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Influence of Ammonium Concentration on the Performance of an Inorganic Biofilter Treating Methane

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Abstract**—**Among the technologies available to reduce methane emitted from the pig industry, biofiltration seems to be an effective and inexpensive solution. In methane (CH_4) biofiltration, nitrogen is an important macronutrient for the microorganisms growth. The objective of this research project was to study the effect of ammonium (NH_4^+) on the performance, the biomass production and the nitrogen conversion of a biofilter treating methane. For NH_4^+ concentrations ranging from 0.05 to 0.5 gN-NH_4^+/L, the CH_4 removal efficiency and the dioxide carbon production rate decreased linearly from 68 to 11.8 % and from 7.1 to 0.5 g/(m^3-h), respectively. The dry biomass content varied from 4.1 to 5.8 kg/(m^3 filter bed). For the same range of concentrations, the ammonium conversion decreased while the specific nitrate production rate increased. The specific nitrate production rate presented negative values indicating denitrification in the biofilter.

Keywords**—**Methane, biofiltration, pig, ammonium, nitrification, denitrification.

I. Introduction

WITH a total production of 109 million tons of pig meat in 2010 [1], the world pork industry was also responsible for water, air and soil pollution [2]. Among the compounds responsible for air pollution, this agricultural sector released volatile fatty acids, ammonia (NH_3), hydrogen sulphide (H_2S) and greenhouse gases (GHG) such as carbon dioxide (CO_2) and methane (CH_4) [3]. In Canada (2009), CH_4 emissions represented 13% of the total GHG emissions (690 Mt eq. CO_2) which corresponds to 90 Mton eq. CO_2[4]. In 2004, the world CH_4 anthropogenic emissions represented around 6.9 Gton eq. CO_2[5]. With a heat of combustion of 890 kJ/mol (25 ^oC, 1 atm) [6], CH_4 is an interesting compound produced by anaerobic digestion of organic matter [3]. However, CH_4 emissions, even if they are lower than CO_2 emissions, are not negletable in terms of global warning because CH_4 has a global warming potential 25 times higher than CO_2 over a period of 100 years [7].

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Even if CH_4 can theoretically be thermally oxidized, the latter requires a minimal CH_4 concentration in air ranging from 5 to 15% (v/v) [8]. In case of CH_4 emitted from slurry storage, the concentrations are generally lower than 3% (v/v), which is not enough to use thermal oxidation [9]. On the other hand, several studies have shown that low CH_4 concentrations can be treated effectively and relatively non-expensively by biofiltration [9]. In order to increase the biofilter performance, some parameters must be controlled such as moisture, temperature and nutrients [10]. Among the nutrients, microorganisms require nitrogen because it represents up to 14% of dry cell weight [11]. Usually, nitrogen is supplied to inorganic bed biofilters as a form of nitrate (NO_3^-) [12] because ammonium (NH_4^+) had a negative effect (inhibiting potential on CH_4 oxidation) on methanotrophic bacteria in soil studies [13, 14], but also had a positive effect (stimulation of CH_4 oxidation) in other soils studies [15].

The objective of this study was to test the effect of NH_4^+ concentration in the nutrient solution of the performance of an inorganic packed bed biofilter treating CH_4. The performance of the biofilter was determined by analyzing the carbon and the nitrogen balance.

II. Materials and Methods

Fig. 1 presents the inorganic packed bed biofilter used for the experiments. The biofilter was a Plexiglas cylinder with an inlet diameter of 15 cm, divided into 3 sections. The biofilter was packed with an inorganic material for a total bed height of 1 m (volume of 18 L). The exact nature of the filter bed cannot be revealed for confidential reasons.

A mixture of pure CH_4 (Praxair) and compressed air containing oxygen (O_2) was fed at the bottom of the biofilter and the treated air was released at the top. In order to avoid filter bed desiccation, the air mixture was previously saturated with water by passing through a humidification column. A nitrate salts medium (NMS) was used to supply nutrients and moisture to the filter bed [17]. At the top of the biofilter, the nutrient solution was fed (1.5 L; once a day) while the leachate was collected at the bottom of the biofilter. Concurrently, NO_3^- (as sodium nitrate) concentration was decreased by 0.05 gN-NO_3^-/L increasing steps and NH_4^+ (as ammonium carbonate)concentration was increased in order to keep the total nitrogen concentration in the nutrient solution at 0.5 gN/L. The NO_3^-concentration was decreased from 0.45 to 0 gN-NO_3^-/L while the NH_4^+ concentration was increased from 0.05 to 0.5 gN-NH_4^+/L.

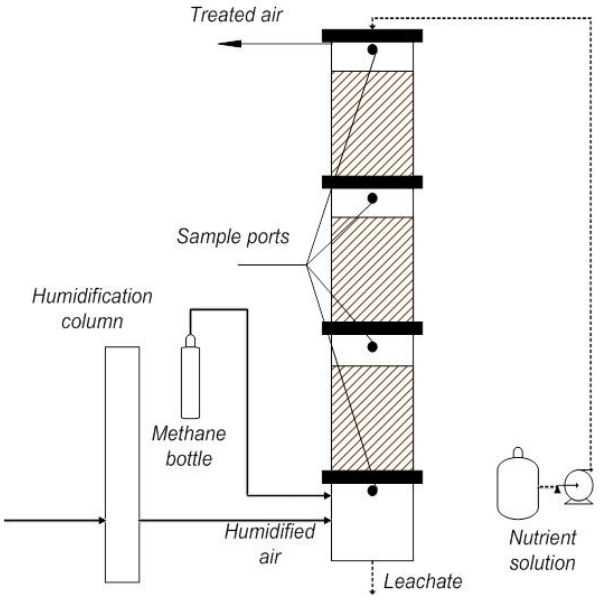

Fig. 1 Biofilter set up for the biofiltration of CH_4

Suspended biomass contained in leachate samples was removed using filter paper. Ionic chromatography (Dionex ICS-1000, Canada) was employed to determinate the concentrations of NH_4^+, NO_3^- and NO_2^- in leachate and nutrient solution [18]. The weight difference of the packing material sample dried at 105 °C and calcined at 500 °C was used to determinate the dry biomass concentration in the packed bed [19].

At the bottom of the biofilter, the CH_4 concentration and air flow rate were respectively set at 1500 ppmv (0.15% v/v) (inlet load of 10 g/(m^3-h)) and 3 L/min. At each sample port, a total hydrocarbon analyser equipped with a continuous flame ionisation detector (Horiba model FIA-510, USA) was utilized to measure the CH_4 concentration in the gas phase. A gas analyser detector (Ultramat 22P, Simens, Germany) was also employed to measure the CO_2 concentration in the gas phase. Table I summarizes the main parameters considered to evaluate the performance of the biofilter. The theoretical dry biomass production rate (DBR), listed in Table I, was used to evaluate the theoretical dry biomass production. This parameter is evaluated by means of a molar balance of CH_4 and CO_2.

III. Results and Discussion

A. Biofilter Performance

Fig. 2 presents the methane removal efficiency (CH_4-RE) and the P_{CO_2} as a function of the NH_4^+ concentration in the nutrient solution. For NH_4^+ concentrations from 0.05 to 0.5 gN-NH_4^+/L, the CH_4-RE decreased linearly from 68 to 12%. For NH_4^+ concentrations ranging from 0.2-0.25 gN-NH_4^+/L, the CH_4-RE decreased quickly from 50 to 24%. For NH_4^+ concentrations ranging from 0.05 to 0.15 gN-NH_4^+/L, the P_{CO_2} increased from 7.1 to 12.4 g/(m^3-h) and from 0.15 to 0.5 gN-NH_4^+/L, the P_{CO_2} decreased from 12.4 to 0.5g/(m^3-h).

The fact that CH_4-RE decreased with the NH_4^+ concentration shows the effect of NH_4^+ on the populations of methanotrophic bacteria present in the biofilter. Many studies have shown that NH_4^+ reduces the CH_4 oxidation rate in soil [20, 21, 22, 23], compost [24] and biofilters [18, 25, 26]. For example, in paddy soil, for CH_4 inlet concentrations of 1500 ppmv, Cai and Mosier [20] found that for an increase of NH_4^+ concentration from 0 to 0.05 mgN-NH_4/kg soil, the CH_4 oxidation rate decreased from 338 to 166 ngC-CH_4/(g soil-h). In the present study, the decrease of CH_4-RE from 68 to 12% (-83%) was more important because, in soil, the nitrifying bacteria are already present, which reduced the NH_4^+ concentration in the filter bed. This could also mean that a NH_4^+ concentration of 0.5 gN-NH_4^+/L has more negative effect on CH_4 oxidation than the NH_4^+ concentration used by Cai and Mosier [20](0.05 mgN-NH_4/kg soil).

Between 0.05 and 0.15 gN-NH_4^+/L, the P_{CO_2} increased from 7.1 to 12.4 g/(m^3-h) (+76%) even if CH_4-RE decreased from 68 to 57% (-16%). This may means that less carbon was used to produce biomass inducing a lower methanotrophic

TABLE I
Main Parameters used to Evaluate the Biofilter Performance

Parameters	Equations	Units
Methane removal efficiency (CH_4-RE)	$CH_4\text{-RE} = \frac{C_{gin} - C_{gout}}{C_{gi}}$	Dimensionless
Carbon dioxide production rate (P_{CO_2})	$P_{CO_2} = \frac{Q*(C_{dout} - C_{din})}{V}$	g/(m^3-h)
Theoretical dry biomass production rate (DBR)	$DBR = \left[\frac{(C_{gin} - C_{gout})}{W_{CH_4}} - \frac{(C_{dout} - C_{din})}{W_{CO_2}}\right]\left(\frac{Q \cdot W_B}{V}\right)$	g biomass/(m^3-h)
Nitrate production rate (P_{NO_3})	$P_{NO_3} = \frac{(NO_{3\,in}^- - NO_{3\,out}^-) \cdot Q_{NS}}{V * DB}$	gN/(g biomass-h)

a: C_{gin} and C_{gout} are the inlet and outlet concentrations of CH_4 (g/m^3) ; Q is the air flow ; V is the volume of the biofilter (0.018 m^3) ; C_{din} and C_{dout} are the inlet and outlet concentrations of carbon dioxide (g/m^3); W_{CH_4}, W_{CO_2} and W_B are the molecular weights of CH_4, CO_2 and biomass produced (g/mol), assuming an empirical formula of $C_5H_7NO_2$ for biomass with an average value of 113 g/mol [16]; $NO_{3\,in}^-$ and $NO_{3\,out}^-$ are the concentration of NO_3^- in the nutrient solution and the leachate, respectively (gN/L) ; Q_{NS} is the flow of nutrient solution (L/h) ; DB is the dry biomass in the filter bed (g biomass/(m^3 filter bed)).

activity, explaining the CH_4-RE decrease. For NH_4^+ concentrations higher than 0.15 gN-NH_4^+/L, the P_{CO_2} followed the same tendency than the CH_4-RE. Between 0.20 and 0.25 gN-NH_4^+/L, the quickly decrease of P_{CO_2} from 9.0 to 4.7 (-48%) confirms the assumption that for this concentration range, a major change in bacteria population occurred in the biofilter as observed in a previous study [19].

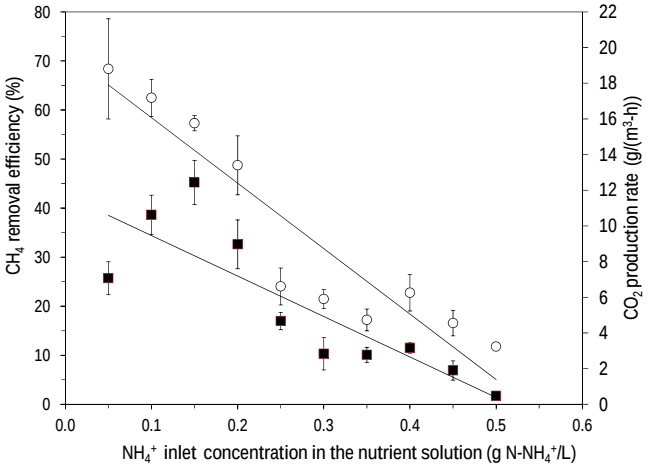

Fig. 2 CO_2 production rate (■) and CH_4 removal efficiency (○) as a function of the NH_4^+ inlet concentration in the nutrient solution

B. Biomass

Fig. 3 presents the average dry biomass content (DB) and the theoretical dry biomass production rate (DBR) as a function of the inlet NH_4^+ concentration in the nutrient solution. For NH_4^+ concentrations ranging from 0.05 to 0.5 gN-NH_4^+/L, the DB decreased with the NH_4^+ concentration and varied from 5.8 to 2.5kg/m^3 filter bed. The DBR decreased also with the NH_4^+ concentration and followed a logarithmic tendency with values ranging from 30 to 5 g/(m^3-h).

The decrease of DBR with the NH_4^+ concentration was also observed by Wilshusen et al. [24]. In order to explain this phenomena, the authors hypothesized that the exopolymeric substances could serve "as a carbon cycling mechanism for type I" methanotrophic bacteria. The fact that DBR decreased could also indicate that more carbon was transformed into CO_2, which explains the decrease of CH-RE observed in Fig. 2 as less new biomass was formed.

The fact that the DB (linear) followed a different tendency than DBR (logarithmic) indicates that some microorganisms other than methanotrophic bacteria (like denitrifying and nitrifying bacteria) can generate biomass. However, a visual inspection of the biofilter shows a decrease of the biomass in the filter bed which may means that the biomass produced by other microorganisms may be more soluble in water. The dry biomass content is also influenced by the amount of biomass washed out of the filter bed at each daily watering. The decrease of DB observed in the filter bed (-57%) was lower than the DBR(-83%). As a consequence, for the NH_4^+ concentrations tested, less biomass would be lost in the leacheate as the NH_4^+ concentration increased.

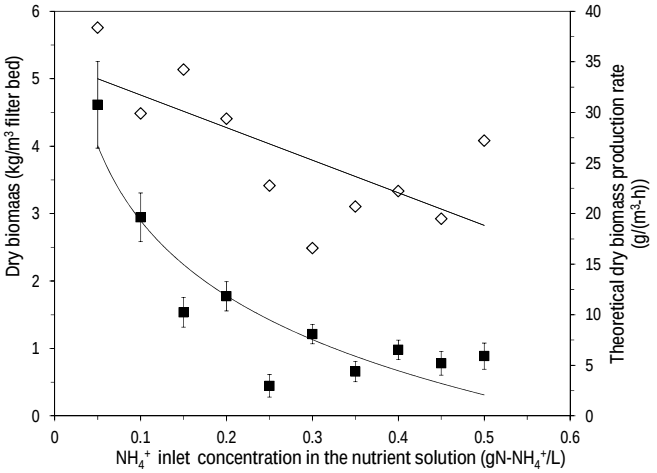

Fig. 3 Dry biomass content (◊) and theoretical dry biomass production rate (■) as a function of the NH_4^+ inlet concentration in the nutrient solution

C. Nitrogen Conversion

Fig. 4 presents the NH_4^+ conversion and the specific NO_3^- production rate (P_{NO_3}) as a function of the NH_4^+ inlet concentration in the nutrient solution. For NH_4^+ concentrations in the nutrient solution ranging from 0.05 to 0.5 gN-NH_4^+/L, the NH_4^+ conversion decreased linearly from 48 to 26 % while the P_{NO_3} increased from -0.01 to 0.16 gN/(m^3-h).

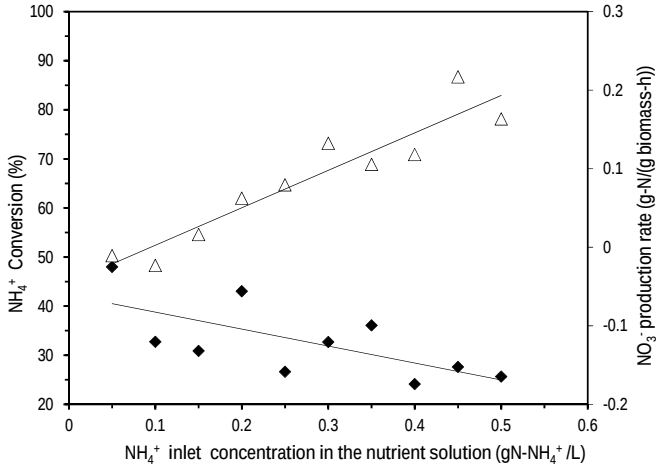

Fig. 4 Ammonium conversion (♦) and specific nitrate production rate (Δ) as a function of the NH_4^+ inlet concentration in the nutrient solution

The fact that the NH_4^+ conversion decreased with the NH_4^+ concentration could be due to the decrease of CH_4-RE (Fig. 2). In fact, the increase of CH_4 concentration could lead to the decrease of NH_4^+ conversion as CH_4 is an inhibitor of nitrifying bacteria [27]. Moreover, the increase of CH_4 concentration in the biofilter could also lead to changes of number and kind of microorganisms specific to NH_4^+ conversion which could lead to the NH_4^+ conversion deacrease. The P_{NO_3} presented some negative values at 0.05 and 0.10 gN-NH_4^+/L of -0.01 and -0.02gN-NO_3^-/(g biomass-

h), respectively. This indicated that there was a consumption of NO_3^- by methanotrophic bacteria or a denitrification.

IV. Conclusion

Increasing the NH_4^+ concentration in the nutrient solution reduced the performance of an inorganic biofilter treating CH_4 at an inlet concentration of 1500 ppmv, as follows: the CH_4-RE, the P_{NO_3} and the dry biomass content decreased respectively from 68 to 12 %, from 7.1 to 0.5 g/(m^3-h) and from 5.8 to 4.1 kg/m^3 filter bed. For the same range of concentrations, the NH_4^+ conversion also decreased from 48 to 26% whereas the P_{NO_3} increased from -0.01 to 0.16 gN/(m^3-h) which suggests that denitrification occurred. This study shows that the nature and the concentration of the macronutrients (nitrogen) present in the nutrient solution are important for the performance of an inorganic biofilter treating CH_4.

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