



RESEARCH ARTICLE

Methane removal using materials from biofilters at composting plants

Loại bỏ khí Mê-tan bằng cách sử dụng vật liệu trong các bể lọc khí sinh học ở các cơ sở sản xuất phân vi sinh

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Methane (CH₄) source of Greenhouse Gases should be considered; CH₄ is formed by composting under anaerobic conditions. Using microbial Methane oxidation is a solution with low cost and effective. In this study, 27 bio-filters and 18 laboratory-scale bioreactors were used to investigate the potential for CH₄ removal in biogas. The CH₄, Dinitrogen monoxide (N₂O) and Carbon dioxide (CO₂) concentrations at the inlet and outlet of the air purifier were measured by gas chromatography. The results showed that the CH₄ concentration decreased in experiments while the CO₂ and N₂O content increased in all experiments. An experiment was conducted with 1 kg of biofilter material with the input of 800 ppm CH₄ contained in a 5-liter flask for 49 hours containing. The results also showed that the CH₄ concentration decreased by 71% after 20 hours and N₂O was formed in the reactor.

Mê-tan (CH₄) là nguồn khí gây nên hiệu ứng nhà kính cần được quan tâm, khí CH₄ được sinh ra trong quá trình ủ vi sinh trong điều kiện kỵ khí. Một giải pháp với chi phí thấp là sử dụng vi sinh vật oxy hóa khí CH₄ cố định trên giá thể là vật liệu sử dụng trong thiết bị lọc sinh học. Trong nghiên cứu này, 27 thiết bị lọc sinh học trên thực tế và 19 bình lọc tại phòng thí nghiệm đã được sử dụng nhằm mục đích khảo sát khả năng loại bỏ CH₄ có trong khí sinh học. Nồng độ khí CH₄, N₂O và CO₂ ở đầu vào và đầu ra bể lọc khí được đo đạc bằng phương pháp sắc ký khí. Kết quả cho thấy nồng độ khí CH₄ giảm sau khi qua hệ thống lọc sinh học ở một số bình, trong khi nồng độ khí CO₂ và N₂O lại tăng lên ở tất cả các bình. Khi khảo sát khả năng oxy hóa CH₄ ở nồng độ 800 ppm của 1kg vật liệu thiết bị lọc sinh học chứa trong bình phản ứng thể tích 5L với thời gian 49 giờ. Kết quả cho thấy nồng độ CH₄ giảm 71% sau 20 giờ. Tuy nhiên, N₂O đã được ghi nhận có hình thành trong bình phản ứng đó.

Keywords: greenhouse gas, emissions, composting, windrows, organic waste, methane, biofilter

1. Introduction

Methane (CH₄) and Dinitrogen monoxide (N₂O) are considered to be strong Greenhouse Gases (GHGs), whereas NH₃ is identified as an odour component and an indirect GHG. According to the Intergovernmental Panel on Climate Change (henceforth IPCC) Report in 2007, the Global Warming Potential (GWP) of CH₄ and N₂O in 100 years are respectively 25 and 298 times higher than that of CO₂. CH₄ emissions from livestock account for 37% of the total emissions of CH₄ in global, mainly for ruminants in digestion. In addition, landfill gas collection has been established to generate electricity and heat in many countries. The CH₄ emitted from landfills is one of the major sources accounting for approximately 30% of total CH₄ emissions (Kára *et al.*, 2010). In other cases, flares are operated to burn CH₄ and other organic trace compounds contained in the landfill gas before releasing to the atmosphere. However, these

processes cannot be applied in cases of low CH₄ concentration. Up to now, the mitigation of emissions with low CH₄ concentrations often is neglected.

CH₄ removal was observed with low gas flows and high concentrations in the soil or in biofilters (Bender & Conrad, 1992). In a biofilter, an autochthonous methanotrophic biofilm can develop and use CH₄ as a carbon source. However, the CH₄ removal in biofilters varied from case to case due to different working conditions e.g. ambient temperature, humidity and nutrient content.

Most of the previous reports (Scheutz *et al.*, 2009; Melse & Van De Werf, 2005 and Bender & Conrad, 1992) showed that a good CH₄ oxidation rates of 20% CH₄ in the supply air and 2.5% CH₄ in the exhaust air. Biofilter has a high flow rate in a combination of low concentrations of CH₄. Low CH₄ concentrations range of below 0.07% CH₄ (700 ppm ~ 460 mg CH₄/m³) in combination with a high exhaust air volume flow in the range of 20,000 - 50,000 m³/h. This results

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in a biofilter had a load of about 100 m³/m³.h. The efficiencies of CH₄ reduction range from 0% - 20% (Scheutz *et al.*, 2009). In addition, Melse and Van De Werf (2005) reported a CH₄ reduction of 80% in the biofilter with a load of 0.75 m³/m³.h.

CH₄ oxidation is therefore considered as an important method to CH₄ emissions reduction. At present, only a few scientific publications on biological waste air treatment are available. Studies related to test the CH₄ removal capacity of a new material have not yet been done. Looking into the real conditions of the biofilter, among different microorganism, CH₄ oxidation bacteria needs to be found. Then, they will be enriched populations, which are added to the biofilter or bioscrubber on demand.

The aim of this work was to investigate CH₄ removal in different biofilters and to develop a new method to find materials for CH₄ oxidation.

2. Materials and methods

2.1 Screening of biofilters

Twenty-seven biofilters in composting plants in Germany were investigated in the study. The study was carried out from 2012 to 2014. An overview of a capsulated biofilter is shown in Figure 1. The gas before and after biofilter was analysed at each plant. At capsulated biofilters, the treated air left the biofilter in a chimney. Here the gases were measured. At the open biofilter of 16m² (4x4m) was covered by a thin foil. Concentrations of the treated gases were measured under the foil.

Exhaust gases were sampled manually by evacuated headspace vials and subsequently analysed for CH₄, CO₂ and N₂O by gas chromatography (ECD/FID, SRI 8610C, USA) in the laboratory in Bonn University, Germany. It was assumed that the volumes of treated and untreated air were the same.

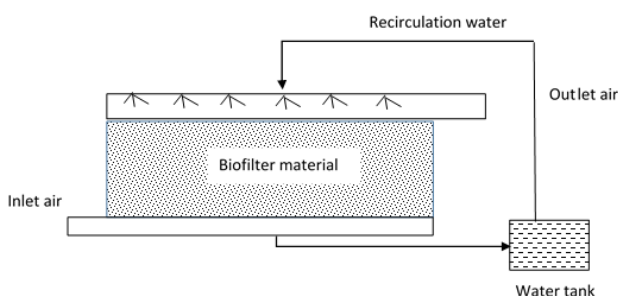


Figure 1. Schematic of a capsulated biofilter

2.2 Experimental setup

After screening of 27 biofilters, solid samples of the biofilters' from the most CH₄ reduction was taken for laboratory experiments. The experiments were carried out in 18 batch reactors (5L) (Figure 2). Each batch reactor contained 1kg biofilter's material at the outset of the experi-

ment (Figure 3). It was assumed that methanotrophic bacteria was available on the material. CH₄ (800 ppm) was mixed with air, humidified and introduced in the 5L reactor. The mixing was pumped into reactors for 5 minutes to push out the existing air in the reactor. After pumping, the reactor was closed and no more Oxygen (O₂) was supplied. The air in the reactor is assumed to contain ~20% O₂ together with the 800ppm CH₄. Samplings of incubated gases were taken to measure the concentrations of CH₄ and O₂.

The gases in the reactor were sampled at intervals of 1, 2, 19, 22, 24, 26 and 49 hours, and analysed for CH₄, CO₂ and N₂O in the laboratory by GC-FID/ECD.



Figure 2. Test kit for determination of CH₄ removal capacity



Figure 3. Material of biofilter for the testing of CH₄ removal capacity

The removal performance was determined by mass balance according to the following equation:

$$CH_4ox_i = \frac{(flux_{in} - flux_{out})}{flux_{in}} \times 100$$

With

CH₄ox_i: At the time *i* oxidized portion of inlet flow [%]

Flux_{in}: CH₄ concentration flow into the reactor at time *i* (*i*= 1, 2, 19, 22, 24, 26 and 49 hours)

Flux_{out}: CH₄ concentration flow out the reactor at time *i* (*i*= 1, 2, 19, 22, 24, 26 and 49 hours)

3. Results and discussion

3.1 CH₄ removal from biofilters at composting plants

The inlet concentration of CH₄ and CH₄ reduction of biofilters were shown in Figure 4. CH₄ was reduced and produced in the biofilters. The removal efficiency ranged from production of -260% to reduction of 80% for CH₄. The mean concentration of CH₄ before biofilter was (106 ± 73) ppm. The average CH₄ removal efficiency was 25% at 13 biofilters. With regard to other literature, CH₄ was reduced by 15% (Amlinger *et al.*, 2008). As waste gas permeates the biofilter layer, CH₄ is oxidized to CO₂ and H₂O by methanotrophic bacteria present in the biofilter's material. The effect on the production of CH₄ emissions in the biofilter may be explained by anaerobic degradation of organic substances in the biofilter (Nguyen & Cuhls, 2016). However, it is not yet well understood.

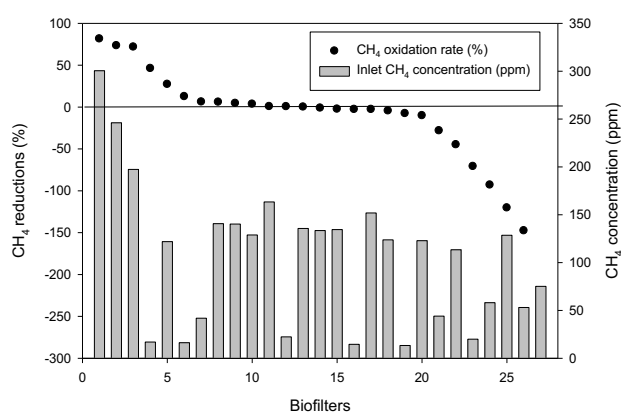


Figure 4. Inlet CH₄ concentrations and removal efficiencies of CH₄ at the studies biofilters

Table 1. Comparison of removal efficiency of biofilters: this study and data from literature (Scheutz *et al.*, 2009)

Reference	CH ₄ removal (%)	CH ₄ removal rate max (g/m ² .day)
This study	7 to 27	5-56
Amlinger <i>et al.</i> , 2008	15	-
Trimborn, <i>et al.</i> , 2003	up to 26	-
Du Plessis <i>et al.</i> , 2003	-	87
Wilshusen <i>et al.</i> , 2004	-	96-276
Streese & Stegmann, 2003	-	341
Melse & Van De Werf, 2005	-	377
Park <i>et al.</i> , 2005	-	435
Sly <i>et al.</i> , 1993	-	586
Haubrichs & Widmann, 2006	-	592

Note: “-” means data was not available

The reductions of CH₄ were lower than in previous studies (Table 1). Melse and Van De Werf (2005) reported the CH₄ reduction of 80% in a biofilter with the load of 0.75 m³/m³.h. However, this loading factor is 130 times lower than in practice. Previous studies illustrated that the process-controlling factors of the CH₄ oxidation in low-concentrations are the O₂ availability, storage density and gas permeability as well as the volume flow of the gas to be treated (Bender & Conrad, 1992; Benstead & King 1997 and Dunfield *et al.*, 1999). In fact, the low CH₄ removal efficiency in practice could be explained by exposure time due to a short duration of the waste air treatment in biofilters.

3.2 Methane oxidation reaction

3.2.1 The value of pH

The pH of biofilter's material was from neutral to a light alkaline (ranged from 7.16 to 7.82). The pH values were suitable for methanotrophic activities. The CH₄ removal process was observed in a broad pH range, from pH < 4 in a sand soil to pH > 9 in a bog soil. The optimal pH for methanotrophs growth is between 6 and 8 (Cao & Staszewska, 2011).

3.2.2 Methane removal and carbon dioxide generation

CH₄ removal and CO₂ generation were investigated for the biofilter's materials. The observed decrease in CH₄ concentration in Figure 5 and 6 can be explained by oxidation since O₂ was available and CO₂ was increased. After an incubation for 49 h at 25°C, 99% of CH₄ was consumed. The CH₄ removal rate increased when the O₂ concentrations increased from 2.5% to 15% (Cao & Staszewska, 2011).

By comparison, the CH₄ concentration in the reactor was 200 ppm after 20 hours (500 ppm reduction); whereas, the CO₂ concentration was 3000 ppm (2500 ppm generation). This could be explained by aerobic decomposition of material in the reactor due to the availability of O₂. Maximum CH₄ consumption and maximum CO₂ generation were observed at the first phase of incubation. Previous studies have shown that the rate of CH₄ removal grows with the increase of CH₄ concentration. The increase of CH₄ concentrations from 2 to 16 % led to 1.1 - 2.5 folds increase of the methanotrophic activity (Pawłowska & Stępniewski, 2004). Another author found that a value (2.3-folds) in the methanotrophic activity increase was observed, where the measured CH₄ concentration varied from 25 to 200 ppm (Whalen & Reeburgh, 1996).

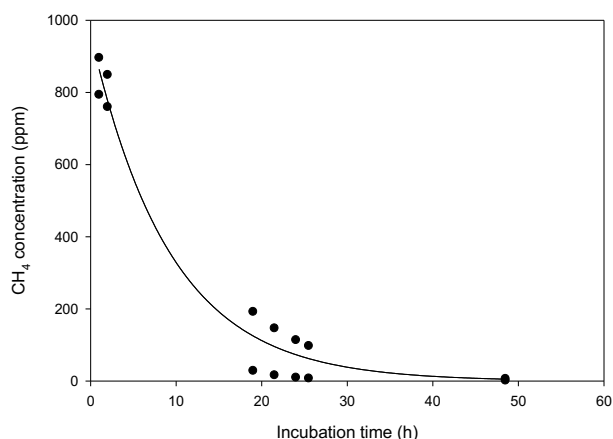


Figure 5. CH₄ concentrations in the reactors during incubation time

CO₂ concentration was increased steadily (Figure 6). CO₂ generation was increased 15 times after 49 hours of incubation (from 3,400 ppm to 57,000 ppm). Although the amounts of CH₄ removal by 3 replications were similar and decreased slightly after 20 hours' incubation, CO₂ generation increased sharply. O₂ is a significant factor influencing the CH₄ oxidation process (Cao & Staszewska, 2011).

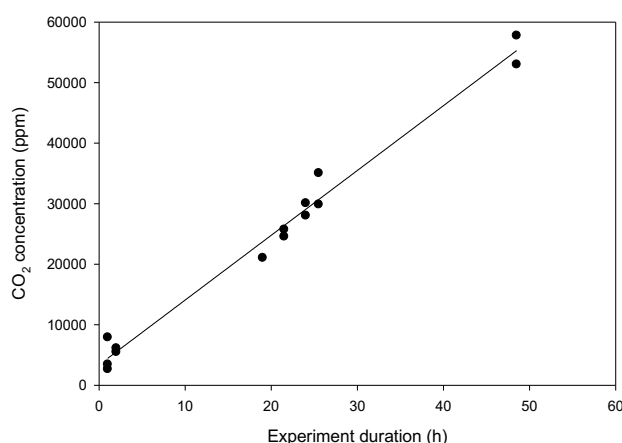


Figure 6. CO₂ concentrations in the reactors during incubation time

3.2.3 Nitrous oxide formation

N₂O generations were low at the start of the experiment and increased steadily to a maximum rate (Figure 7). The increase in N₂O concentrations during the experiment is attributed to the nitrification process.

The formation of N₂O during the further duration of the experiment indicates that some N₂O production occurred in the biofilter material. The increase of N₂O may be explained by the fact that N is converted to N₂O by nitrification due to continuous aerobic conditions in the biofilters (Melse & Van der Werf, 2005). According to previous studies, around one third NH₃ that enters biofilters can be transformed and released as N₂O (Trimborn, 2003). Similarly, Clemens and Cuhls (2003) reported that 26% of NH₃ was transformed into N₂O in biofilters.

The total cumulative N₂O generation after 50h incubation was 1.4 ppm was much lower than the reduction of CH₄ (823 ppm). After the end of the experiment, the contribution of N₂O to the total GHG concentration in the outlet air is insignificant.

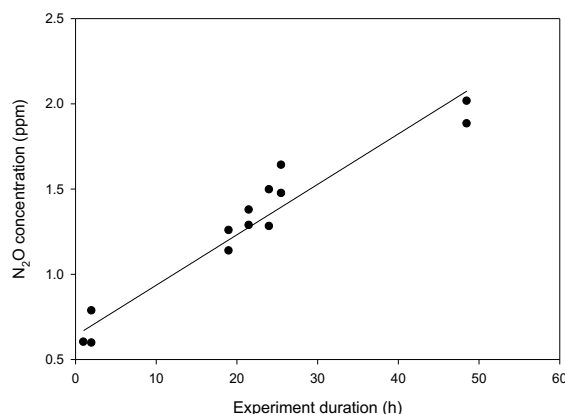


Figure 7. N₂O concentrations in the reactors during incubation time

4. Conclusions

Biofilter has the capacity of CH₄ removal and reduction. This is an attractive option for CH₄ removal at low concentration in the organic waste treatment plants.

Results from experiments using biofilter's material showed that the material was an excellent property as a carrier for CH₄ oxidation processes. Application of the microbial oxidation is a promising way to control the CH₄ emission from organic waste treatment.

CH₄ reduction rates in some biofilters were significantly lower than other. In biofilters, CH₄ is either oxidized or produced due to the O₂ availability. The CH₄ oxidation rate was lower in some part of biofilters because of the anaerobic condition. Therefore, the designing the biofilters correspondingly should effectively promote the microbial CH₄ removal of exhausted gas.

Further study is needed to understand and explain the CH₄ formation and removal in the biofilter in order to optimize the CH₄ and N₂O reduction processes. More studies with the continues reactor should be carried out because GHG emission of N₂O in the outlet air of the batch reactor was 3 times higher than the inlet gases. If it is the same tendency in the continuous reactor, it will be concerned more when the concentration of CH₄ (GPW =25) decreases 15 times when that of N₂O (GPW = 298) increases three times in biofilter.

5. References

- [1] Amlinger, F., Peyr, S. and Cuhls, C. 2008. Greenhouse gas emissions from composting and mechanical biological treatment. Waste Management and Research, 26, 47-60.

- [2] Bender, M. and Conrad, R. 1995. Effect of CH₄ Concentrations and Soil Conditions on the Induction of CH₄ Oxidation Activity. *Soil Biol. Biochem.* 27: 1517-1527.
- [3] Bender, M. & Conrad, R. 1992. Kinetics of CH₄ oxidation in oxic soils exposed to ambient air or high CH₄ mixing ratios. *FEMS Microbiology Ecology* 101: 261-270.
- [4] Benstead, J. & King, G.M. 1997. Response of methanotrophic activity in forest soil to Methane availability. *FEMS Microbiology Ecology* 23: 333-340.
- [5] Cao, Y. and Staszewska, E. 2011. Methane Emission Mitigation from Landfill by Microbial Oxidation in Landfill Cover, International Conference on Environmental and Agriculture Engineering, IPCBEE vol.15, IACSIT Press, Singapore.
- [6] Clemens, J. and Cuhls, C. 2003. Greenhouse gas emissions from mechanical and biological waste treatment of municipal waste. *Environmental Technology*, 24: 745-754.
- [7] Du Plessis, C.A., Strauss, J.M., Sebapalo, E.M.T. & Riedel, K.-H.J. 2003. Empirical model for Methane oxidation using a composted pine bark biofilter. *Fuel*, 82: 1359–1365.
- [8] Dunfield, P., Knowles, R., Dumont, R. & Moore, T.R. 1993. Methane production and consumption in temperate and subarctic peat soils: response to temperature and pH. *S Soil Biology and Biochemistry*, 25: 321–325.
- [9] Haubrichs, R. & Widmann, R. 2006. Evaluation of aerated biofilter systems for microbial Methane oxidation of poor landfill gas. *Waste Management*, 26: 408–416.
- [10] IPCC. 2007. Climate change 2007- the Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the IPCC. Cambridge University Press, Cambridge, UK.
- [11] Melse, R. W. and Van der Werf, A. W. 2005. Biofiltration for mitigation of Methane emission from animal husbandry. *Environmental Science and Technology*, 39: 5460-5468.
- [12] Nguyen, T. P., Cuhls, C. 2016. The effect of turning frequency on methane generation during composting of anaerobic digestion material, *J. Viet. Env.*, 8(1): 50-55.
- [13] Park, J.-R., Moon, S., Ahn, Y.M., Kim, J.Y. & Nam, K. 2005. Determination of environmental factors influencing Methane oxidation in a sandy landfill cover soil. *Environmental Technology*, 26: 93–102.
- [14] Kára, J., Janča, E., and Herák, D. 2010. Exploitation of anaerobic fermentation of bio-degradable waste. *Res. Agr. Eng.* 56(1): 8–17.
- [15] Scheutz, C., Bogner, J., De Visscher, A., Gebert, J., Hilger, H., Huber-Humer, M., Kjeldsen, P., Spokas, K. 2009. Microbial Methane oxidation processes and technologies for mitigation of landfill gas emissions. *Waste Management & Research*, 27: 409-455.
- [16] Sly, L.I., Bryant, L.Y., Cox, J.M. & Anderson, J.M. 1993. Development of a biofilter for the removal of Methane from coal mine ventilation atmospheres. *Journal of Applied Microbiology and Biotechnology*, 39: 400–404.
- [17] Stępniewski, W., Pawłowska, M. and Rożej A. 2009. Microbial Oxidation of Methane in a Mineral-Based Aerated Biofilter – Model Studies. The International Conference on Solid Waste Management Technical, Environmental and Socio-economical Contexts – Waste Safe, Khulna, Bangladesh. 55-64.
- [18] Streese J. & Stegman, R. 2003. Microbial oxidation of CH₄ from old landfills in biofilters. *Waste Management*, 23: 573–580.
- [19] Trimborn, M., Goldbach, H., Clemens, J., Cuhls, C. and Breeger, A., 2003. Reduction of greenhouse gases in the exhaust air of biofilters at biowaste treatment plants. In: Band 14 der Bonner Agrikulturchemischen Reihe, Abschlußbericht.
- [20] Whalen, S.C., Reeburgh, W.S. and Sandbeck, K.A. 1990. Rapid Methane Oxidation in a Landfill Cover Soil. *Appl Environ Microbiol.* 56(11): 3405-3411.
- [21] Wilshusen, J.H., Hettiaratchi, J.P.A., De Visscher, A. & Saint-Fort, R. 2004. Methane oxidation and formation of EPS in compost: Effect of Oxygen concentration. *Environmental Pollution*, 129, 305–314.