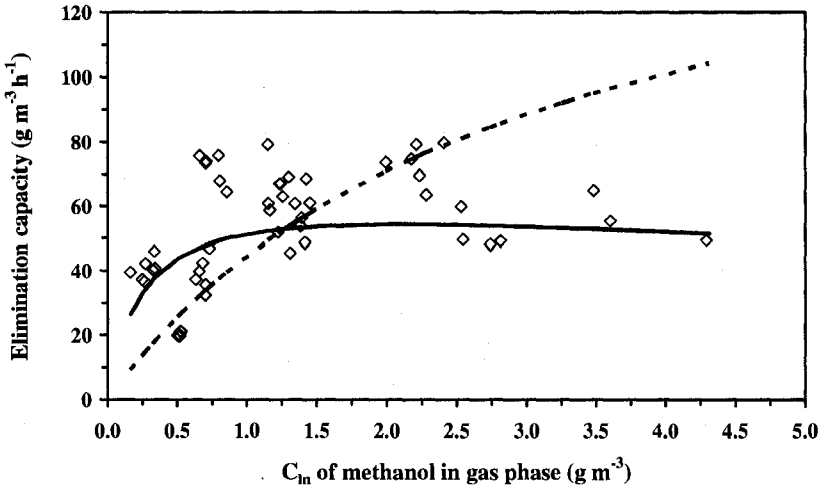


Figure 6.6. Specific growth rate for biofilters packed with clay spheres treating a) methanol and b) toluene as a function of methanol or toluene concentration in biofilm. Experimental μ (◊), tendency of μ (—).

a)



b)

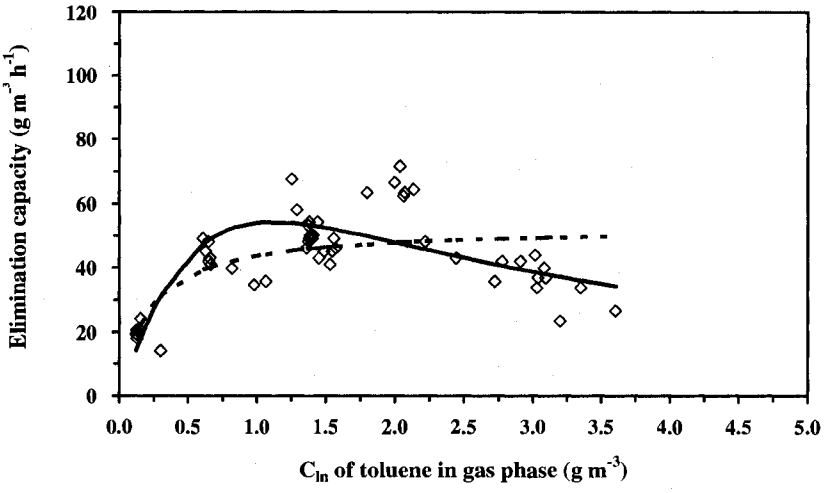


Figure 6.7. Elimination capacity as a function of a) methanol and b) toluene concentration in gas phase of biofilters packed with clay spheres. Experimental elimination capacity (◊), elimination capacity estimated with Michaelis-Menten type model (- - -), elimination capacity estimated with Haldane type model (——).

Figure 6.6-b shows that toluene produced a higher inhibitory effect than methanol; μ_{max} was smaller and μ dropped drastically to 0.001 h^{-1} when inhibition occurred. Since toluene is a

non-polar compound, it passes easily the hydrophobic cell membrane and is able to leak essential metabolites and cofactors, which kill the cells (RAJAGOPAL, 1996).

Figures 6.7-a and 6.7-b show the experimental EC for BF treating methanol at a C_{ln} from 0 to 4.5 g m^{-3} and toluene at a C_{ln} from 0 to 4 g m^{-3}. Figures 6.7-a and 6.7-b show that for both VOCs, the EC estimated with the Haldane type model (solid line) fitted the experimental data (lozenges) better than the Michaelis-Menten type model (dashed line). The experimental EC_{max} for methanol was 80 g m^{-3} h^{-1} at a methanol C_{ln} of around 1.5 g m^{-3}. The EC_{max} estimated with the Haldane type model was 70 g m^{-3} h^{-1} and with the Michaelis-Menten type model was 175 g m^{-3} h^{-1}. In the case of toluene, the EC_{max} observed was 65 g m^{-3} h^{-1} at a toluene C_{ln} of 2 g m^{-3}. The EC_{max} estimated with Haldane and Michaelis-Menten type models was 55 g m^{-3} h^{-1}, but with the Haldane type model EC_{max} occurred at a toluene C_{ln} of 1 g m^{-3} while with the Michaelis-Menten type model it occurred at a C_{ln} higher than 4.0 g m^{-3}. The experimental EC for methanol and toluene were better fitted by the model based on the Haldane model than the Michaelis-Menten model because both VOCs caused inhibition.

A comparison of Figures 6.7-a and 6.7-b confirms that toluene produced a higher inhibition than methanol. For toluene EC_{max} was 20% smaller and EC dropped quicker than for the BF treating methanol. For example, at a VOC C_{ln} of 3.5 g m^{-3}, the BF treating methanol presented an EC of 55 g m^{-3} h^{-1} while the EC of toluene was 30 g m^{-3} h^{-1}.

6.3.4. Fourth phase: Energy indicators

Effect of volatile solids on carbon dioxide production rate

Figure 6.8 shows the carbon dioxide production rate (PCO_2) as a function of the content of volatile solids present in the biofilm for methanol and toluene biofiltration. As shown in Figure 6.8, the PCO_2 for both pollutants had a similar linear tendency. PCO_2 increased with the volatile solids content in biofilm and the lines passing through the origin signify that CO_2 would not be produced in the absence of volatile solids. The microorganisms represent a part of the total volatile solids contained in the biofilm and an increase of total volatile solids signifies an increase of microorganisms. The correlation between PCO_2 and volatile solids content presents the advantage that the measurement of CO_2 concentration in the gas phase is easier and faster than the volatile solids content in the biofilm.

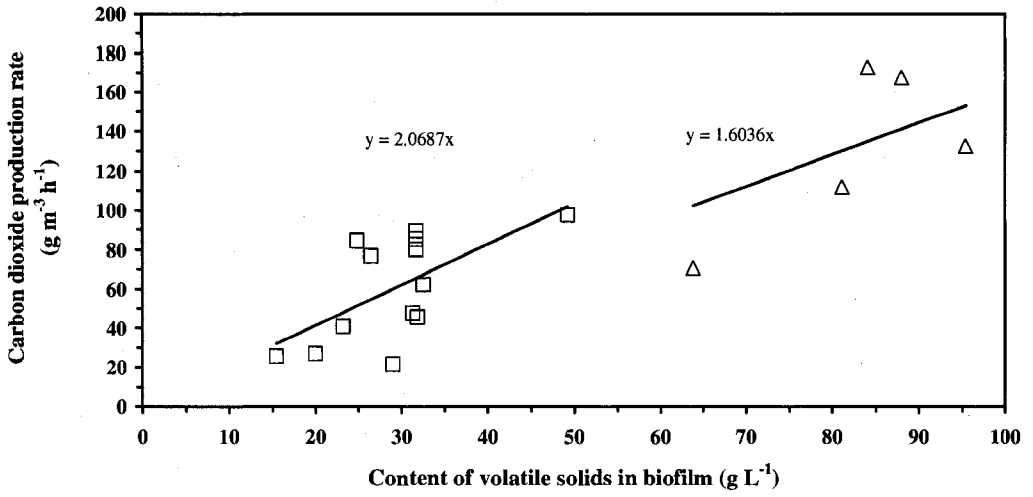


Figure 6.8. Carbon dioxide production rate (PCO_2) as a function of content of volatile solids in biofilm for biofilters treating methanol (□) and toluene (Δ). Tendency of PCO_2 (——).

Relationship between carbon dioxide production rate and packing bed temperature

Figure 6.9-a shows the difference of temperature (ΔT) between the packing bed and the environment as a function of the PCO_2 for methanol and toluene for BF. The tendency for both compounds and both packing materials was similar. The ΔT presented a linear tendency with PCO_2 with a slope of 0.024 °C per g of CO_2 produced m^{-3} h^{-1}. The slope represents the rate at which increases the temperature in the BF by the effect of the energy produced and released during the VOC biodegradation and which was associated to the PCO_2. The line passing through the origin shows that if the bioreaction does not occur, the packing bed would present the same temperature as the environment.

Figure 6.9-b shows the ΔT as a function of PCO_2 for the BTF treating methanol. For BTF the slope is higher than for BF, 0.15 °C (g of CO_2 produced m^{-3} $h^{-1})^{-1}$, but in this case the line does not pass through the origin and the ordinate is 6.8 °C. The ordinate represents the temperature which had the BTF if there is no microbial activity. As opposed to the BF, in the BTF, the lixiviate was recovered and recirculated to the top of the packing bed. When the lixiviate was pumped, it absorbed some of the energy dissipated by the pump and when it trickled down

through the BTF it heated the packing bed and produced a ΔT with respect to the environment. Daily measures of temperature in the holding reservoir showed that the nutrient solution presented an average ΔT of 7°C, which was near the value of the ordinate of 6.8°C in Figure 6.9-b. The energy recovered by the nutrient solution caused that the BTF presented a higher ΔT per unit of PCO_2 than the BF.

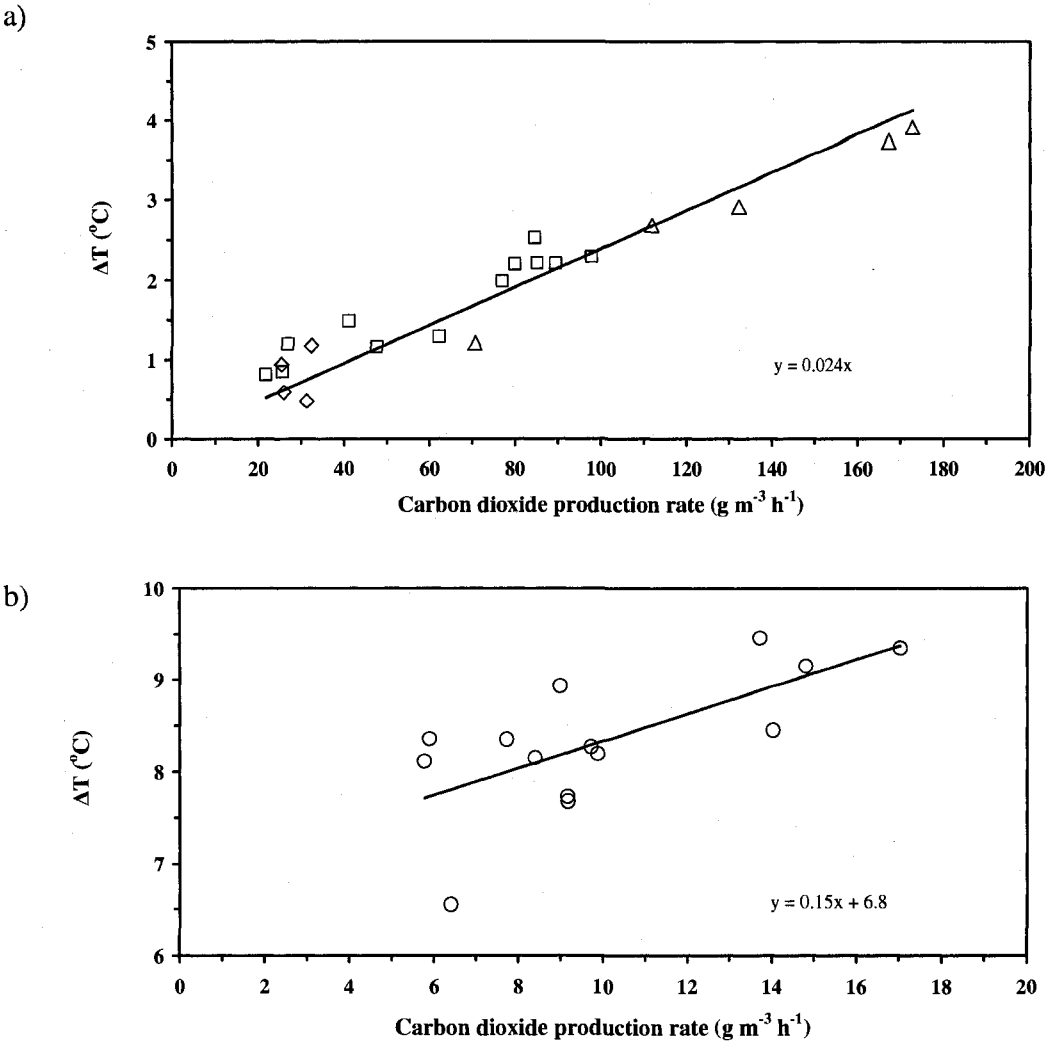


Figure 6.9. Difference of temperature between the packing bed and the environment as a function of the carbon dioxide production rate (PCO_2): a) Biofilters treating methanol and packed with clay spheres (□), methanol and polypropylene spheres (◊), toluene and clay spheres (Δ); b) biotrickling filters treating methanol. Tendency of PCO_2 for both figures (——).

In aerobic biosystems, the reactions of biodegradation of VOCs are exothermic. The chemical species which participate in these reactions are donors or acceptors of electrons. The exothermic energy produced in these reactions is the result of electron transfer from donor to acceptor. A percentage of this energy is recovered by the cells and used for maintenance and synthesis of new cells or storage compounds. When the electron donor and the carbon source are the carbon atoms contained in the molecule of VOC, the PCO_2 can be associated to the energy generated during the reaction of VOC biodegradation because there are no other element like N or S involved in energy generation (XIAO and coll., 2006). The microorganisms are not able to recover the total energy produced in bioreactions, they commonly present an efficiency of energy capture around 0.6 (VAN BRIESEN and coll., 2000). The energy which is not recovered dissipates in the system by different ways, such as conductive and convective heat transfer and causes the increase of temperature in the packing bed (ACUÑA and coll., 1999; GUTIÉRREZ-ROJAS and coll., 1996). The association of PCO_2 with the energy produced during the VOC biodegradation could lead to the calculation of the energy dissipated through the packing bed and the estimation of its temperature by means of an easy measurement of gas concentration.

Elemental composition and heat of combustion of biofilm

Table 6.3 shows the empirical formula calculated for biofilm formed in BFs treating methanol and toluene. The average empirical formula for biofilm formed in methanol biofiltration was $CH_{1.99}O_{0.64}N_{0.11}$ and in toluene biofiltration $CH_{1.98}O_{0.44}N_{0.18}$. These empirical formulas were nearly similar to that reported by BAILEY *et al.* (1986) of $CH_2O_{0.5}N_{0.2}$ as an average of elemental composition of biomass. The elemental composition calculated in the present study for the biofilm was nearly constant whatever the operating conditions. But this does not mean that the biofilm presented a constant composition in terms of macromolecules. For example, FARRUGIA (1999) showed that the protein and polysaccharide content in biofilm varied with operating conditions in methanol biofiltration. The biomass formed during methanol biofiltration had 20 % more oxygen than the biomass during toluene biofiltration. This could be due to the capability of methylotrophs to produce exo-polymers containing oxygen ANTHONY (1982).

Table 6.3. Heat of combustion and elemental composition of dry biofilm developed in biofilters packed with clay spheres for treating methanol and toluene.

a) Biofilters packed with clay spheres for treating methanol

Variable: Nitrogen concentration (gN L^{-1})	Combustion heat (cal g^{-1} of dry biofilm)	Elemental composition
0.03	3705	$C\ H_{2.02}\ O_{0.72}\ N_{0.09}$
0.1	3505	$C\ H_{2.01}\ O_{0.66}\ N_{0.09}$
2.4	3360	$C\ H_{2.05}\ O_{0.69}\ N_{0.09}$
Methanol inlet concentration (g m^{-3})		
0.8	3600	$C\ H_{1.97}\ O_{0.63}\ N_{0.11}$
3.0	3705	$C\ H_{2.00}\ O_{0.64}\ N_{0.10}$
4.3	3820	$C\ H_{1.99}\ O_{0.63}\ N_{0.11}$
Empty bed residence time (s)		
260	4240	$C\ H_{1.95}\ O_{0.53}\ N_{0.16}$
130	3865	$C\ H_{1.98}\ O_{0.64}\ N_{0.11}$
33	3880	$C\ H_{1.92}\ O_{0.64}\ N_{0.10}$
21	4465	$C\ H_{1.98}\ O_{0.64}\ N_{0.11}$
Average	3815	$C\ H_{1.99}\ O_{0.64}\ N_{0.11}$
standard deviation	330	-

b) Biofilters packed with clay spheres for treating toluene

Toluene inlet concentration (g m^{-3})	Combustion heat (cal g^{-1} of dry biofilm)	Elemental composition
0.4	3445	$C\ H_{1.95}\ O_{0.44}\ N_{0.19}$
1.1	4170	$C\ H_{1.97}\ O_{0.42}\ N_{0.17}$
1.9	4250	$C\ H_{1.98}\ O_{0.43}\ N_{0.17}$
2.7	4250	$C\ H_{1.99}\ O_{0.46}\ N_{0.19}$
3.5	3870	$C\ H_{2.00}\ O_{0.44}\ N_{0.19}$
Average	3995	$C\ H_{1.98}\ O_{0.44}\ N_{0.18}$
standard deviation	345	-

Table 6.3 also shows the heat of combustion for dry biofilm developed in the BF treating methanol or toluene. The values vary widely for both compounds from 3360 to 4465 cal g^{-1} of biofilm and this suggests that the biofilm composition in terms of chemical species varied with operating conditions. The dry biofilm formed in BF treating toluene presented an average heat of combustion of 3995 ± 345 cal g^{-1} of biofilm calculated with five samples. The dry biofilm developed in BF treating methanol presented an average of heat of combustion of 3815 ± 330 cal g^{-1} of biofilm calculated with ten samples. Table 6.3 shows that the energy

stocked in the bonds of chemical species contained in the biofilm was not constant for all the operating conditions tested. The values of heat of combustion are useful for energy balances of BF and BTF (BATTLEY, 2003; MYSLIWIEC and coll., 2001; SANDLER, 1991) which leads to the estimation of the heating and cooling utilities in bioprocess applied to industrial scale.

6.4. Conclusion

The microkinetics and macrokinetics of biofiltration with and without percolation of methanol and toluene were analyzed. Microkinetic models were expressed as functions of parameters which are easy followed, such as the concentration of volatile organic compound (VOC) in the gas phase. The specific growth rate μ in biotrickling filters treating methanol was 0.037 h^{-1}. For biofilters treating methanol, μ was in the range from 0.0001 to 0.0095 h^{-1} and for toluene from 0.001 to 0.007 h^{-1}. In biofilters, μ was function of VOC concentration in biofilm. Biofilters treating methanol showed that μ was also a function of N concentration in nutrient solution and kind of packing bed material.

The models of Michaelis-Menten and Haldane were adapted to estimate the elimination capacities of biofilters with and without percolation. The Michaelis-Menten type model fitted to EC of biotrickling filters treating methanol. The Haldane type model fitted to EC of biofilters treating methanol and toluene because biofilters presented inhibition by VOC concentration.

The carbon dioxide production rate presented a linear correlation with the content of volatile solids in the biofilm and with the difference of temperature between the packing bed and the environment. The carbon dioxide production rate was identified as an indicator of the energy produced during the VOC biodegradation in order to estimate the heat transfer and the temperature in the packing bed.

Biofilters packed with clay spheres presented a biofilm with a constant elemental composition of $CH_{1.99}O_{0.64}N_{0.11}$ for methanol and $CH_{1.98}O_{0.44}N_{0.18}$ for toluene. However, the heat of combustion of dry biofilm formed in the biofiltration of methanol (3815 ± 330 cal g^{-1} of biofilm) and toluene (3995 ± 345 cal g^{-1} of biofilm) suggests that the composition of biofilm in terms of macromolecules and other chemical species was not constant. This suggested that energy stored in the biofilm in the form of chemical bonds varied with operating conditions.

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Conclusion générale

Le présent travail montre que la biofiltration avec et sans percolation est un bioprocédé efficace pour le traitement de l'air pollué par de composés organiques volatils (COV).

Des vapeurs de méthanol, d'éthanol et de toluène ont été traitées dans des biofiltres avec et sans percolation garnis avec des matériaux inertes, tels l'argile et le polypropylène. Les biofiltres percolateurs traitant le méthanol et l'éthanol n'ont pas présenté de phénomène d'inhibition. Les capacités d'élimination du méthanol et de l'éthanol ont atteint la valeur de 2160 et 970 g m^{-3} h^{-1} respectivement, soit supérieures à celles reportées dans la littérature.

Les résultats obtenus démontrent que la solution nutritive a un effet bénéfique sur le biofiltre percolateur traitant des COV solubles dans l'eau. La solution nutritive permet de fournir les nutriments essentiels aux microorganismes et d'augmenter la disponibilité des COV solubilisés. La quantité de polluant absorbé par la solution nutritive est fonction de la charge à l'entrée. La solution nutritive agit aussi comme une voie d'élimination des vapeurs de méthanol et d'éthanol et peut représenter jusqu'à 80% d'élimination du méthanol enlevé de la phase gazeuse.

La solution nutritive a aussi le rôle de capter l'énergie émise par les microorganismes, ce qui permet d'homogénéiser la température du lit filtrant autour de 32°C. Du fait que la température ne varie pas, les microorganismes qu'utilisent le méthanol ou l'éthanol ont opéré dans des gammes de températures optimales pour leur croissance. Les profils de concentration du dioxyde de carbone sur la hauteur du lit filtrant montrent que le taux de réaction est homogène dans les biofiltres percolateurs. Le coefficient de partition du méthanol à 32°C a été déterminé et vaut 2.64×10^{-4} [mole L^{-1}]$_{gaz}$/[mole L^{-1}]$_{liquide}$. La mise au point de la méthode de la détermination du coefficient de partition est un apport important de la présente étude. Dans la littérature, à notre connaissance, il n'existe pas de travaux relatifs à la détermination des coefficients de partition pour des biofiltres percolateurs opérant en régime permanent.

La performance des biofiltres percolateurs a été affectée par les conditions opératoires, telles la concentration de méthanol à l'entrée, la concentration d'azote dans la solution nutritive, le temps de résidence du gaz à l'intérieur du biofiltre percolateur. Pour les deux alcools, méthanol et éthanol, le taux de conversion a augmenté avec le temps de résidence et la

concentration d'azote pendant qu'il a diminué avec la charge. Quant à la biotransformation des COV, les coefficients de rendement de la biomasse et du dioxyde de carbone augmentent avec la concentration d'azote et le temps de résidence. Les rendements diminuent avec la concentration à l'entrée des polluants.

Dans la présente étude, les biofiltres percolateurs ont opéré à une faible concentration d'azote de 0.005 gN L^{-1} dans une solution nutritive constituée par seulement trois composés : urée, sulfate de potassium et acide phosphorique neutralisé avec l'hydroxyde de sodium. Les taux de conversion et les capacités d'élimination obtenus démontrent que les biofiltres percolateurs peuvent opérer efficacement avec des solutions nutritives peu complexes. De plus, la méthode développée pour contrôler le contenu de biomasse dans le lit filtrant a permis d'utiliser les biofiltres percolateurs pendant 45 jours sans laver le lit filtrant. De ce fait, il n'y a pas eu de problèmes de colmatage du lit; le lit filtrant était lavé uniquement pour stabiliser la performance des biofiltres et non pour enlever la biomasse.

Un autre bioréacteur étudié était le biofiltre traditionnel. Des vapeurs de méthanol et de toluène ont été traités dans des biofiltres garnis de matériaux inertes. Les deux COV ont eu un effet inhibiteur sur les microorganismes. Pour le méthanol, les effets des conditions d'opération sur certains paramètres du lit filtrant et du biofilm ont été étudiés. Deux garnissages ont été testés, une argile poreuse qui a donné des taux de conversion plus élevés que le polypropylène non poreux. Pour les deux garnissages, la performance des biofiltres augmente avec la concentration d'azote présente dans la solution nutritive. Cependant, pour la concentration maximale d'azote de 2.4 gN L^{-1}, la production de biomasse et la densité cellulaire de méthylotrophes ont diminué. Le contenu d'eau dans le lit filtrant a été fonction du contenu de biomasse présent dans le matériel non poreux. La capacité d'élimination a été associée à la densité cellulaire des méthylotrophes. La charge critique de méthanol a été de 80 g m^{-3} h^{-1} et s'est présentée avec la densité cellulaire des méthylotrophes la plus élevée. Une méthode pour calculer la moyenne pondérée de la biomasse présente dans le lit filtrant a été développée. Cette méthode a permis d'une part d'effectuer des bilans de carbone dans le biofiltre et d'autre part de calculer les paramètres cinétiques de croissance microbienne sous des conditions d'opération réelles.

Les paramètres cinétiques de croissance microbienne et de dégradation de polluants ont été calculés pour l'ensemble des biofiltres et des biofiltres percolateurs. Dans le cas de la

croissance microbienne, une nouvelle méthode pour calculer les paramètres cinétiques du méthanol a été développée. L'algorithme mathématique a été construit à partir des bilans de matière reliés à la bioconversion du méthanol en biomasse et dioxyde de carbone. Les hypothèses établies, pour simplifier l'algorithme mathématique, ont été validées avec les résultats obtenus. Quand les concentrations de méthanol dans le gaz et le biofilm s'approchent de l'équilibre thermodynamique, il a été ainsi observé que la diminution de la concentration de méthanol dans la phase gazeuse était contrôlée par le taux de biodégradation du méthanol dans le biofilm; ce dernier étant constant tout au long de chaque expérience. La vitesse de croissance spécifique répond au modèle d'Haldane, étant donné que le méthanol inhibe les microorganismes. La vitesse de croissance maximale observée est de 0.049 h^{-1} pour le biofiltre garni avec sphères d'argile et de 0.007 h^{-1} pour le biofiltre garni avec boulettes de compost, tandis que les valeurs calculées avec le modèle d'Haldane sont respectivement de 0.044 et 0.007 h^{-1}.

La vitesse de croissance spécifique de la biomasse a été calculée pour les biofiltres avec et sans percolation sous des conditions réelles d'opération. La vitesse pour le biofiltre percolateur a été calculée en régime permanent. La concentration de biomasse dans le lit filtrant, approximée à celle du lixiviat, a été utilisée pour calculer la vitesse spécifique pour le biofiltre percolateur traitant du méthanol qui vaut 0.037 h^{-1}. Dans le cas du biofiltre traditionnel, la vitesse spécifique de croissance microbienne du méthanol et du toluène a été calculée sous chaque condition d'opération en suivant la biomasse présente dans le lit filtrant. Les vitesses spécifiques sont fonction des conditions d'opération, telle la concentration d'azote dans la solution nutritive, le garnissage, la concentration de toluène et de méthanol dans le biofilm.

La cinétique de biodégradation des polluants a été analysée en terme de capacité d'élimination. Deux modèles cinétiques avec une structure mathématique similaire aux modèles de Michaelis-Menten et d'Haldane ont été validés. Dans les cas des biofiltres percolateurs, la capacité d'élimination du méthanol s'est ajustée au modèle du type Michaelis-Menten, puisque les biofiltres percolateurs n'ont pas présenté d'inhibition. Dans le cas des biofiltres traditionnels, la capacité d'élimination pour le méthanol et le toluène s'est ajustée au modèle du type Haldane puisque les biofiltres ont présenté de l'inhibition à concentration élevée de polluants. Les capacités d'élimination maximales estimées avec les modèles

cinétiques sont proches des valeurs expérimentales. Le modèle cinétique incluant un terme d'inhibition pour calculer la capacité d'élimination n'avait jamais été utilisé à notre connaissance.

Une brève analyse des indicateurs énergétiques des biofiltres avec et sans percolation a été faite. Plus spécifiquement, le taux de production de dioxyde de carbone a été associé avec la différence de température entre le lit filtrant et l'environnement. Dans les biofiltres percolateurs, la solution nutritive agit comme régulateur de la température en absorbant et en émettant de la chaleur provenant de la bioréaction et de la pompe centrifuge.

Le biofilm développé dans des biofiltres traditionnels à une composition élémentaire moyenne de $CH_{1.99}O_{0.64}N_{0.11}$ pour le méthanol et de $CH_{1.98}O_{0.44}N_{0.18}$ pour le toluène, ces compositions restant constantes pour toutes les conditions d'opération testées. Par contre, les chaleurs de combustion du biofilm suggèrent que la composition du biofilm en terme des espèces chimiques, telles les protéines et les exo-polysaccharides, n'est pas constante. Les chaleurs de combustion varient dans une gamme de 3440 à 4460 cal g^{-1} de biofilm. Ces données de composition élémentaire et de chaleur de combustion du biofilm sont utiles dans le développement des modèles mathématiques intégrant une approche énergétique.

En résumé, les études présentées dans cette thèse sont une contribution à une meilleure appréhension de la biofiltration avec et sans percolation et ont permis de développer de nouvelles méthodes facilitant la caractérisation des propriétés physico-chimiques et biologiques des biofiltres.

Références

ACUÑA, M. E., PÉREZ, F., AURIA, R., REVAH, S. (1999) *Microbiological and kinetic aspects of a biofilter for the removal of toluene from waste gases*, Biotechnology and Bioengineering, vol. 63, n° 2, p. 175-184.

ALCANTARA, S., ESTRADA, I., VASQUEZ, M. S., REVAH, S. (1999) *Carbon Disulfide Oxidation by a Microbial Consortium from a Trickling Filter*, Biotechnology Letters, vol. 21, n° 9, p. 815-821.

ALLEN, L., ELLIS, S. (2000) *Laboratory evaluation of trickling biofiltration for treatment of kraft mill noncombustion air emissions*, TAPPI 2000 International Environmental Conference, Denver, CO.

ALONSO, C., SUIDAN, M. T., SORIAL, G. A., SMITH, F. L., BISWAS, P., SMITH, P. J., BRENNER, R. (1997) *Gas treatment in trickle-bed biofilters: Biomass, how much is enough?*, Biotechnology and Bioengineering, vol. 54, n° 6, p. 583-594.

ALONSO, C., ZHU, X. Q., SUIDAN, M. T., KIM, B. R., KIM, B. J. (2000) *Parameter estimation in biofilter systems*, Environmental Science & Technology, vol. 34, n° 11, p. 2318-2323.

ALONSO, C., ZHU, X. Q., SUIDAN, M. T., KIM, B. R., KIM, B. J. (1999) *Mathematical model for the biodegradation of VOCs in trickle bed biofilters*, Water Science & Technology, vol. 39, n° 7, p. 139-146.

AMANULLAH, S., FAROOQ, S., VISWANATHAN, S. (1999) *Modeling and simulation of a biofilter*, Industrial and Engineering Chemistry Research, vol. 38, n° 7, p. 2765-2774.

ANTHONY, C. (1982) *The biochemistry of methylotrophs*, Academic Press, London, p. 431.

APHA – AMERICAN PUBLIC HEALTH ASSOCIATION (1999) *Standard Methods for the Examination of Water and Wastewater*, 20th ed. United Book Press, Inc., Baltimore, MD, pp. 2-55 – 2-56.

ARCANGELI, J. P., ARVIN, E. (1992) *Modelling of toluene biodegradation and biofilm growth in a fixed biofilm reactor*, Water Science and Technology, vol. 26, n° 3-4, p. 617-626.

ARULNEYAM, D., SWAMINATHAN, T. (2000) *Biodegradation of ethanol vapour in a biofilter*, Bioprocess Engineering, vol. 22, n° 1, p. 63-67.

AURIA, R., AYCAGUER, A.-C., DEVINNY, J. S. (1998) *Influence of water content on degradation rates for ethanol in biofiltration*, Journal of the Air & Waste Management Association, vol. 48, n° 1, p. 65-70.

AVALOS RAMIREZ, A., BÉNARD, S., GIROIR-FENDLER, A., JONES, J. P., HEITZ, M. (accepted on February 2008) *Treatment of methanol vapours in biofilters packed with inert materials*, Journal of Chemical Technology and Biotechnology.

AVALOS RAMIREZ, A., JONES, J. P., HEITZ, M. (2007a) *Treatment of methanol emissions by biofiltration with or without percolation*, 9th Ontario-Quebec Biotechnology Meeting, oral presentation, University of Toronto, Ontario, Canada.

AVALOS RAMIREZ, A., JONES, J. P., HEITZ, M. (2007b) *Biotrickling filtration of air contaminated with ethanol*, Journal of Chemical Technology and Biotechnology, vol. 82, n° 2, p. 149-157.

AVALOS RAMIREZ, A., JONES, J. P., HEITZ, M. (2007c) *Characterization of a biotrickling filter treating methanol vapours*, In: Biotechniques for air pollution control, Chapter: VOC removal in conventional and biotrickling filters, Eds. KENNES, C., VEIGA, M. C. Servicio de Publicacions, Universidade da Coruña, La Coruña, pp 379-384.

AVALOS RAMIREZ, A., JONES, J. P., HEITZ, M. (2005) *Methanol and ethanol treatment by biotrickling filtration: an experimental study*, In: Biotechniques for air pollution control, Chapter: Mixed VOCs and industrial applications, Eds. KENNES, C., VEIGA, M. C. Servicio de Publicacions, Universidade da Coruña, La Coruña, Espagne, p. 385-389.

BAILEY, J. E., OLLIS, D. F. (1986) *Biochemical engineering fundamentals*, 2nd ed. McGraw-Hill, New York, NY, p. 984.

BAKKE, R., TRULEAR, M. G., ROBINSON, J. A., CHARACKLIS, W. G. (1984) *Activity of Pseudomonas aeruginosa in biofilms: Steady state.* Biotechnology and Bioengineering, vol. 26, n° 12, p. 1418-1424.

BALTZIS, B. C., DE LA CRUZ, D. S. (1996) *Removal of xylene vapors in a biotrickling filter*, In Proceedings of the 89th Annual Meeting and Exhibition of the Air and Waste Management Association, AWMA, Nashville, TN.

BALTZIS, B. C., SHAREEFDEEN, Z. (1992) *Principles of packed-bed biofilter modeling and design*, In mini-symposium of Bioscrubbing of gaseous emissions, Rutgers University, New Brunswick, 18 November 1992.

BALTZIS, B. C., MPANIAS, C. J., BHATTACHARYA, S. (2001) *Modeling the removal of VOC mixtures in biotrickling filters*, Biotechnology and Bioengineering, vol. 72, n° 4, p. 389-401.

BARTON, J. W., KLASSON, K. T., KORAN, L. J., DAVISON, B. H. (1997) *Microbial removal of alkanes from dilute gaseous waste streams: Kinetics and mass transfer considerations*, Biotechnology Progress, vol. 13, n° 6, p. 814-821.

BARTON, J. W., DAVISON, B. H., KLASSON, K. T., GABLE III, C. C. (1999) *Estimation of mass transfer and kinetics in operating trickle-bed bioreactors for removal of VOCs*, Environmental Progress, vol. 18, n° 2, p. 87-92.

BATTLEY, E.H. (2003) *Absorbed heat and heat of formation of dried microbial biomass, Studies on the thermodynamics of microbial growth*, Journal of Thermal Analysis and Calorimetry, vol. 74, n° 3, p. 709-721.

BISHOP, P. L. (1997) *Biofilm structure and kinetics*, Water Science and Technology, vol. 36, n° 1, p. 287-294.

CHANG, K.; LU, C.; LIN, M.-R. (2001) *Treatment of volatile organic compounds from polyurethane and epoxy manufacture by a trickle-bed air biofilter*, Journal of Bioscience & Bioengineering, vol. 92, n° 2, p. 126-130.

CHANG, M.-K., VOICE, T. C., CRIDDLE, C. S. (1993) *Kinetics of competitive inhibition and cometabolism in the biodegradation of benzene, toluene, and p-xylene by two Pseudomonas isolates*, Biotechnology and Bioengineering, vol. 41, n° 11, p. 1057-1065.

CHETPATTANANONDH, P., NITIPAVACHON, Y., BUNYAKAN, C., (2005) *Biofiltration of air contaminated with methanol and toluene*, Songklanakarin Journal of Science and Technology, vol. 27, n° 3, p. 761-773.

CHOU, M. S., HUANG, J. J. (1997) *Treatment of methylethylketone in air stream by biotrickling filters*, Journal of Environmental Engineering-Asce, vol. 123, n° 6, p. 569-576.

CHOU, M. S., HSIAO, C. C. (1998) *Treatment of styrene-contaminated airstream in biotrickling filter packed with slags*, Journal of Environmental Engineering-Asce, vol. 124, n° 9, p. 844-850.

CHRISTEN, P., DOMENECH, F., AURIA, R., REVAH, S. (2001) *Effect of medium salt concentration on the performances of an ethanol biofilter*, In Proceedings of the 94th Annual Meeting and Exhibition of the Air and Waste Management Association, AWMA, Orlando, FL.

CHRISTEN, P., DOMENECH, F., MICHELENA, G., AURIA, R., REVAH, S. (2002) *Biofiltration of volatile ethanol using sugar cane bagasse inoculated with Candida utilis*, Journal of Hazardous Materials, vol. 89, n° 2-3, p. 253-265.

CIOCI, F., LAVECCHIA, R., FERRANTI, M. M. (1997) *High-performance microbial removal of ethanol from contaminated air*, Biotechnology Techniques, vol. 11, n° 12, p. 893-898.

COMMUNICATION CANADA (2003) *Notice with respect to substances in the National Pollutant Release Inventory for 2003*, Canada Gazette Part I, vol. 137, n° 1, p. 8-32.

COOPER, C. D., ALLEY, F.C. (2002) *Air pollution Control, A design approach*, 3e edition, Waveland Press, Prospect Heights, IL, p. 429-442.

COX, H. H. J., DESHUSSES, M. A. (2000a) *Innovative experimental setup for the parallel operation of multiple bench scale biotrickling filters for waste air treatment*, Environmental Technology, vol. 21, n° 4, p. 427-435.

COX, H. H. J., DESHUSSES, M. A. (1999a) *Biomass control in waste air biotrickling filters by protozoan predation*, Biotechnology and Bioengineering, vol. 62, n° 2, p. 216-224.

COX, H. H. J., DESHUSSES, M. A. (1999b) *Chemical removal of biomass from waste air biotrickling filters: Screening of chemicals of potential interest*, Water Research, vol. 33, n° 10, p. 2383-2391.

COX, H. H., NGUYEN, T. T., DESHUSSES, M. A. (2000b) *Toluene degradation in the recycle liquid of biotrickling filters for air pollution control*, Applied Microbiology and Biotechnology, vol. 54, n° 1, p. 133-137.

COX, H. H., SEXTON, T., SHAREEFDEEN, Z. M., DESHUSSES, M. A. (2001) *Thermophilic biotrickling filtration of ethanol vapors*, Environmental Science and Technology, vol. 35, n° 12, p. 2612-2619.

CRUEGER, W., CRUEGER, A. (1990) *Biotechnology: A textbook of industrial microbiology*, 2eme, Sinauer Associates, Sunderland, MA, p. 357.

DASTOUS, P., SOREANU, G., NIKIEMA, J., HEITZ, M. (accepted on 2007) *Elimination of methanol and ethanol by biofiltration: an experimental study*. Journal of Water, Air, and Soil Pollution.

DASTOUS, P.-A., NIKIEMA, J., SOREANU, G., HEITZ, M. (2005) *Biofiltration of Two Alcohols on a Mature Bed Compost*, Paper No. 1038, Annual Meeting and Exhibition of the Air and Waste Management Association, AWMA, Pittburgh, PA.

DELHOMÉNIE, M. C. (2002) *Biofiltration of air contaminated by volatil organic compounds in a compost-based bed*, Ph. D. Thesis, Université de Sherbrooke, Québec, Canada, p. 222.

DELHOMÉNIE, M. C., BIBEAU, L., GENDRON, J., BRZEZINSKI, R., HEITZ, M. (2001) *Toluene removal by biofiltration: influence of the nitrogen concentration on operational parameters*, Industrial and Engineering Chemistry Research, vol. 40, n° 23, p. 5405-5414.

DELHOMÉNIE, M. C., BIBEAU, L., HEITZ, M. (2005) *A study of the biofiltration of high-loads of toluene in air: Carbon and Water Balances, temperature changes and nitrogen effect*, Canadian Journal of Chemical Engineering, vol. 83, n° 2, p. 153-160.

DELHOMÉNIE, M. C., HEITZ, M. (2005) *Biofiltration of air: A review*. Critical Reviews in Biotechnology, vol. 25, n° 1, p. 53-72.

DELHOMÉNIE, M. C., HEITZ, M. (2003) *Elimination of chlorobenzene vapors from air in a compost-based biofilter*, Journal of Chemical Technology and Biotechnology, vol. 78, n° 5, p. 588-595.

DESHUSSES, M. A. (1997) *Transient behavior of biofilters: start-up, carbon balances, and interactions between pollutants*, Journal of Environmental Engineering, vol. 123, n° 6, p. 563-568.

DESHUSSES, M. A., HAMER, G., DUNN, I. J. (1995a) *Behavior of biofilters for waste air biotreatment. 1. Dynamic model development*, Environmental Science & Technology, vol. 29, n° 4, p. 1048-1058.

DESHUSSES, M. A., HAMER, G., DUNN, I. J. (1995b) *Behavior of biofilters for waste air biotreatment. 2. Experimental evaluation of a dynamic model*, Environmental Science & Technology, vol. 29, n° 4, p. 1059-1068.

DEVINNY, J. S., HODGE, D. S. (1995) *Formation of acidic and toxic intermediates in overloaded ethanol biofilters*, Journal of the Air & Waste Management Association, vol. 45, n° 2, p. 125-131.

DIKS, R. M. M. (1992) *The removal of dichloromethane from waste gases in a biological trickling filter*, Ph. D. Thesis, Technische Universiteit Eindhoven, Eindhoven, Netherlands, 217 p.

DIKS, R.M.M, OTTENGRAF, S.P.P, (1991) *Verification studies of a simplified model for the removal of dichloromethane from waste gas using a biological trickling filter: part I and part II*, Bioprocess Engineering, vol. 6, n° 4, p. 93-99, 131-140.

DIKS, R.M.M, OTTENGRAF, S.P.P, VRIJLAND, S. (1994) *The existence of a biological equilibrium in a trickling filter for waste gas purification*, Biotechnology and Bioengineering, vol. 44, n° 11, p. 1279-1287.

DION St-PIERRE, M.-C., BIBEAU, L., HEITZ, M. (2006) *Biofiltration of contaminated air by styrene vapors on an inorganic filtering media*, In: Proceedings of the 99th Annual Meeting and Exhibition of the Air and Waste Management Association, AWMA, Pittburgh, PA.

DUMONT, E., ANDRES, Y., LE CLOIREC, P. (2005) *Enhancement of oxygen transfer in bioprocess by the use of an organic phase: effect of silicone oil on volumetric mass transfer coefficient of oxygen (k_La)*, In: Biotechniques for air pollution control, Chapter: Kinetics, mass transfer, and modelling, Eds. Kennes, C., Veiga, M. C. Servicio de Publicacions, Universidade da Coruña, La Coruña, Espagne, p. 163-170.

ECKENFELDER, W.W. (1989) *Industrial water pollution control.* 2eme, McGraw-Hill, New York, NY, p. 400.

EDWARDS, F. G., NIRMALAKHANDAN, N. (1996) *Biological treatment of airstreams contaminated with VOCs: An overview*, Water Science and Technology, vol. 34, n° 3-4, p. 565-571.

ENVIRONNEMENT CANADA. (2003) *Inventaire National des rejets des polluants, Compte rendu national 2001 - rejets*, http://www.ec.gc.ca/inrp [accessed may 2007]

ENVIRONMENT AUSTRALIA (2006) *National Pollutant Inventory: Emission estimation techniques manual for bread manufacturing Version 1.1*, http://www.npi.gov.au [accessed may 2006].

ENVIRONMENTAL PROTECTION AGENCY – EPA (1992) *Alternative control technology document for bakery oven emissions, ed. by Office of Air Quality Planning and Standards*, Research Triangle Park, North Carolina, p. 126.

EPA - ENVIRONMENTAL PROTECTION AGENCY (1990) *Clean Air Act as amended (42 U.S.C. 7401 et seq.)*, US Government, Washington, DC.

FANG, Y. (2002) *New developments of biotrickling filters: Experiments and theories*, Ph. D. Thesis, University of Cincinnati, OH, p. 295.

FARRUGIA, V. M. (1999) *The development and properties of biofilms in biofilters*, Ph. D. Thesis, University of Toronto, Toronto, Canada, 175 p.

FORTIN, N. Y., DESHUSSES, M. A. (1999) *Treatment of methyl tert-butyl ether vapors in biotrickling filters. 1. Reactor startup, steady state performance, and culture characteristics*, Environmental Science & Technology, vol. 33, n° 17, p. 2980-2986.

GAI, S. L., BAUMANN, K. H (2001) *The role of the liquid phase in the degradation of toluene and m-cresol within a biofilm trickle-bed reactor*, Engineering Life Science, vol. 24, n° 4, p. 159-172.

GARNER, J (1996) *Methanol emission control options meet EPA "cluster" requirements*, Pulp and Paper, vol. 70, n° 8, p. 59-62.

GOVIND, R., WANG, Z. (1997) *Biofiltration kinetics for volatil organic compounds (VOCs) and development of a structure-biodegradability relationship*, In: Proceedings of the 90th Annual Meeting and Exhibition of the Air and Waste Management Association, AWMA, Pittsburgh, PA.

GREEN, P. N. (1992) *Taxonomy of methylotrophic bacteria*, In: Biotechnology Handbooks V5 – Methane and methanol utilizers, Eds. Murrell, J. C., Dalton, H. Plenum Press, New York, NY, p. 23-84.

GRIBBINS, M. J., LOEHR, R.C. (1998) *Effect of media nitrogen concentration on biofilter performance*, Journal of the Air and Waste Management Association, vol. 48, n° 3, p. 216-226.

GROENESTIJN, J. W., LAKE, M. E. (1999) *Elimination of alkanes from off-gases using biotrickling filters containing two liquid phases*, Environmental Progress, vol. 18, n° 3, p. 151-155.

GUPTA, A. K., TEJA, A. S., CHAI, X. S., ZHU, J. Y. (2000) *Henry's constants of n-alkanols (methanol through n-hexanol) in water at temperatures between 40°C and 90°C*, Fluid Phase Equilibria, vol. 170, n° 2, p.183-192.

GUTIÉRREZ-ROJAS, M., HOSN, S. A. A., AURIA, R., REVAH, S., FAVELA-TORRES, E. (1996) *Heat transfer in citric acid production by solid state fermentation*, Process Biochemistry, vol. 31, n° 4, p. 363-369.

HART, T. D., CHAMBERLAIN, A. H. L., LYNCH, J. M., NEWLING, B., McDONALD, P. J. (1999) *A stray field magnetic resonance study of water diffusion in bacterial exopolysaccharides*. Enzyme and Microbial Technology, vol. 24, n° 5-6, p. 339-347.

HEKMAT, D., VORTMEYER, D. (1994) *Modelling of biodegradation processes in trickle-bed bioreactors*, Chemical Engineering Science, vol. 49, n° 24A, p. 4327-4345.

HEKMAT, D., LINN, A., STEPHAN, M., VORTMEYER, D. (1997) *Biodegradation dynamics of aromatic compounds from waste air in trickle-bed reactor*, Applied Microbiology and Biotechnology, vol. 48, n° 1, p. 129-134.

HIRAI, M., OHTAKE, M., SHODA, M. (1990) *Removal kinetics of hydrogen sulfide, methanethiol and dimethyl sulfide by peat biofilters*, Journal Fermentation and Bioengineering, vol. 70, n° 5, p. 334-339.

HODGE, D. S., DEVINNY, J. S. (1994) *Biofilter treatment of ethanol vapors*, Environmental Progress, vol. 13, n° 3, p. 167-173.

HODGE, D. S., DEVINNY, J. S. (1995) *Modeling removal of air contaminants by biofiltration*, Journal of Environmental Engineering, vol. 121, n° 1, p. 21-32.

HODGE, D. S., DEVINNY, J. S. (1997) *Determination of transfer rate constants and partition coefficients for air phase biofilters*, Journal of Environmental Engineering, vol. 123, n° 6, p. 577-585.

HODGE, D. S., MEDINA, V. F., DEVINNY, J. S. (1991) *Biological methods for air decontamination: Modeling hydrocarbon removal*, In Environmental Engineering: Proceedings of the 1991 Specialty Conference, Reno, NV.

HOLUBAR, P., ANDORFER, C., BRAUN, R. (1999) *Effects of nitrogen limitation on biofilm formation in a hydrocarbon-degrading trickle-bed filter*, Applied Microbiology and Biotechnology, vol. 51, n° 4, p. 536-540.

HUGLER, W., ACOSTA, C., REVAH, S. (1999) *Biological removal of carbon disulfide from waste air streams*, Environmental Progress, vol. 18, n° 3, p. 173-177.

IKEMOTO, S., JENNINGS, A. A., SKUBAL, K. L. (2006) *Modeling hydrophobic VOC biofilter treatment in the presence of nutrient stimulation and hydrophilic VOC inhibition*, Environmental Modelling and Software, vol. 21, n° 10, p. 1387-1401.

IRANPOUR, R., SAMAR, P., STENSTROM, M. K., CLARK, J. H., CONVERSE, B. M., SCHROEDER, E. D., COX, H. H. J., DESHUSSES, M. A. (2001) *Biological treatment of odor and VOCs in biofilters and biotrickling filters: survey of field experience*, In: Proceedings of the 94th Annual Meeting and Exhibition of the Air and Waste Management Association, AWMA, Pittsburgh, PA.

JONES, K., MARTINEZ, A., MAROO, K., DESHPANDE, S. (2004) *Kinetic evaluation of H_2S and NH_3 biofiltration for two media used for wastewater lift station emissions*, Journal of the Air and Waste Management Association, vol. 54, n° 1, p. 24-35.

JORIO, H., BIBEAU, L., HEITZ, M. (2000) *Biofiltration of air contaminated by styrene: effect of nitrogen supply, gas flow rate, and inlet concentration*, Environmental Science and Technology, vol. 34, n° 9, p. 1764-1771.

JORIO, H., BRZEZINSKI, R., HEITZ, M. (2005) *A novel procedure for the measurement of the kinetics of styrene biodegradation in a biofilter*, Journal of Chemical Technology and Biotechnology, vol. 80, n° 7, p. 796-804.

JORIO, H., HEITZ, M. (1999) *Traitement de l'air par biofiltration*, Canadian Journal of Civil Engineering, vol. 26, n° 4, p. 402-424.

JORIO, H., KIARED, K., BRZEZINSKI, R., LEROUX, A., VIEL, G., HEITZ, M. (1998) *Treatment of air polluted with high concentrations of toluene and xylene in a pilot-scale biofilter.* Journal of Chemical Technology and Biotechnology, vol. 73, n° 3, p. 183-196.

JUTEAU, P. (1997) *Analyse fonctionnelle de la microflore d'un biofiltre à base de compost utilisé pour le traitement d'effluents gazeux contenant du toluène*, Ph. D. Thesis, Université Laval, Québec, Canada, p. 199.

KENNES, C., THALASSO, F. (1998) *Waste gas biotreatment technology*, Journal of Chemical Technology and Biotechnology, vol. 72, n° 4, p. 303-319.

KIARED, K., BIBEAU, L., BRZEZINSKI, R., VIEL, G., HEITZ, M. (1996) *Biological elimination of VOCs in biofilter*, Environmental Progress, vol. 15, n° 3, p. 148-152.

KIARED, K., WU, G., BEERLI, M., ROTHENBÜHLER, M., HEITZ, M. (1997) *Application of biofiltration to control of VOC emissions*, Environmental Technology, vol. 18, n° 1, p. 55-63.

KIM, D., SORIAL, G. A. (2007) *Role of biological activity and biomass distribution in air biofilter performance*, Chemosphere, vol. 66, n° 9, p. 1758-1764.

KIRCHNER, K., WAGNER, S., REHM, H. J. (1996) *Removal of organics from exhaust gases in the trickle-bed bioreactor: Effect of oxygen*, Applied Microbiology and Biotechnology, vol. 45, n° 3, p. 415-419.

KONG, Z., FARHANA, L., FULTHORPE, R. R., ALLEN, D. G. (2001) *Treatment of volatile organic compounds in a biotrickling filter under thermophilic conditions*, Environmental Science and Technology, vol. 35, n° 21, p. 4347-4352.

KORNBERG, A. (1995) *Inorganic polyphosphate: Toward making a forgotten polymer unforgettable*, Journal of Bacteriology, vol. 177, n° 3, p. 491-496.

KRAILAS, S., PHAM, Q. T. (2000a) *Transient model of methanol and water movements in packed bed biofilter*, In: Proceedings of the 93rd Annual Meeting and Exhibition of the Air and Waste Management Association, AWMA, Pittburgh, PA, p. 2214-2231.

KRAILAS, S., PHAM, Q. T. (2002) *Macrokinetic determination and water movement in a downward flow biofilter for methanol removal*, Biochemical Engineering Journal, vol. 10, n° 4, p. 299-305.

KRAILAS, S., PHAM, Q. T., AMAL, R., JIANG, J. K., HEITZ, M. (2000b) *Effect of inlet mass loading, water and total bacteria count on methanol elimination using upward flow and downward flow biofilters*, Journal of Chemical Technology and Biotechnology, vol. 75, n° 2, p. 103-113.

LEAK, D. J. (1992) *Biotechnological and applied aspects of methane and methanol utilizers*, In: Biotechnology Handbooks V5 – Methane and methanol utilizers, Eds. Murrell, J. C., Dalton, H. Plenum Press, New York, NY, p. 245-279.

LE CLOIREC (1998) *Les composés organiques volatils (COV) dans l'environnement*, Technique & Documentation, Paris.

LE CLOIREC, P., HUMEAU, P., RAMIREZ-LOPEZ, E. M., *Biotreatments of odours: control and performances of a biofilter and a bioscrubber*, Water Science and Technology, vol. 44, n° 9, p. 219-226 (2001).

LEHNINGER, A. L., NELSON, D. L., COX, M. M. (1993) *Principles of biochemistry*, 2e edition, Worth Publishers, New York, p. 70-71, 116, 181, 288-293, 688-696.

LESON, G., CHAVIRA, R., WINER, A. M., HODGE, D. (1995) *Experiences with a Full-Scale Biofilter for Control of Ethanol Emissions*, In: Proceedings of the 88th Annual Meeting and Exhibition of the Air and Waste Management Association, AWMA, Pittburgh, PA, p. 11.

LESON, G., HODGE, D. S., TABATAI, F., WINER, A. M. (1993) *Biofilter demonstration projects for the control of ethanol emission*, In: Proceedings of the 86th Annual Meeting and Exhibition of the Air and Waste Management Association, AWMA, Pittburgh, PA, p. 14.

LESON, G., TABATAI, F., WINER, A. M. (1993) Control of hazardous and toxic air emissions by biofiltration, in Proceedings of the 85th Annual Meeting and Exhibition of the Air and Waste Management Association, AWMA, Pittburgh, PA, p. 12.

LI, M., BANDO, Y., TANIGAWARA, R., KAMIYA, T., YASUDA, K., NAKAMURA, M. (2001) *Effect of packed structure on flow behaviour in a trickle bed biofilter*, The Canadian Journal of Chemical Engineering, vol. 79, n° 4, p. 602-607.

LIDE, D. R. (2006) *Handbook of chemistry and physics*. 87th CRC Press, Boca Raton, FL.

LIM, K.-H. (2005) *The treatment of waste-air containing mixed solvent using a biofilter: 2. Treatment of waste-air containing ethanol and toluene in a biofilter*, Korean Journal of Chemical Engineering, vol. 22, n° 2, p. 228-233.

LIM, K.-H., PARK, S.-W. (2004) *The treatment of waste-air containing mixed solvent using a biofilter: 2. Transient behavior of biofilter to treat waste-air containing ethanol*, Korean Journal of Chemical Engineering, vol. 21, n° 6, p. 1161-1167.

LIN, J.-H., CHOU, M.-S. (2006) *Henry's law constant variations of volatile organic compounds in wastewater and activated sludge*, Aerosol and Air Quality Research, vol. 6, n° 2, p. 180-192.

LIU, Y. (2007) *Overview of some theoretical approaches for derivation of the Monod equation*. Applied Microbiology and Biotechnology, vol. 73, n° 6, p. 1241-1250.

LIU, Y., LIN, Y.-M., YANG, S.-F. (2003) *A thermodynamic interpretation of the Monod equation*. Current Microbiology, vol. 46, n° 3, p. 233-234.

LOBO, R., REVAH, S., VIVEROS-GARCIA, T. (1999) *An analysis of a trickle-bed bioreactor : Carbon disulfide removal*, Biotechnology and Bioenginnering, vol. 63, n° 1, p. 98-109.

LU, C., LIN, M.-R., CHU, C. (1999) *Temperature effects of trickle-bed biofilter for treating BTEX vapors*, Journal of Environmental Engineering, vol. 125, n° 8, p. 775-779.

LU, C. S., LIN, M.-R., LIN, J. (2000) *Removal of acrylonitrile vapor from waste gases by a trickle-bed air biofilter*, Bioresource Technology, vol. 75, n° 1, p. 35-41.

LU, C.S., LIN, M.-R., LIN, J.C. (2001a) *Treatment of methylacetate waste gas using a trickle-bed air biofilter*, Waste Management, vol. 21, n° 6, p. 489-498.

LU, C. S., LIN, M.-R., LIN, J. (2001b) *Removal of styrene vapor from waste gases by a trickle-bed air biofilter*, Journal of Hazardous Materials, vol. 82, n° 3, p. 233-245.

LU, C., LIN, M.-R., WEY, I. (2002) *Removal of acrylonitrile and styrene mixtures from waste gases by a trickle-bed air biofilter*, Bioprocess Biosystems Engineering, vol. 25, n° 1, p. 61-67.

LU, C. S., LIN, M .R., LIN, J. C., CHANG, K. (2001c) *Removal of ethylacetate vapor from waste gases by a trickle-bed air biofilter*, Journal of Biotechnology, vol. 87, n° 2, p. 123-130.

MATHESON TRI-GAS (2004) *Material safety data sheet*, MDL Information Systems, Inc., Parsippany, NJ, p. 6.

MILLE, Y., BENEY, L., GERVAIS, P. (2005) *Compared tolerance to osmotic stress in various microorganisms: towards a survival prediction test.* Biotechnology and Bioengineering, vol. 92, n° 4, p. 479-484.

MOE, W. M., IRVINE, R. L. (2001) Effect of nitrogen limitation on performance of toluene degrading biofilters, Water Research, vol. 35, , n° 6, p. 1407-1414.

MONOD, A., DOUSSIN, J. F., CHEBBI, A., CARLIER, P. (1998) *Transformations chimiques des COV dans la troposphère. Impact sur la qualité de l'air*, In : Les composés organiques volatils (COV) dans l'environnement, Ed. Le Cloirec P., Technique & Documentation, Paris, p. 119-162.

MORALES, M., REVAH, S., AURIA, R. (1998) *Start-up and the effect of gaseous ammonia additions on a biofilter for the elimination of toluene vapors*, Biotechnology & Bioengineering, vol. 60, n° 4, p. 483-491.

MORGAN-SAGASTUME, F., SLEEP, B. E., ALLEN, D. G. (2001) *Effects of biomass growth on gas pressure drop in biofilters*, Journal of Environmental Engineering, vol. 127, n° 5, p. 388-396.

MORGENROTH, E., SCHROEDER, E. D., CHANG, D. P. Y., SCOW, K. M. (1996) *Nutrient limitation in a compost biofilter degrading hexane*, Journal of the Air and Waste Management Association, vol. 46, n° 4, p. 300-308.

MPANIAS, C. J., BALTZIS, B. C. (1998a) *An experimental and modeling study on the removal of mono-chlorobenzene vapor in biotrickling filters*, Biotechnology and Bioengineering, vol. 59, n° 3, p. 328-343.

MPANIAS, C.J., BALTZIS, B.C. (1998b) *Biocatalytic removal of mono-chlorobenzene vapor in trickling filters*, Catalysis Today, vol. 40, n° 1, p. 113-120.

MYSLIWIEC, M. J., VANDERGHEYNST, J. S., RASHID, M. M. (2001) *Dynamic volume - Average model of heat and mass transport within a compost biofilter: I. Model development*, Biotechnology and Bioengineering, vol. 73, n° 4, p. 282-294.

NIKIEMA, J., BIBEAU, L., LAVOIE, J., BRZEZINSKI, R., VIGNEUX, J., HEITZ, M. (2005) *Biofiltration of methane: An experimental study*, Chemical Engineering Journal, vol. 113, n° 2-3, p. 111-117.

NPRI - NATIONAL POLLUTANT RELEASE INVENTORY (2007) *NPRI, Methanol 67-56-1, Releases 2005*, Environnement Canada, QC, Canada, http://www.ec.gc.ca/pdb/querysite/query_e.cfm [accessed november 2007].

NUKUNYA, T., DEVINNY, J. S., TSATSIS, T. T. (2005) *Application of a pore network model to a biofilter treating ethanol vapor*, Chemical Engineering Science, vol. 60, n° 3, p. 665-675.

OBLINGER, J. L., KOBURGER, J. A. (1975) *Understanding and Teaching the Most Probable Number Technique*, Journal of Milk and Food Technology, vol. 38, n° 9, p. 540-545.

OCKELOEN, H. F., OVERCAMP, T. J., GRADY, Jr., C. P. L. (1992) *A biological fixed-film simulation model for the removal of volatile organic air pollutants*, In: Proceedings of the 85th Annual Meeting and Exhibition of the Air and Waste Management Association, AWMA, Pittburgh, PA.

OKKERSE, W. J. H., OTTENGRAF, S. P. P., DIKS, R. M. M., OSINGA-KUIPERS, B., JACOBS, P. (1999a) *Long term performance of biotrickling filters removing a mixture of volatile organic compounds from an artificial waste gas: dichloromethane and methylmethacrylate*, Bioprocess engineering, vol. 20, n° 1, p. 49-57.

OKKERSE, W. J. H., OTTENGRAF, S. P. P., OSINGA-KUIPERS, B., OKKERSE, M. (1999b) *Biomass accumulation and clogging in biotrickling filters for waste gas treatment. Evaluation of a dynamic model using dichloromethane as a model pollutant*, Biotechnology & Bioengineering, vol. 63, n° 4, p. 418-430.

OKPOKWASILI, G. C., NWEKE, C. O. (2005) *Microbial growth and substrate utilization kinetics*. African Journal of Biotechnology, vol. 5, n° 4, p. 305-317.

OPPT – OFFICE OF POLLUTION PREVENTION AND TOXICS (2007) *Chemicals in the Environment: Methanol (CAS NO. 67-56-1)*, http://www.epa.gov/chemfact/f_methan.txt [accessed july 2007].

OTTENGRAF, S. P. P. (1986) *Exhaust gas purification*, In: *Biotechnology, Volume 8 Microbial degradations*, eds. Rehm H.-J., Reed G. and Schönborn, VCH, Weinheim, p. 425-452.

OTTENGRAF, S. P. P., VAN der OEVER, A. H. C. (1983) *Kinetics of organic compound removal from waste gases with a biological filter*. Biotechnology and Bioengineering, vol. 25, n° 12, p. 3089-3102.

PASSANT, N. R., RICHARDSON, S. J., SWANNELL, R. P. J., GIBSON, N., WOODFIELD, M. J. (1993) *Emission of volatile organic compounds (VOCs) from the food and drink industries of the European Community*, Atmospheric Environment, vol. 27A, n° 16, p. 2555-2566.

PEDERSEN, A. R., ARVIN, E. (1999) *The function of a toluene-degrading bacterial community in a waste gas trickling filter*, Water Science and Technology, vol. 39, n° 7, p. 131-137.

PEIXOTO, J., MOTA, M. (1998) *Biodegradation of toluene in a trickling filter*, Bioprocess engineering, vol. 19, n° 5, p. 393-397.

PINNETTE, J. R., DWINAL, C. A., GIGGEY, M. D., HENDRY, G. E. (1995) *Design implications of the biofilter heat and moisture balance*, In: Proceedings of the 1995 Conference on Biofiltration, Eds. Hodge, D., Reynolds, E., University of Southern California, Los Angeles, CA, p. 85-98.

POPOV, V. O., BEZBORODOV, A. M. (1999) *Industrial technology of microbiological purification of wastes gases*, Applied Biochemistry and Microbiology, vol. 35, n° 5, p. 570-577.

PRADO, O. J., VEIGA, M. C., KENNES, C. (2005) *Treatment of gas-phase methanol in conventional biofilters packed with lava rock*, Water Research, vol. 39, n° 11, p. 2385-2393.

PRADO, O. J., VEIGA, M. C., KENNES, C., (2004) *Biofiltration of waste gases containing a mixture of formaldehyde and methanol*, Applied Microbiology and Biotechnology, vol. 65, n° 2, p. 235-242.

RAJAGOPAL, A. N. (1996) *Growth of gram-negative bacteria in the presence of organic solvents*. Enzyme and Microbial Technology, vol. 19, n° 8, p. 606-613.

RAMIREZ-LOPEZ, E. M., MONTILLET, A., COMITI, J., LE CLOIREC, P. (2000) *Biofiltration of volatile organic compounds – application to air treatment*, Water Science and Technology, vol. 41, n° 12, p. 183-190.

REAY, D. S., NEDWELL, D. B. (2004) *Methane oxidation in temperate soils: effects of inorganic N*, Soil Biology and Biochemistry, vol. 36, n° 12, p. 2059-2065.

RIHN, M. J., ZHU, X. Q., SUIDAN, M. T., KIM, B. J., KIM, B. R. (1997) *The effect of nitrate on VOC removal in trickle-bed biofilters*, Water Research, vol. 31, n° 12, p. 2997-3008.

RUOKOJÄRVI, A., AATAMILA, M., HARTIKAINEN, T., OLKKONEN, M., SALMI, J., RUUSKANEN, J., MARTIKAINEN, P. J. (2000) *Removal of dimethyl sulphide from off-gas mixtures containing hydrogen sulphide and methanethiol by a biotrickling filter* Environmental Technology, vol. 21, n° 10, p. 1173-1180.

SANDLER, S. I. (1991) *Microbial growth thermodynamics*. Fluid Phase Equilibria, vol. 70, n° 2-3, p. 141-163.

SCHÖNDUVE, P., SARA, M., FRIEDL, A. (1996) *Influence of physiologically relevant parameters on biomass formation in a trickle-bed bioreactor used for waste gas cleaning*, Applied Microbiology and Biotechnology, vol. 45, n° 1-2, p. 286-292.

SHAREEFDEEN, Z., BALTZIS, B. C. (1994) *Biofiltration of toluene vapor under steady-state and transient conditions: theory and experimental results*, Chemical Engineering Science, vol. 49, n° 24A, p. 4347-4360.

SHAREEFDEEN, Z., BALTZIS, B. C., OH, Y.-S., BARTHA, R. (1993) *Biofiltration of methanol vapor*, Biotechnology and Bioengineering, vol. 41, n° 5, p. 512-524.

SLUITER, A., HAMES, B., RUIZ, R., SCARLATA, C., SLUITER, J., TEMPLETON, D. (2005) *Determination of total solids in biomass*. http://www.nrel.gov/biomass/pdfs/9361.pdf [accessed january 2007].

SMITH, F. L. (1999) *Pilot-scale development of trickled bed air biofiltration employing deep biofilms, for the purification of air polluted with biodegradable VOCs*, Ph. D. Thesis, University of Cincinnati, Cincinnati, OH, p. 149.

SMITH, A. J., HOARE, D. S. (1977) *Specialist phototrophs, lithotrophs, and methylotrophs: a unity among a diversity of prokaryotes?* Bacteriological Reviews, vol. 41, n° 1, p. 419-448.

SMITH, F. L., SORIAL, G. A., SUIDAN, M. T., BISWAS, P., BRENNER, R. C. (2002) *Development and demonstration of an explicit lumped-parameter biofilter model and design equation incorporating Monod kinetics*, Journal of the Air & Waste Management Association, vol. 52, n° 2, p. 208-219.

SMITH, F. L., SORIAL, G. A., SUIDAN, M. T., BISWAS, P., BRENNER, R. C. (1994) *Trickle bed biofilter performance-biomass control and N-nutrient effects*, In: Proceedings of the 67th Annual conference and exposition of the Water Environment Federation. Chicago, IL, p. 553-564.

SMITH, F. L., SORIAL, G. A., SUIDAN, M. T., BREEN, A. W., BISWAS, P., BRENNER, R. C. (1996) *Development of two biomass control strategies for extended, stable operation of highly efficient biofilters with high toluene loadings*, Environmental Science & Technology, vol. 30, n° 5, p. 1744-1751.

SMITH, F. L., SORIAL, G. A., SUIDAN, M. T., PANDIT, A., BISWAS, P., BRENNER, R. C. (1998) *Evaluation of trickle bed air biofilter performance as a function of inlet VOC concentration and loading, and biomass control*, Journal of the Air and Waste Management Association, vol. 48, n° 7, p. 627-636.

SOLOGAR, V. S., LU, Z., ALLEN, D. G. (2003) *Biofiltration of concentrated mixtures of hydrogen sulfide and methanol*, Environmental Progress, vol. 22, n° 2, p. 129-136.

SONG, J. H., KINNEY, K. A. (2000) *Effect of vapor-phase bioreactor operation on biomass accumulation, distribution, and activity: linking biofilm properties to bioreactor performance*, Water Research, vol. 37, n° 18, p. 4497-4505.

SONG, J. H., RAMIREZ, J., KINNEY, K. A. (2003) *Nitrogen utilization in a vapor-phase biofilter*, Biotechnology and Bioengineering, vol. 68, n° 5, p. 508-516.

SORIAL, G. A., SMITH, F. L., SUIDAN, M. T., PANDIT, A., BISWAS, P., BRENNER, R. C. (1997) *Evaluation of trickle bed air biofilter performance for BTEX removal*, Journal of Environmental Engineering-Asce, vol. 123, n° 6, p. 530-537.

SPEITEL, G. E., McLAY, D. S. (1993) *Biofilm reactors for treatment of gas streams containing chlorinated solvents*, Journal of Environmental Engineering, vol. 119, n° 4, p. 658-678.

STREESE, J., SCHLEGELMILCH, M., HEINING, K., STEGMANN, R. (2005) *A macrokinetic model for dimensioning of biofilters for VOC and odour treatment*, Waste Management, vol. 25, n° 9, p. 965-974.

SWANSON, W. J., LOEHR, R. C. (1997) *Biofiltration: fundamentals, design and operations principles, and applicaions*, Journal of Environmental Engineering, vol. 123, n° 6, p. 538-546.

TANG, H.-M., HWANG, S.-J., WANG, W. C. (1997) *Degradation of acetone in a biofilter*, Environmental Engineering Science, vol. 14, n° 4, p. 219-226.

TEJA, A. S., GUPTA, A. K., BULLOCK, K., CHAI, X.-S., ZHU, J. (2001) *Henry's constants of methanol in aqueous systems containing salts*, Fluid Phase Equilibria, vol. 185, n° 1-2, p. 265-274.

TERAN PEREZ, W., DOMENECH, F., ROGER, P., CHRISTEN, P. (2002) *Effect of mineral salts addition on the behaviour of an ethanol biofilter*, Environmental Technology, vol. 23, n° 9, p. 981988.

TRESSE, O., LORRAIN, M. J., RHO, D. (2002) *Population dynamics of free-floating and attached bacteria in a styrene-degrading biotrickling filter analyzed by denaturing gradient gel electrophoresis*, Applied Microbiology and Biotechnology, vol. 59, n° 4-5, p. 585-590.

TRI-EXPLORER – TOXICS RELEASE INVENTORY-EXPLORER (2005) *Releases: Chemical Report, Methanol, U.S., 2005*, http://www.epa.gov/triexplorer/ [accessed july 2007].

VAN BRIESEN, J. M., RITTMANNTANG, B. E. (2000) *Mathematical description of microbiological reactions involving intermediates*, Biotechnology and Bioengineering, vol. 67, n° 1, p. 35-52.

WANI, A., LAU, A. K., BRANION, M. R. M. (1999) *Biofiltration control of pulping odors – hydrogen sulfide: performance, macrokinetics and coexistence effects of organo-sulfur species*. Journal of Chemical Technology and Biotechnology, vol. 74, n° 1, p. 9-16.

WECKHUYSEN, B., VRIENS, L., VERACHTERT, H. (1993) *The effect of nutrient supplementation on the biofiltration removal of butanal in contaminated air*, Applied Microbiology and Biotechnology, vol. 39, n° 3, p. 395-399.

WÜBKER, S. M., FRIEDRICH, C. (1996) *Reduction of biomass in a bioscrubber for waste gas treatment by limited supply of phosphate and potassium ions*, Applied Microbiology and Biotechnology, vol. 46, n° 5-6, p. 475-480.

WÜBKER, S. M., LAURENZIS, A., WERNER, U., FRIEDRICH, C. (1997) *Controlled biomass formation and kinetics of toluene degradation in a bioscrubber and in a reactor with periodically moved trickle-bed*, Biotechnology and Bioengineering, vol. 55, n° 4, p. 686-692.

XIAO, J., VAN BRIESEN, J. M. (2006) *Expanded thermodynamic model for microbial true yield prediction*, Biotechnology and Bioengineering, vol. 93, n° 1, p. 110-121.

YANG, H., MINUTH, B., ALLEN, D. G. (2002) *Effects of nitrogen and oxygen on biofilter performance*, Journal of the Air and Waste Management Association, vol. 52, n° 3, p. 279-286.

ZAROOK, S. M., SHAIKH, A. A., ANSAR, Z. (1997) *Development, experimental validation and dynamic analysis of a general transient biofilter model*, Chemical Engineering Science, vol. 52, n° 5, p. 759-773.

ZHU, X., ALONSO, C., SUIDAN, M. T., CAO, H., KIM, B. J., KIM, B. R. (1998) *The effect of liquid phase on VOC removal in trickle-bed biofilters*, Water Science & Technology, vol. 38, n° 3, p. 315-322.

ZHU, X., RIHN, M. J., SUIDAN, M. T., KIM, B. J., KIM, B. R. (1996) *The effect of nitrate on VOC removal in trickle bed biofilters*, Water Science and Technology, vol. 34, n° 3-4, p. 573-581.

ZHU, X., SUIDAN, M. T., ALONSO, C., YU, T., KIM, B. J., KIM, B. R. (2001) *Biofilm structure and mass transfer in a gas phase trickle-bed biofilter*, Water Science & Technology, vol. 43, n° 1, p. 285-293.