Use of biochar to enhance methane oxidation for MSW landfill bio-cover

Utilisation du biochar pour améliorer l'oxydation du méthane pour la bio-couverture de décharge de DSM

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ABSTRACT: Biochar is an organic material produced from biomass through pyrolysis. Its highly porous structure and high organic matter content can favour the microbial activity, which has been recently considered as a potential soil amendment material to enhance methane oxidation in the bio-cover of municipal solid waste (MSW) landfill. In this study, laboratory batch tests were conducted on soils modified by three different types of biochar (wood chip, corn stalk and rice stalk) to characterise their methane oxidation capacity. Test results showed that the methane oxidation rate of three biochar modified soils was around 3 to 5 times that of untreated soil. The oxidation rate is influenced by water content (*WC*) and biochar content (*BC*). It increases with increasing *WC*/*BC* until reaching a maximum value at the optimum *WC*/*BC*. Thereafter it decreases with further increasing *WC*/*BC*. The liquidity index is used as a normalised parameter of *WC*. For the three biochars tested in this study, the maximum oxidati on rate occurs at the liquidity index ranging between -0.6 and -0.3. On the other hand, the optimum *BC* is between 20% and 30% of dry weight of soil. It should be noted that biochar alone does not have any methane oxidation capacity.

RÉSUMÉ : Le biochar est une matière organique produite à partir de la biomasse par pyrolyse. Sa structure très poreuse et sa teneur élevée en matière organique peuvent favoriser l'activité microbienne, qui a été récemment considérée comme un matériau potentiel de modification du sol pour améliorer l'oxydation du méthane dans la bio-couverture de décharge de déchets solides municipaux (DSM). Dans cette étude, des essais de lots de laboratoire ont été effectués sur des sols modifiés par trois types différents de biochar (copeau de bois, tige de maïs et paille de riz) pour caractériser leur capacité d'oxydation du méthane. Les résultats des essais ont montré que le taux d'oxydation du méthane de trois sols modifiés par le biochar était d'environ 3 à 5 fois celui du sol non traité. Le taux d'oxydation est influencé par la teneur en eau (*WC*) et la teneur en biochar (*BC*). Il augmente avec l'augmentation de *WC*/*BC* jusqu'à atteindre une valeur maximale à l'optimum *WC*/*BC*. Ensuite, il diminue avec l'augmentation de *WC*/*BC*. L'indice de liquidité est utilisé comme paramètre normalisé de *WC*. Pour les trois biochars testés dans cette étude, le taux d'oxydation maximum se produit à l'indice de liquidité entre -0,6 et -0,3. D'autre part, l'optimum *BC* est entre 20% et 30% du poids sec du sol. Il faut noter que le biochar seul n'a pas de capacité d'oxydation du méthane.

KEYWORDS: biochar, methane oxidation, bio-activity, water content.

1 INTRODUCTION

A bio-cover is a novel soil cover system that mitigates methane emission of municipal solid waste (MSW) landfill by using the methanothropic bacteria to oxidise methane (Huber-Humer et al. 2009, Stern et al. 2007, Humer and Lechner 1999). In general, the biocover consists of an upper oxidation enhancing layer overlying a gas distribution layer. Past studies have shown that organic rich materials such as compost and sewage sludge are commonly used in the bio-cover to optimise the environmental conditions for the activity of methanotrophic bacteria, thus enhance methane oxidation (Bohn et al. 2011, Huber-Humer et al. 2011).

Biochar is an organic material produced from biomass through pyrolysis. Its highly porous structure and high organic matter content can favor the microbial activity, which has been recently considered as a potential soil amendment material to enhance methane oxidation in the bio-cover (Sadasivam and Reddy 2015, Reddy et al. 2014). Yargicoglu et al. (2015) showed that a high variability in the physical and chemical properties of different biochars was observed due to different feedstocks and production processes. In this study, laboratory batch tests were conducted on a soil modified by three different types of biochar (wood chip, corn stalk and rice stalk) to determine the effects of biochar content (*BC*) and water content (*WC*) on their methane oxidation capacity. Then the test results are compared with the physical and chemical properties of the modified soils to identify the favourable conditions for methane oxidation.

2 MATERIALS AND METHODOLODY

2.1 *Materials*

The tested soil was a mixture of 13% silica sand, 75% silica fines and 12% kaolin. The basic physical and chemical properties of soil samples were conducted in accordance with the procedures given in GB/T 50123-1999 (1999), LYT 1232-1999 (1999) and LYT 1239-1999 (1999). Figure 1 depicts the grain size distribution of the tested soil, which consists of around 90% fines (< 0.075 mm). The liquid limit (*LL*) and plastic limit (*PL*) are 27% and 19%, respectively. According to the Unified Soil Classification System (USCS), the soil is classified as clay of low plasticity (CL). Three different types of biochar were used in this study. They are derived from wood chip (*W*), corn straw (*C*) and rice straw (*R*). The grain size distribution curves depicted in Figure 1 indicate that biochars are coarse materials, which consist of over 50% of grain size larger than 0.075 mm.

The modified soil samples were formed by mixing air-dried biochar and soil thoroughly inside a mixer to achieve *BC* ranging from 10% to 50% of dry mass of soil. Addition of biochar can modify the basic physical and chemical properties of the tested soil. Figure 2 shows the classification of modified soils with 10% and 20% *BC*. It is apparent that the soil changes from CL to MH with higher *BC*. Table 1 summarises the other basic physical and chemical properties of modified soils with 20% *BC* and untreated soil. It can be seen that addition of biochar decreases the specific gravity (G_s), but increases *pH*, organic matter content (*OC*) and phosphorus content (*PC*) of modified soils.

2.2 *Methane oxidation batch tests*

Laboratory methane oxidation batch tests were conducted to determine the methane oxidation capacity of the biochar modified soils. Table 2 summarises the testing conditions of batch tests. Two series of batch tests were conducted to study the effects of *BC* and *WC* on the methane oxidation capacity of the biochar modified soils.

Air-dried samples of biochar and soil were mixed thoroughly and water was added to reach the target *WC* as shown in Table 2. 10 g of dry soil mixture (the actual weight depends on the water content) was placed inside each 135 ml gas container. The test procedures followed those recommended by Albanna and Fernandes (2009). In the beginning of the experiment, 10 ml of air inside the container was replaced by 10 ml of mixture of CH_4 and CO_2 (volumetric ratio of 1:1) which corresponds to the initial state of methane oxidation. Thereafter the container was placed inside an environmental chamber under a constant temperature of 25 ºC for 24 hours. Then 10 ml of gas sample was extracted from each container and the volume fraction of CH_4 was measured by gas chromatography. After extracting gas sample, the container was flushed by fresh air for at least an hour. Then 10 ml of mixture of CH_4 and CO_2 was injected to replace 10 ml of air inside the container. As a result, the same initial volume fractions of gases were maintained. The above procedures were repeated and the gas sample was extracted for each subsequent 24 hours. The batch tests lasted for a total of 30 days. The initial volume fraction of CH_4 is assumed as that measured from the gas sample taken from the container two hours after the first gas injection. The methane oxidation rate per unit dry mass per unit of time (μg CH_4 g^{-1} day^{-1}) is calculated as the difference of volume of methane at a given time of incubation and its initial volume.

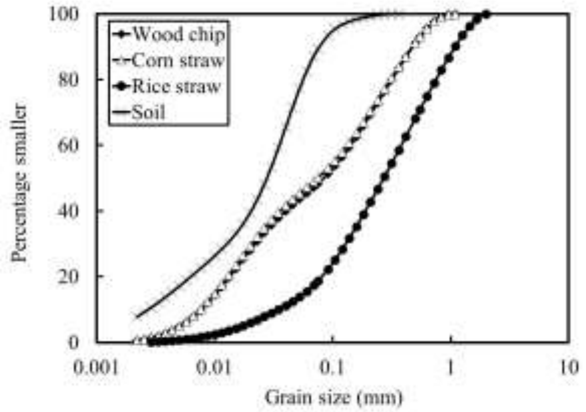

Figure 1. Grain size distribution curves of biochars and tested soil.

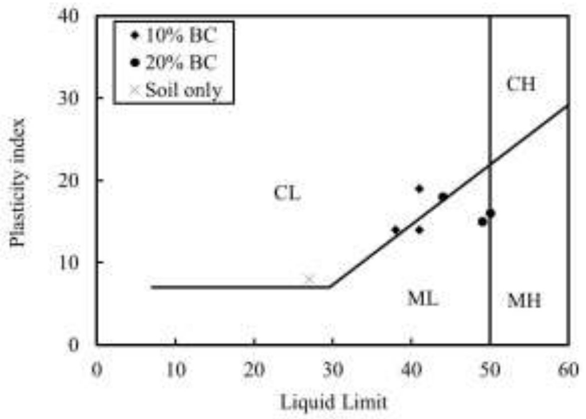

Figure 2. Classification of biochar modified soils.

Table 1. Basic physical and chemical properties of modified soils (20% *BC*) and untreated soil.

Soil Type	G_s	*PC(g/kg)*	*pH*	*OC(%)*
Untreated soil	2.62	0.5	5.8	1.8
W modified soil	2.36	7.0	8.6	14.0
C modified soil	2.47	7.2	9.9	14.2
R modified soil	2.47	6.2	10.4	13.1

Table 2. Test conditions of methane oxidation batch tests.

Test series	*BC* (%)	*WC* (%)
1	10 – 50	20
2	20	10 – 40

3 TEST RESULTS AND DISCUSSION

3.1 *Effect of biochar content*

The test results of three biochar modified soils are very similar. For illustration, the methane oxidation – time relationship of soil modified by wood chip biochar at a *WC* of 20% is shown in Figure 3. The test results of untreated soil and pure biochar are also shown in the figure for comparison. As shown in the figure, biochar alone exhibits negligible methane oxidation throughout the 30-day incubation period. On the other hand, the other five specimens exhibit a similar trend where the methane oxidation rate increases with time and reaches a peak value (MO_p), beyond which it reduces to a negligible value at the end of the 30-day incubation period. It is apparent from the test results that the peak methane oxidation rate is influenced significantly by *BC*. By adding a 20% of biochar, MO_p increases from 60 to 218 μg CH_4 g^{-1} day^{-1}.

Figure 3 also indicates that after reaching MO_p, methane oxidation rate decreases with time. Similar trend was observed in past studies on other soils (Kightley et al. 1995; Hilger et al. 2000; De Visscher and Van Cleemput 2003) and composts (Wilshusen et al. 2004; Mor et al. 2006). The reason for this phenomenon may be due to the exopolymeric substances (EPS), products of methane oxidation activities. It is postulated that the amount of methane oxidising bacteria reduces with the accumulation of EPS and depletion of soil nutrients leading to a lower methane oxidation rate. As the impact of EPS on methane oxidation activity is a very complex process, further study is required.

Figure 4 depicts the effect of *BC* content on MO_p of three biochar modified soils. All three biochars exhibit a similar trend. It can be seen from the test results that there is an optimum *BC* which corresponds to a maximum MO_p. The optimum *BC* is between 20% and 30%. There are many factors that influence the methane oxidation process in soils, for example, soil texture, organic matter content, water content, pH, nutrients, temperature, CH_4 and O_2 concentrations (Wilshusen et al. 2004, Börjesson et al. 2001). Soils with coarser grains and higher organic matter contents exhibit higher oxidation efficiency (Humer and Lechner 2001). However, the oxidation process is also affected by the pH of soil because methanotrophic bacteria are sensitive to the pH. Past studies have shown that all types of methanotropic bacteria can grow in pH values ranging from 5.8 to 7.4 and they cannot grow at pH values below 5 (Whittenbury et al. 1970, Hanson and Hanson 1996). As shown in Figure 1 and Table 1, addition of biochar can increase the amount of coarser grains, phosphorus content and organic matter content of the modified soils, from which the oxidation capacity may be enhanced. On the other hand, the pH values of biochar modified soils are higher than the reported optimal range for the growth of methanotropic bacteria. It is postulated that the strong alkalinity at high *BC* content may reduce the activity of methanotrophic bacteria leading to a reduction in the oxidation rate. As past studies have focused on the effect of acidity, further study is required to understand the effect of alkalinity.

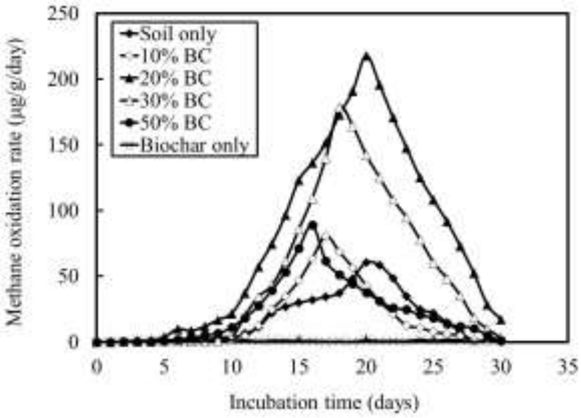

Figure 3. Methane oxidation – time relationship of soil modified by wood chip biochar at a *WC* of 20%.

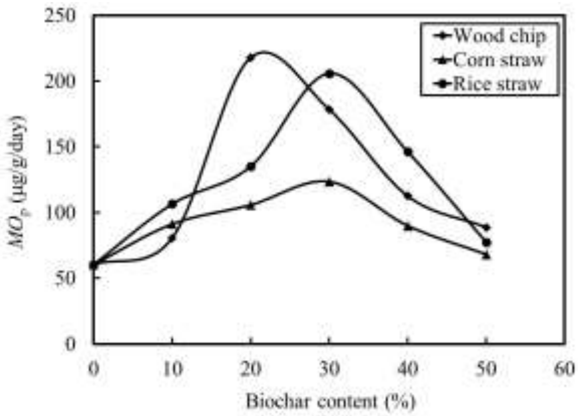

Figure 4. Effect of biochar content (*BC*) on MO_p of three biochar modified soils.

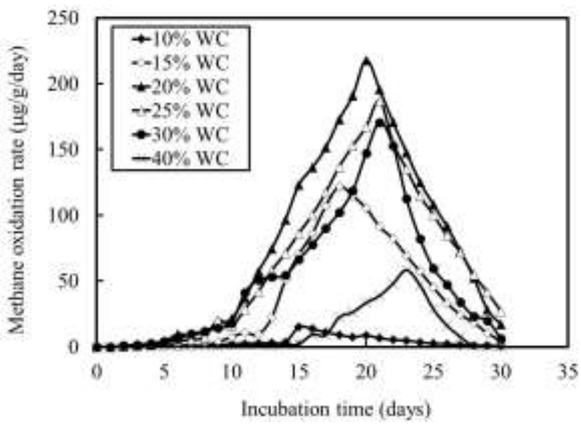

Figure 5. Methane oxidation – time relationship of soil modified by wood chip biochar with a *BC* of 20% .

3 .2 *Effect of water content*

Figure 5 shows the methane oxidation – time relationship of soil modified by wood chip biochar at a *BC* of 20%. All six specimens exhibit the similar trend as depicted in Figure 3, where the methane oxidation rate increases with time and reaches a peak value (MO_p), beyond which it reduces to a negligible value at the end of the 30-day incubation period. It is apparent that MO_p is influenced by the *WC*. The effect of *WC* on MO_p of soils modified by three different biochars is shown in Figure 6. The test results of untreated soil is also shown in the figure for comparison. Negligible methane oxidation is observed at a water content of 10%. As a certain amount of water is required to maintain the activities of methanotrophic bacteria, a low *WC* can inhibit the oxidation process. Beyond 10% *WC*, MO_p increases substantially with increasing *WC* until reaching a maximum MO_p, beyond which MO_p decreases with further increasing *WC*. High *WC* also does not favour the oxidation process because it decreases the flow of O_2 into the soil. For the biochar modified soils tested in this study, the optimum range of *WC* is between 20% and 30%. The results are consistent with those reported in the literature. Past studies have indicated that the optimum range of *WC* is influenced by the soil texture and organic matter content (Park et al. 2002, Christophersen et al. 2000). Coarse-grained soils exhibit a lower optimum *WC* than fine-grained soils. The optimum *WC* also increases with increasing organic matter content, for example, composts can exhibit an optimum *WC* ranging from 45% to 110% (Mor at al. 2006).

WC can be normalised by some basic physical indices of soil. For example, liquidity index is a parameter which scales the *WC* of soil with respect to the *PL* (= 0 at *PL* and = 1 at *LL*). It may be used to characterise the relative amount of pores filled with water in the soil. Figure 7 depicts the relationships between liquidity index and MO_p. Compared to Figure 6, it is apparent that the optimum liquidity indices corresponding to the maximum values of MO_p of the three modified soils lie close to each other, which ranging between -0.6 and -0.3. It should be noted a negative value of liquidity index indicates the soil is dessicated where sufficient amount of pores is available for the gas flow, thus enhancing the oxidation process.

4 CONCLUSIONS

Three different biochars (wood chip, corn straw and rice straw) were used to enhance the methane oxidation capacity of a low plasticity clay. Two series of laboratory batch tests were conducted to study the effects of biochar content (*BC*) and water content (*WC*) on the methane oxidation rate of the modified soils. The following conclusions can be drawn from the test results:

(1) Addition of biochar changes the basic physical and chemical properties of soil, namely it increases the amount of coarser grains, plasticity, pH, organic matter content and phosphorus content of the modified soil.
(2) The peak methane oxidation rate (MO_p) measured in the batch tests is influenced by *BC* and *WC*. There is an optimum *BC*/*WC* which corresponds to the maximum MO_p .
(3) For the three biochars tested in this study, the optimum *WC* ranges between 20% and 30%. It is postulated that liquidity index, a normalised *WC*, may be used to identify the favourable condition for methane oxidation. For the tested biochars, the optimum liquidity index ranges between -0.6 and -0.3.
(4) It should be noted that biochar alone does not exhibit any oxidation capacity. The optimum *BC* ranges between 20% and 30%. It is suggested that the strong alkalinity of high

BC may inhibit the activity of methanotrophic bacteria, thus retarding the oxidation process.

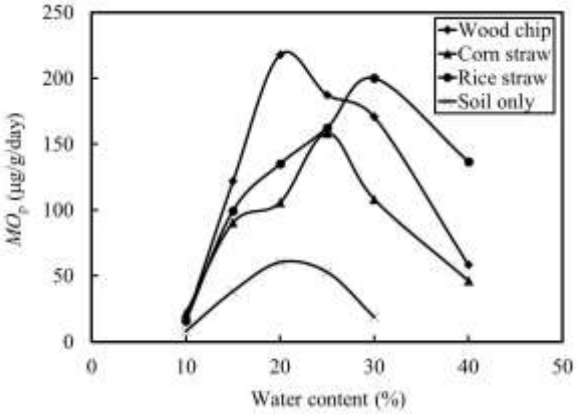

Figure 6. Effect of water content on MO_p of three biochar modified soils.

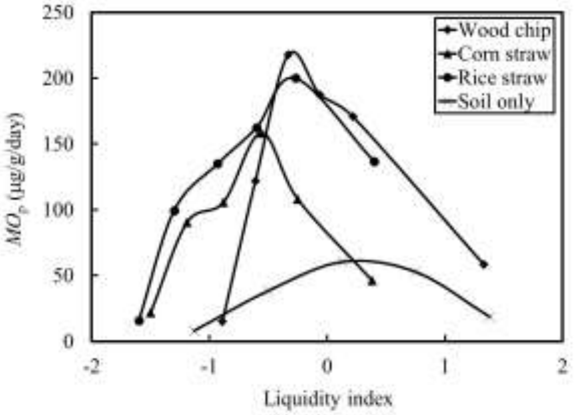

Figure 7. Effect of liquidity index on MO_p of three biochar modified soils.

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6 REFERENCES

Albanna M. and Fernandes L. 2009. Effects of Temperature, moist ure content, and fertilizer addition on biological methane oxid ation in landfill cover soils. Practice Periodical of Hazardous, Toxic, and Radioactive Waste Management 13(3), 187-195.

Bohn S., Brunke P., Gebert J. and Jager J. 2011. Improving the a eration of critical fine-grained landfill top cover material by v egetation to increase the microbial methane oxidation efficienc y. Waste Management 31(5), 854-863.

Börjesson G., Chanton J. and Svensson B.H. 2001. Methane oxida tion in two Swedish landfill covers measured with carbon-13 t o carbon-12 isotope ratios. Journal of Environmental Quality 3 0, 369-376.

Christophersen M., Linderod L., Jensen P.E. and Kjeldsen. P. 200 0. Methane oxidation at low temperatures in soil exposed to l andfill gas. Journal of Environmental Quality 29, 1989-1997.

De Visscher A. and Van Cleemput O. 2003. Induction of enhance d CH_4 oxidation in soils: NH_4^+ inhibition patterns. Soil Biolog y and Biochemistry 35, 907-913.

GB/T 50123-1999 1999. Standard for soil test method. Ministry of Construction, P.R. China. [In Chinese]

Hanson R.S. and Hanson T.E. 1996. Methanotrophic bacteria. Mic robiological Reviews 60, 439-471.

Hilger H.A., Cranford D.F. and Barlaz M.A. 2000. Methane oxida tion and microbial exopolymer production in landfill cover soi l. Soil Biology and Biochemistry 32(4), 457-467.

Huber-Humer M., Roder S. and Lechner P. 2009. Approaches to assess biocover performance on landfills. Waste Management 29, 2092-2104.

Huber-Humer M., Tintner J., Böhm K. and Lechner P. 2011. Scru tinizing compost properties and their impact on methane oxida tion efficiency. Waste Management 31(5), 871-883.

Humer M. and Lechner P. 2001. Design of a landfill cover layer to enhance methane oxidation results of a two year field inve stigation. In: Proceedings of the 8th International Waste Manag ement and Landfill Symposium 2, 541-550.

Humer M. and Lechner P. 1999 . Alternative approach to the elimination of greenhouse gases from old landfills. Waste Management and Research 17, 443-452.

Kightley D., Nedwell D.B. and Cooper M. 1995. Capacity for me thane oxidation in landfill cover soils measured in laboratory-s cale soil microcosms. Applied and Environmental Microbiolog y, 61, 592-610.

LY/T 1232-1999 1999. Determination of total phosphorus in forest soil. Forestry Standards, P.R. China. [In Chinese]

LY/T 1239-1999 1999. Determination of pH value in forest soil. Forestry Standards, P.R. China. [In Chinese]

Mor S., De Visscher A., Ravindra K., Dahiya R.P., Chandra A. a nd Van Cleemput O. 2006. Induction of enhanced methane ox idation in compost: Temperature and moisture response. Waste Management 26(4), 381-388.

Park S, Brown K.W. and Thomas J.C. 2002. The effect of variou s environmental and design parameters on methane oxidation i n a model biofilter. Waste Management and Research 20, 434 -444.

Reddy K.K., Yargicoglu E.N., Yue D. and Yaghoubi P. 2014. Enh ance microbial methane oxidation in landfill cover soil amend ed with biochar. Journal of Geotechnical and Geoenvironmenta l Engineering 140(9), 04014047.

Sadasivam B.Y. and Reddy K.R. 2015. Adsorption and transport o f methane in biochars derived from waste wood. Waste Mana gement 43, 218-229.

Stern J.C., Chanton J., Abichou T., Powelson D., Yuan L., Escoriz a S. and Bogner J. 2007. Use of biologically active cover to reduce landfill methane emissions and enhance methane oxidat ion. Waste Management 27, 1248-1258.

Whittenbury R, Phillips K.C. and Wilkinson J.F. 1970. Enrichment, isolation and some properties of methane utilizing bacteria. Jo urnal of General Microbiology 61, 205-218.

Wilshusen J.H., Hettiaratchi J.P.A. and Stein V.B. 2004. Long-term behaviour of passively aerated compost methanotrophic biofilt er columns. Waste Management 24, 643-653.

Yargicoglu E.N., Sadasivam B.Y., Reddy K.R. and Spokas K. 201 5. Physical and chemical characterization of waste wood deriv ed biochars. Waste Management 36, 256-268.