

Available online at www.sciencedirect.com



Journal of Environmental Sciences 2010, 22(5) 769-776

JOURNAL OF ENVIRONMENTAL SCIENCES ISSN 1001-0742 CN 11-2629/X www.jesc.ac.cn

Effect of bio-column composed of aged refuse on methane abatement – A novel configuration of biological oxidation in refuse landfill

Dan Han, Youcai Zhao*, Binjie Xue, Xiaoli Chai

State Key Laboratory of Pollution Control and Resource Reuse, Tongji University, Shanghai 200092, China. E-mail: 3824932@163.com

Received 24 August 2009; revised 20 February 2010; accepted 24 February 2010

Abstract

An experimental bio-column composed of aged refuse was installed around the exhaust pipe as a new way to mitigate methane in refuse landfill. One of the objectives of this work was to assess the effect of aged refuse thickness in bio-column on reducing CH₄ emissions. Over the study period, methane oxidation was observed at various thicknesses, 5 cm (small size), 10 cm (middle size) and 15 cm (large size), representing one to three times of pipeline diameters. The middle and large size both showed over 90% methane conversion, and the highest methane conversion rate of above 95% occurred in the middle-size column cell. Michaelis-Menten equation addressed the methanotrophs diffusion in different layers of the bio-columns. Maximum methanotrophic activity (V_{max}) measured at the three thicknesses ranged from 6.4×10^{-3} to 15.6×10^{-3} units, and the half-saturation value ($K_{\rm M}$) ranged from 0.85% to 1.67%. Both the highest $V_{\rm max}$ and $K_{\rm M}$ were observed at the middle-size of the bio-column, as well as the largest methanotrophs population, suggesting a significant efficiency of methane mitigation happened in the optimum zone with greatest affinity and methanotrophic bacteria activities. Therefore, bio-column is a potential style for methane abatement in landfill, and the aged refuse both naturally formed and artificially placed in the column plays a critical role in CH₄ emission.

Key words: methane; landfill; aged refuse; bio-column; thickness

DOI: 10.1016/S1001-0742(09)60175-3

Introduction

Methane is a potent greenhouse gas due to its efficiency at absorbing and re-emitting infrared radiation. The global warming potential of CH₄ is 23 times higher than that of CO₂ (USEPA, 2002). On a global scale, approximately 653 Tg/yr of waste is landfilled, and annual global CH₄ emissions from landfills range from 16 to 22 Tg (Bogner and Matthews, 2003; Simpson et al., 2006), accounting for about 10%-19% of annual global CH₄ emissions (Kumar et al., 2004; USEPA, 2006). In the United States, landfills are the largest sources of anthropogenic methane emissions, which have been estimated to be 140.9 Tg CO₂, accounting for about 25% of the total CH₄ emissions of USA (USEPA, 2006), and in Canada, methane emissions from landfill sites represent 26% of all anthropogenic sources of this greenhouse gas (Nikiema et al., 2005). Although, at this time, important improvements are being made towards landfill management, it is believed that by the year 2050, CH₄ emission from landfills could increase by up to 81 Tg/yr (Kreileman and Bouwman, 1994) or even 93 Tg/yr (van Amstel et al., 1993). As methane from landfills is closely related to human activities, together with CH₄ emissions from the fossil fuel sector, landfill CH₄ emissions are the most practical ones to mitigate to

* Corresponding author. E-mail: zhaoyoucai@tongji.edu.cn

stabilize the CH₄ concentration in atmosphere.

Within landfills, the percentage of the natural biological elimination of the generated methane is estimated to be only approximately 10% (USEPA, 2005). Biological treatment depending mainly on the methanotrophs, are able to consume various polluting compounds present in biogas, such as methane, while only generating water, carbon dioxide, salts and biomass as oxidation products, being much less harmful for the environment than the initial biogas components. Hence, methanotrophs are capable of efficiently converting CH₄ (Hanson and Hanson, 1996; Hakemian and Rosenzweig, 2007), in spite of the increasing use of systems for gas emissions collection, for only between 40% and 60% (V/V) of the biogas formed is effectively recovered, and the residual quantities are dissipated into the surrounding soil and air (Nikiema et al., 2005).

However, the quantitative significance of the reduction, which depends on the availability of CH₄ (Bender and Conrad, 1995; Stein and Hettiaratchi, 2001; Pawlowska and Stepniewski, 2006), as well as on several environmental factors, need to be determined in the field. Soil material has been used to create landfill covers that oxidize the methane produced in the layer of wastes. It can bring about a considerable reduction up to 35% in emissions of methane in this way from one of the more important

anthropogenic sources (Reeburgh, 1996). And, experiments conducted in the past by several authors have shown that various compost materials constitute adequate cover media for methane abatement. Indeed, with such composts, reaction times are reduced and overall conversions are often greater and longer than those obtained with other cover materials, e.g., soils. Best results were obtained in composts when the organic matter is almost completely stable and the 7-day respiratory activity value is lower than $10 \text{ mg } O_2/g$ of dry matter (Humer and Lechner, 2001).

Apart from soil, methane oxidation material is usually made of sand or clay, and used as the daily and final cover of the wastes in landfills. Additionally, aged refuse, available in many landfills, is considered as a potential natural medium to be the covering on the top of the landfills recently. Generally, after 8–10 years of placement, there are few explosive gases and liquid leachate produced from the refuse, the ratio of biochemical oxygen demand and chemical oxygen demand (BOD₅/COD_{Cr}) descents to 0.3, COD_{Cr} level decreases to 25–50 mg/L, and the content of organic matters is less than 10%, which suggests that the refuse has been stabilized and could be defined as "aged refuse" (Zhao and Shao, 2004). The aged refuse contains a wide spectrum and large quantity of microorganisms which have been proved to have a strong decomposition capability for both biodegradable and refractory organic matter appeared in some wastewaters (Zhao et al., 2007). There are 2.2 million tons of municipal solid wastes produced per day in Shanghai, the largest city in China, and over 25 million tons of aged refuse in total at Shanghai Refuse Landfill. The quantity of aged refuse may account for 100 million tons in the urban areas in Chinese cities. The excavation and recycling of aged refuse has received much more attention in recent years, as the dumping sites have been urbanized and the aged refuse placed there should be removed and the land remediated (Zhao and Shao, 2004). Recently, researches have focused on utilizing the characteristics of huge surface proportion and abundance of microbes in aged refuse to design bio-filters for treating landfill leachate and various wastewaters (Chai et al., 2007). Furthermore, aged refuse could behave better when sufficient nutrients are provided and the moisture levels optimized.

The means for the abatement of anthropogenic methane emissions is also quite significant other than methane oxidation material. Biocover and biofilter as important zones for methanotrophic bacteria developing, are the most common forms applied at landfills in the initial phase of operation, old landfills or sites containing material of low gas generation rate (Hilger et al, 2000; Nikiema et al., 2005; Stern et al., 2007). Comparing with gas extracting, landfill cover is much cheaper and more effective for reducing emissions in smaller and older landfills with lower amounts of CH₄ generation, which becomes inefficient at low CH₄ contents. The application of biofilter was proved increasingly popular in Europe when the EC landfill directive (1999/31) becomes effective in 2005, which stipulates that only material of low biological activity may be deposited. Streese and Stegmann (2003) and Humer and Lechner (2001) used compost as oxidation material and reported about the formation of extrapolymeric substances (EPS) in biofilters and landfill covers. These block pore space and hamper substrate supply to the microorganisms, thus impairing optimum methanotrophic activity. However, comparing landfill covers and biofilters, landfill covers in general receive by far less methane than biofilters and are also usually not optimized for the purpose of methane oxidation with regard to parameters such as gas distribution, gas permeable pore space (i.e., mass transfer, methane and oxygen supply), or water content (Gebert and Gröngröft, 2006).

In fact, landfill cover as an important exit for methane escaped to outside has been studied, but another main exit - ventilation pipe seems no way to control, and little work has been done. The exhaust pipe is the passage for over 60% of methane (Themelis and Ulloa, 2007). As a new potential style of biological methane oxidation, in this study, bio-column filled with aged refuse was placed around the exhaust pipeline in landfill to evaluate the properties of aged refuse in such high methane concentration zone to optimize the environment for methanotrophic bacteria and mitigate greenhouse gas emission. The relationship between thickness of the bio-column and methane oxidation, the carbon dioxide production was examined. Meanwhile, the kinetics of methane oxidation process was deduced to analyze the methanotrophs at different bio-column thickness and supply a foundation with engineering application in practice in the future.

1 Materials and lysimeter set-up

1.1 Origin and characteristics of aged refuse

The aged refuse used in the study was excavated from different landfill units in Shanghai Laogang Refuse Landfill, China, with over 8 yeas of placement. The larger inorganic substances, such as stones, glass, bottles, etc., were manually separated and removed. The air-dried aged refuse was screened by a conventional mechanical screener and a granule size of less than 2 mm was employed in this work. For further basic characteristics analysis, the aged refuse was broken into small pieces by a hammer. At least 5 kg aged refuse was sampled and its characteristics in different landfill time such as moisture, organic content, oxidation-reduction potential (ORP), and distribution of particles in various sizes were measured in triplicate (Table 1).

In order to stimulate the methane oxidation bacteria in aged refuse, methanotrophs were inoculated in nitrate mineral salts (NMS) agar slant with 20% CH₄ (*V/V*) in the headspace and incubated at 25°C in the dark for three days before the aged refuse is taken to use. The NMS was prepared as follows: 1 L NMS contains NaNO₃ 0.85 g, KH₂PO₄ 0.53 g, Na₂HPO₄ 2.17 g, MgSO₄·7H₂O 0.037 g, K₂SO₄ 0.17 g, CaCl₂·2H₂O 0.007 g, 1 mol/L H₂SO₄ 0.5 mL, FeSO₄·7H₂O 11.2 mg, CuSO₄·5H₂O 2.5 mg, and trace element solution 2 mL. pH value was adjusted to 7.0. One liter of trace element solution contains (g)

Table 1 Main characteristics of aged refuse used in the experiment

Property	Value
Placement time (yr)	16
Moisture (%)	3.2
pH	7.76
Eh (mV)	143
TN (%)	0.18
Organic content (%)	4.37
Distribution fraction of particle size (%)	
> 4 mm	45.23
0.45-4 mm	31.41
0.3-0.45 mm	5.03
0.2 –0.3 mm	5.03
0.15-0.2 mm	5.03
0.125-0.15 mm	0.75
< 0.125 mm	7.52

ZnSO₄·7H₂O 0.204, MnSO₄·4H₂O 0.223, H₃BO₃ 0.062, Na₂MoO₄·2H₂O 0.048, CoCl₂·6H₂O 0.048, and KI 0.083.

1.2 Experimental scenarios

1.2.1 Experimental set-up

The column test was performed in three 38 L PVC columns, 35 cm in diameter and 40 cm in height (Fig. 1). A ventilation pipeline with 5 cm in diameter and 45 cm in length was put in the center of each column. Aged refuse with 16 years of placement time added with NMS nutrient was installed around the ventilation pipelines in columns with thickness of 5, 10, and 15 cm, respectively, and plastic nets were installed to hold the aged refuse. The moisture of the aged refuse was standardized in relation to their water-holding capacities by humidifier to maintain the same water content in aged refuse.

The columns were placed in a temperature-controlled $(37^{\circ}C)$ chamber. Chemical synthetic gas $(50\% \text{ CH}_4/50\% \text{ CO}_2)$ was mixed with air before crossing the humidifier and then was fed to the columns from the lower ektexine. The gas flow rates were adjusted by rotameters. The injected bottle mixing gas and air were 0.3 L/min (methane in each column is 50 mL/min) and 0.75 L/min (oxygen in each column is 50 mL/min), respectively, corresponding to an aeration ratio of $1 \text{ mol } O_2$ in $1 \text{ mol } CH_4$ for the incomplete oxidation of CH_4 simulating the total oxygen

distribution around the ventilation pipe. Outlet gas was analyzed once 4 days through a silica tube, and the tube end was kept 1 cm under the surface of the water in a cylinder.

1.2.2 Analytical methods

Biogas compositions were analyzed by a gas chromatograph (GC, Shimadzu GC-14B, Japan) equipped with a gas thermal conductivity detector (TCD) and a stainless steel column with nitrogen as a carrier gas at a flow rate of 30 mL/min. The temperatures of injector, detector, and column were kept at 40, 80, and 40°C, respectively. Measurements of total solid, pH, ORP were performed according to the standard methods (APHA, 1995).

The number of methanotrophic bacteria was determined by the rolling tube method in five replicates (Min and Zinder, 1990) with NMS medium.

2 Results and discussion

2.1 Methane oxidation by aged refuse as bio-column with different thicknesses

The three bio-columns, used in this experiment, were operated over a period of more than one month, under the same moisture content 15% and temperature 37°C. The production of carbon dioxide relative to the quantity of eliminated methane, which depends on the concentration changes between the bio-column inlet and outlet, is the key indicator of the effectiveness of the treatment process. Bio-column thickness, the most important parameter of the bio-column design, took effect on methane oxidation with time in Fig. 2, and the rate of production of CO_2 (P_{CO_2}) as a function of the elimination of CH_4 (E_{CH_4}) was expressed in concentration fraction change (%) (Fig. 3). Where, P_{CO_2} and E_{CH_4} can be represent as follows:

$$P_{\text{CO}_2} = (C_{\text{CO}_2,\text{out}} - C_{\text{CO}_2,\text{in}})/C_{\text{CO}_2,\text{out}}$$
 (1)

$$E_{\text{CH}_4} = (C_{\text{CH}_4,\text{in}} - C_{\text{CH}_4,\text{out}})/C_{\text{CH}_4,\text{in}}$$
 (2)

From Fig. 2, methane conversion for the middle and large size bio-columns both increased slowly during the measuring time, while the small size fell to a significant

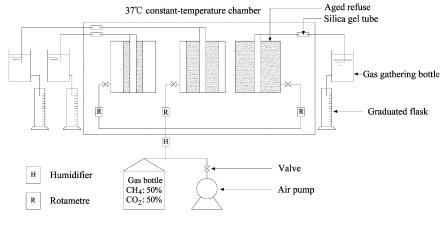


Fig. 1 Column set-up in the experiment.

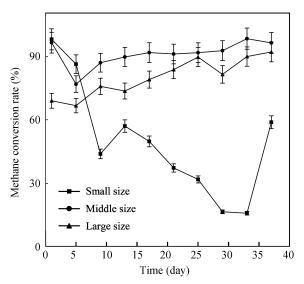


Fig. 2 Methane conversion with time for three sizes of bio-columns. Error bars represent 5% error of the mean of measuring day.

degree at day 9, and then fell to an even lower level (17%), followed by a gentle increase. Although a great rebound was observed in the last four days, the conversion of small size was still much lower than the other two sizes, and it seemed that the middle size was more stable and efficient on methane conversion than the large size. For the middle cell, methane conversion rate waved at 90%, and reached its highest value of 95% after one month, while a gradual rising appeared for the large cell, and finally reached 90%. Therefore, the middle size was considered as optimum thickness for bio-column to control methane.

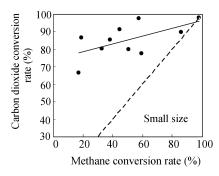
The present aged refuse with proper thickness appeared to have a sufficient level of biological stabilization for being used in methane oxidation applications, as indicated by gas production proportion (and also by the dominance of methane oxidation over the microbial activity of the columns as discussed later). In Fig. 3, for a theoretical bio-column composed only of methanotrophs, the curve in Fig. 2 describing the relationship of CO_2 productions and CH_4 eliminations should pass through the origin, meaning that a lack of methane consumption causes the carbon dioxide production to cease. However, all the P_{CO_2} in Fig. 3 did not follow a direct proportionality, yet produced less CO_2 (with P_{CO_2} -to- E_{CH_4} ratio being 0.3786 for small size, 0.5031 for middle size and 0.4731 for large size) than

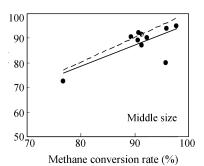
the stoichiometric ratio of 1. What is more, the relative positions of each liner regression for the three sizes to the theoretical curves were above, crossing, and below, respectively, indicating different biomass production in aged refuse. The middle size produced more CO₂ compared with the small and large sizes, thus sustained lower level of aged refuse layer clogging due to reduced rate of biomass production within it, which favored oxygen to access and transfer faster and farther. This is mainly because that the production rate of carbon dioxide is proportional to the growth rate of methanotrophic bacteria in the aged refuse. The biological degradation reaction of methane is given by Reaction (3).

$$CH_4 + wO_2 \rightarrow xCO_2 + yH_2O + z$$
 (Bacterial biomass) (3)

The greater the mass of CO₂ produced per gram of methane eliminated, the lesser is the proliferation of microorganisms within the aged refuse, which influences the rate of aged refuse clogging and gas accessing. In the case of total methane oxidation, supposing that no biomass is generated (theoretical reaction, w = 2, x = 1, y = 2 and z = 0), the mol-basis stoichiometric ratio for the maximum CO_2 production P_{CO_2}/E_{CH_4} is 1, expressed by the theoretical straight line in Fig. 3. The present gas ratios in the study were a little higher than those reported by Kettunen et al. (2006) in engineering soil columns and by Einola et al. (2008) in biocover utilized end-product of mechanical-biological waste treatment, indicating that aged refuse in bio-column is equally or better suited to support microbial methane oxidation than the materials studied previously.

The thickness profiles of methane oxidation in the biocolumns were governed by O₂ availability, as there was an inward decrease in CH₄ oxidation potential following the falling of O₂ concentration in cross section. In bio-column, like landfill cover, there is an optimum zone for CH₄ oxidation, where optimum conditions for the growth of methanotrophic bacteria, oxygen and CH₄ ratio, retaining time and suitable environmental condition exists. CH₄ oxidation potentials were the greatest where the vertical and horizontal profiles of O₂ and CH₄ overlapped. Bender and Conrad (1994), Czepiel et al. (1996) and Stein and Hettiaratchi (2001) have shown that, by increasing O₂ concentration from 3% to 20% (V/V) in the gas mixture, the CH₄ conversion rate varied slightly (less than 10%),





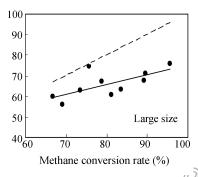


Fig. 3 Production of CO₂ as a function of elimination capacity for CH₄. The solid lines represent the relationships of CO₂ and CH₄ conversion rate, and the dashed lines are theoretical lines which are same with one slope in three figures.

whereas, a decrease of O_2 concentrations from 3% to 1% caused the fall off of CH_4 oxidation of more than 50%. However, during the experiments of Stein and Hettiaratchi (2001), the maximal CH_4 elimination was obtained at O_2 concentration between 0.75 and 1.6%.

Besides the oxygen distribution, thickness of aged refuse is related to the retention time in media determined by adsorption ability, and the microorganism function determined by the aged refuse components, for aged refuse is a kind of porous media with high adsorption of gas. It is known that the normal impacting radius of pipeline in landfills is considered 25 m, and gas is diffused and gathered in the range, finally enters the pipeline or escaped outside from the landfill cover. Therefore, proper thickness of the bio-column resulted in increased retention times for transported CH₄ and higher fraction oxidation. In fact, the significant deviation of three curves from the theoretical line is typically observed in the microbial oxidation processes; it described the partial conversion of CH₄ into biomass. Additionally, it is possible for a small fraction of the produced CO2 to accumulate in the wet biofilm as HCO₃⁻, H₂CO₃ or CO₃²⁻ ionic species (Delhoménie et al., 2002; Jorio et al., 1998).

Since the scales of landfills are different, one to three times of the pipeline diameters were chosen to represent different proportions of the bio-column and pipeline, which also can be scaled up in practice. Furthermore, similar to the landfill cover, in order to reduce the influence of temperature, and the problems related to O_2 diffusion, the use of multi-layer (Streese and Stegmann, 2003; Berger et al., 2005) in bio-column is believed to be developed in the future.

2.2 Characteristics and kinetics of the methane oxidation process

According to the normal concentration in the exhaust gas, the concentration of methane in the influent was changed across the range of 3.0%–40.0% (V/V). Changes in the concentrations of gases (CH₄, CO₂ and O₂) in the exit were analyzed over several days. The kinetics of the methane oxidation process in aged refuse point to a reaction proceeding in line with the kinetics described by

the Michaelis-Menten equation (Eq. (4)):

$$V = V_{\text{max}} \times 1/(1 + K_{\text{m}}/C) \tag{4}$$

where, V (m³/(m³·sec)) is the actual methane oxidation rate, $V_{\rm max}$ (m³/(m³·sec)) is the maximum methane oxidation rate, $K_{\rm M}$ (%) is Michaelis constant for CH₄, C (%) is the CH₄ concentration. The kinetic parameters to the reaction ($V_{\rm max}$ and $K_{\rm M}$) as regards CH₄ were designated using the linearization method after Lineweaver-Burke (Kloczewiak, 1984).

The values obtained for $V_{\rm max}$ in the experiment described here were in the range 6.4×10^{-3} to 15.6×10^{-3} units (Fig. 4a). These were similar to the potential methanotrophic activity measured by Gebert et al. (2003) in crushed expanded clay in biofilter, being equal to 11.8×10^{-3} , while lower than that in soil from landfill cover, being equal to 40.7×10^{-3} (Table 2).

Values of $K_{\rm M}$ for CH₄ measured in field conditions or in conditions of the simulation of a landfill cover or biofilter and included in the literature are shown to vary between $0.8 \times 10^3\%$ (De Visscher et al., 2001) and 2.6% (Bogner et al., 1997). The $K_{\rm M}$ values noted in this study did not depart from the results gained by other authors (Table 2), being in the range 0.85% to 1.67%. The relatively high values for $K_{\rm M}$ in comparison with some obtainable in soils from the places exposed to lower concentrations of CH₄ in Table 2 pointed to the limited affinity for CH₄ of the microorganisms responsible for the methanotrophic process in aged refuse. This affinity was several orders of magnitude greater in the case of forest soils, in which the constant $K_{\rm M}$ varied from 0.8×10^{-3} (Benstead and King, 1997) to $9.9 \times 10^{-3}\%$ of methane (Whalen and Reeburgh, 1996).

Figure 4b shows the differentiation of methanotrophs in the profile for the column in relation to affinity for CH_4 . Lower affinity was demonstrated by the populations of bacteria in the center part of the column. In the further parts of the profile (at the thickness of 35 cm), the affinity for CH_4 was higher, while the value for K_M was even twice as high as in the inner layer.

From Fig. 4, $V_{\rm max}$ and $K_{\rm M}$ did not increase as the thickness of aged refuse increased, whereas they changed at such a zone as the aged refuse is saturated. Before

Table 2 Characteristics of kinetic parameters for methane oxidation in different habitats (Malgorzata and Witold, 2006)

Material	CH ₄ concentration range (V/V)	$V_{\text{max}} (\text{m}^3/(\text{m}^3 \cdot \text{sec}))$	$K_{\rm M}$ for CH ₄ (V/V)	Reference
Composite of soil from landfill cover	0.00017-1.0	0.88-0.0011 ^a	0.18	Whalen et al., 1990
Coarse sand soil from landfill cover	0.050-5.0	6.5-0.0073	2.4	Kightley et al., 1995
Clay topsoil from landfill	0.016-8.0	0.0047	2.6	Bogner et al., 1997
Soil with agricultural origin	0.0050-3.0	1.5-0.17	0.15-0.50	De Visscher et al., 1999
Sandy loamy cover soil from landfill	< 2.0	0.52-0.011	0.080 - 0.50	De Visscher et al., 2001
Loam from landfill cover	< 10	0.0062	0.75	Stein and Hettiaratchi, 2001
Crushed expanded clay in biofilter	0.20-10	0.011	1.1	Gebert et al., 2003
Soil from landfill cover	0.0-23	0.041	2.0	
Forest camb soil	0.000002-0.030	0.000022a	0.0022	Bender and Conrad, 1992
The Alaskan soil	0.00017-0.12			Whalen and Reeburgh, 1996
Bog		0.0015	0.084	
Forest		4.9-0.000057	2.9-0.0099	
Forest soil	0.00017-0.10	0.0000062	0.00080	Benstead and King, 1997

a Per kg of wet weight.

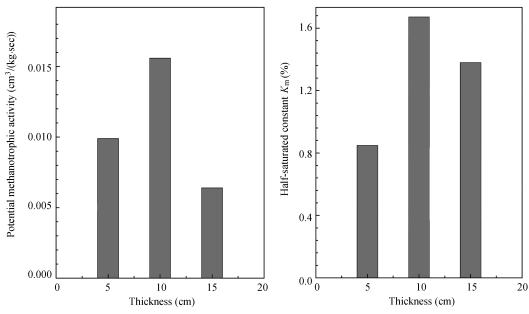


Fig. 4 Profile for potential activity of methane oxidation V_{max} (a) and half-saturated constant K_{M} (b) in simulated bio-column. Values for V_{max} and CH₄ (K_{M}) were obtained by the graphical method of Line weaver-Burke.

and after saturating, methanotrophs are not the same in the aged refuse. In the zone close to the exhaust pipe, methanotrophs characterized by their high potential activity ($V_{\rm max}$) and low affinity ($K_{\rm M}$) in relation to high methane concentrations are dominant, while microorganism exposed to the low or normal atmospheric levels of CH₄ seemed to distribute in the edge of the column, where methane concentration was declined by adsorption instead of oxidation. That is to say, the middle-size column seemed to have both active methanotrophic bacteria and good affinity, which methane is mitigated by adsorption and oxidation efficiently.

The existence of a zone of maximal methanotrophic activity is dependent on many factors, of which the most important is the granulometric composition of aged refuse, as this determines the diffusion of gases and the surface area available to microorganisms, as well as temperature, moisture, the concentration of CH₄ in biogas and the rate at which it moves through the layer of aged refuse. Possibly the explanations all serve to describe different efficiencies in different thicknesses of bio-column in landfill.

2.3 Characteristics of methanotrophs in the aged refuse

After purging with landfill gas for more than one month, the average numbers of methanotrophic cells in 5-, 10- and 15-thickness layers were 0.92×10^9 , 5.48×10^9 and 8.62×10^8 , respectively, which are a little lower than the numbers of PLFA-derived methanotrophic cells found in field landfill biofilters in northern Germany (Gebert et al., 2004), but more than the population in the landfill cover soil sampled at four different depth of the columns reported by Park et al. (2008). In the landfill cover soil, the number of methanotrophs was in the range of $2.0 \times 10^7 - 4.0 \times 10^7$ CFU/g, and changed to $4.6 \times 10^7 - 10.0 \times 10^7$ CFU/g and $1.1 \times 10^7 - 2.7 \times 10^7$ CFU/g, respectively, if the cover soil was amended with earthworm cast and PAC.

The largest bacteria population appeared in the 10 cm-thickness zone, in agreement with the results above. Taking the aged refuse in middle-size column cell to identify the type of the methanotrophs, it was found that the average number of type I methanotrophs in the analyzed layers was more than triple higher than that of type II methanotrophs. This indicated the dominance of type I methanotrophs in the bio-column purged with landfill gas. Furthermore, comparing the population of methanotrophs in the original aged refuse obtained in previous work (12.5 \times 10⁷ CFU/g), it appears evident that it is possible to enrich high methanotrophic populations in methane oxidizing processes as the populations of methanotrophs found in landfill gas-exposed environments are of one to two orders of magnitude higher than that in initial phase.

In fact, methanotrophs activity period could be divided into two phases: the lag phase and the growth phase. The lag phase follows the construction of the experimental plot when the methane oxidation bacteria are essentially identical. After about one month under laboratory conditions (the temperature is not optimal condition), the steady state conditions needed for growing methanotrophs in bio-column are established. During the second phase, the number of abundant methane bacteria increases with time, particularly in the region close to oxygen, until reach maximum value. Our analyses of the bacterial population in the study suggests that the difference in the number and activity of methanotrophic bacteria in LFG-applied biocolumn may be explained by the fact that CH₄ in the LFG plays a key role in inducing the growth of methanotrophs in aged refuse. Further, elevation for active methanotrophic populations may be equal to strengthening tolerance for high LFG levels.

Since the bio-column is a potential mean to mitigate methane discharged from the exhaust pipe, there is one point to be mentioned. In landfills, the refuse distributed around the gas pipeline could be stable naturally after 8–10 years to become aged refuse; hence, the partition of refuse is able to oxidize the methane *in situ* landfill. And it is assumable to believe the capacity of the aged refuse conversed by the original refuse naturally is greater with the placement time. Thereby, the practical methane emission is less than the theoretical value, except the difference due to biological oxidation by covers in landfills.

3 Conclusions

The proposed bio-columns filled with aged refuse was constructed and placed around the exhaust pipeline to oxidize the methane discharged from exhaust pipelines in landfills. From the results presented, twice of pipeline diameter was the optional thickness for the bio-column, and methane conversion reached 95% during 37 days. Methanotrophs diffusion in different layers of aged refuse in the bio-column was described using the Michaelis-Menten equation, and it was found that maximum methanotrophic activity ($V_{\rm max}$) of the three sizes ranged from 6.4 × 10⁻³ to 15.6 × 10⁻³ units, and the half-saturation value ($K_{\rm M}$) ranged from 0.85% to 1.67%. The middle-size of bio-column cell showed the highest $V_{\rm max}$ and $K_{\rm M}$, and the largest bacteria population is 5.48 × 10⁹.

Acknowledgments

This work was financially supported by the Hi-Tech Research and Development Program (863) of China (No. 2007AA06Z349).

References

- APHA (American Public Health Association), 1995. Standard Methods for the Water and Wastewater (19th ed.). Washington, DC, USA.
- Bender M, Conrad R, 1994. Methane oxidation activity in various soils and freshwater sediments Occurrence, characteristics, vertical profiles, and distribution on grain size fractions. *Journal of Geophysical Research: Atoms*, 99(D8): 16531–16540.
- Bender M, Conrad R, 1995. Effect of CH₄, concentrations and soil conditions on the induction of CH₄ oxidation activity. *Soil Biological and Biochemistry*, 27: 1517–1527.
- Benstead J, King G M, 1997. Response of methanotrophic activity in forest soil to methane availability. *FEMS Microbiology Ecology*, 23: 333–340.
- Berger J, Fornés L V, Ott C, Jager J, Wawra B, Zanke U, 2005. Methane oxidation in a landfill cover with capillary barrier. *Waste Management*, 25: 369–373.
- Bogner J, Spokas K, Burton E, 1997. Kinetics of methane oxidation in a landfill cover soil: temporal variations, a whole-landfill oxidation experiment, and modeling of net CH₄ emissions. *Environmental Science and Technology*, 31: 2504–2514.
- Bogner J, Matthews E, 2003. Global methane emissions from landfills: New methodology and annual estimates 1980–1996. *Global Biogeochemical Cycle*, 17: 1065.
- Chai X L, Guo Q, Li Y L, Zhao Y C, 2007. Adsorption characteristics of phenolic compound by aged refuse. *Environmental Chemistry*, 2: 164–167.

- Czepiel P M, Mosher B, Crill P M, Harriss R C, 1996. Quantifying the effect of oxidation on landfill methane emissions. *Journal of Geophysical Research: Atoms*, 101: 16721–16729
- Delhoménie M C, Bibeau L, Bredin N, Roy S, Broussau S, Brzezinski R et al., 2002. Biofiltration of air contaminated with toluene on a compost-based bed. Advance in Environmental Research, 6: 239–254.
- De Visscher A, Schippers M, van Cleemput O, 2001. Short-term kinetic response of enhanced methane oxidation in landfill cover soils to environmental factors. *Biological Fertility of Soil*, 33: 231–237.
- De Visscher A, Thomas D, Boeckx P, van Cleemput O, 1999. Methane oxidation in simulated landfill cover soil environments. Environmental Science and Technology, 33:1854–1859.
- Einola J K M, Karhu A E, Rintala J A, 2008. Mechanicallybiologically treated municipal solid waste as a supported medium for microbial methane oxidation to mitigate landfill greenhouse emissions. *Waste Management*, 28: 97–111.
- Gebert J, Gröengröeft A, Miehlich G, 2003. Kinetics of microbial landfill methane oxidation in biofilters. *Waste Management*, 23: 609–619.
- Gebert J, Gröngröft A, 2006. Performance of a passively vented filed-scale biofilter for the microbial oxidation of landfill methane. Waste Management, 26: 399–407.
- Gebert J, Gröngröft A, Schloter M, Gattinger A, 2004. Community structure in a methanotroph biofilter as revealed by phospholipid fatty acid analysis. FEMS Microbiology Letters, 240: 61–68.
- Hakemian A S, Rosenzweig A C, 2007. The biochemistry of methane oxidation. *Annual Reviews in Biochemistry*, 76: 223–241.
- Hanson R S, Hanson T E, 1996. Methanotrophic bacteria. Microbiological Reviews, 60: 439–471.
- Hilger H A, Cranford D F, Barlaz M A, 2000. Methane oxidation and microbial exopolymer production in landfill cover soil. *Soil Biology and Biochemistry*, 32: 457–467.
- Humer M, Lechner P, 2001. Microbial methane oxidation for the reduction of landfill gas emissions. *Journal of Solid Waste Technology Management*, 27: 146–151.
- Jorio H, Kiared K, Brzezinski R, 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*, 73: 183–196.
- Kettunen R H, Einola J K M, Rintala J A, 2006. Landfill methane oxidation in organic soil columns at low temperature. *Water, Air and Soil Pollution*, 177: 313–334.
- Kightley D, Nedwell D B, Cooper M, 1995. Capacity for methane oxidation in landfill cover soils measured in laboratory-scale soil microcosms. Applied and Environmental Microbiology, 61: 592–601.
- Kloczewiak M, 1984. Kinetyka Reakcji Enzymatycznych, w: Elementy enzymologii, red. J. Wytwicki, W Ardelt, PWN, Warszawa, 111–129.
- Kreileman G J J, Bouwman A F, 1994. Computing land use emissions of greenhouse gases. Water, Air and Soil Pollution, 76: 231–258
- Kumar S, Gaikwad S A, Shekdar A V, Kshirsagar P S, Singh R N, 2004. Estimation method for national methane emission from solid waste landfills. *Atmospheric Environment*, 38: 3481–3487.
- Malgorzata P, Witold S, 2006. An influence of methane concentration on the methanotrophic activity of a model landfill

- cover. Ecology Engineering, 26: 392-395.
- Min H, Zinder S H, 1990. Isolation and characterization of a thermophilic sulfatereducing bacterium *Desulfotomaculum* thermoacetoxidans sp. nov. Archives of Microbiology, 153: 399–404.
- Nikiema J, Bibeau L, Lavoie J, Brzezinski R, Vigneux J, Heitz M, 2005. Biofiltration of methane: An experimental study. *Chemical Engineering Journal*, 113: 111–117.
- Park S, Lee I, Cho C, Sung K, 2008. Effects of earthworm cast and powdered activated carbon on methane removal capacity of landfill cover soils. *Chemosphere*, 70: 1117– 1123.
- Pawlowska M, Stepniewski W, 2006. An influence of methane concentration on the methanotrophic activity of a model landfill cover. *Ecology Engineering*, 26: 392–395.
- Reeburgh W S, 1996. "Soft spot" in the global methane budget. In: Microbial Growth on C1 Compounds (Lidstrom M E, Tabita F R, eds.). Kluwer Academic Publishers, The Netherlands. 334–342.
- Simpson I J, Rowland F S, Meinardi S, Blake D R, 2006. Influence of biomass burning during recent fluctuations in the slow growth of global tropospheric methane. *Geophysical Research Letters*, 33: L22808.
- Stein V B, Hettiaratchi J P A, 2001. Methane oxidation in three Alberta soils: influence of soil parameters and methane flux rates. *Environmental Technology*, 22: 101–111.
- Stern J C, Chanton J, Abichou T, Powelson D, Yuan L, Escoriza S et al., 2007. Use of a biologically active cover to reduce landfill methane emissions and enhance methane oxidation. *Waste Management*, 27: 1248–1258.

- Streese J, Stegmann R, 2003. Microbial oxidation of methane from old landfills in biofilters. Waste Management, 23: 573– 580
- Themelis N J, Ulloa P A, 2007. Methane generation in landfills. *Renewable Energy*, 32: 1243–1257.
- USEPA, 2002. Greenhouse gases and global warming potential values. In: Inventory of US Greenhouse Emissions and Sinks: 1990–2000. 16.
- USEPA, 2005. Inventory of US greenhouse gas emissions and sink: 1990–2003. US Environmental Protection Agency, Washington, USA.
- USEPA, 2006. Global Mitigation of Non-CO₂ Greenhouse Gas.
 3. Landfill Sector. US Environmental Protection Agency, Washington DC, USA.
- van Amstel A R, Swart R J, Kroll M S, Beck J P, Bouwman A F, van der Hoek K W, 1993. In: Methane, the Other Greenhouse Gas. RIVM Report No 48 150700 1, The Netherlands.
- Whalen S C, Reeburgh W S, 1996. Moisture and temperature sensitivity of CH₄ oxidation in boreal soils. *Soil Biology and Biochemistry*, 28: 1271–1281.
- Whalen S C, Reeburgh W S, Sandbeck K A, 1990. Rapid methane oxidation in a landfill cover soil. *Applied and Environmental Microbiology*, 56: 3405–3411.
- Zhao Y C, Lou Z Y, Guo Y L, Xu D M, 2007. Treatment of sewage using an aged-refuse based bioreactor. *Journal of Environmental Management*, 82: 32–38.
- ZhaoY C, Shao F, 2004. Use of an aged-refuse biofilter for the treatment of feedlots wastewaters. *Environmental Engineering Science*, 21: 349–360.

