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# Effects of mixed ratio, moisture content, nutrient addition and cover thickness on methane oxidation in landfill bio-cover

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## ABSTRACT

*Landfill bio-cover plays a significant role in methane reducing. It inhabits methane-oxidizing bacteria which reduce methane emissions to the atmosphere and supply carbon dioxide for photosynthesis. Full factorial $3^4$ experimental design using simulation columns was conducted to investigate statistically the effects of mixed ratio, moisture content, nutrient addition and cover thickness on the $CH_4$ oxidation efficiency through a landfill bio-cover sewage sludge modified by coal ash. The results from all experiment sets showed that all factors definitely influence methane oxidation ability. The $CH_4$ oxidation efficiencies were different under different experimental and operating conditions. Synthesize the maximum $CH_4$ oxidation efficiency and $V(CH_4)$, the optimal conditions was 1:1 mixed ratio of coal ash and sewage sludge, added 0.05 mL/g NMS nutrients to 400 mm thickness in landfill bio-cover which made moisture content of material reached 40%. The maximum $CH_4$ oxidation efficiency and $V(CH_4)$ were 88.6% and 0.75 mmol/(kg•d) under the optimal conditions. Additionally, the decrease in the $CH_4$ concentration and the increase in $CO_2$ concentration in the headspace gas were clear indication that there was $CH_4$ oxidation process.*

**Key words:** landfill bio-cover, methane oxidation, mixed ratio, moisture content, NMS nutrient, cover thickness.

## INTRODUCTION

Solid waste is delivered to landfills, and then the waste is generally spread out, compacted, and covered with a fresh layer of daily cover soil. The amount of biodegradable waste deposited in landfills decomposes by microbial action to form mainly methane ($CH_4$ 50-65%), carbon dioxide ($CO_2$ 35-50%), and water [1,2].It is common knowledge that $CO_2$ is green gas which has a bad influence on global climate. But contrary to methane, $CO_2$ formed inside landfills and released into the atmosphere produces a negligible effect on the environment due to the global warming potential(GWP) of $CH_4$ is 23 times that of an equal mass of $CO_2$ over a period of 100 years and atmospheric $CH_4$ has more than doubled in concentrations over the last 150 years. It is estimated that $CH_4$ will become No.1 green gas which get the heel of $CO_2$ in 2030[3,4]. Landfill $CH_4$ emissions have been cited as one of the anthropogenic gas releases that can and should be controlled to reduce global climate change. Nevertheless methane is the most valuable component of landfill gas; it can be extracted and utilized as a form of energy. For example it used to generate electricity or fuel in large-scale landfill. Some small-scale landfill may choose the simplest disposal option to combustion of landfill gas. Landfill gas extraction systems and utilize $CH_4$ are an ideal way to reduce landfill gas emission to atmosphere, but are mainly feasible for large landfill sites and the cost involved is high. In order to know how many the uncontrolled landfill gas emissions, we study a large landfill in Guangzhou. It treatments about 8000t rubbish every day and collect landfill gas for generate electricity. Our study showed that the $CH_4$ emission rate is 4.93 $mol/m^2 \cdot h$ in landfill cover soil and the whole emission amount of methane was $0.20\times10^7$ $m^3/a$, which accounted for 11.7 percent of total methane collected. The uncontrolled $CH_4$ emissions which escape into the atmosphere may significantly contribute to the effects of global warming.

When installation of a gas extraction system is inefficient at large landfill and the methane production is too low for energy recovery or flaring at small or older landfill, another effective method to reduce $CH_4$ emissions from landfill is the use of biological cover for $CH_4$ oxidation [5].A great quantity of literature has demonstrated a high oxidation capacity in diverse bio-covers due to it is rich in microorganism [6-8]. Such as composts, sewage sludge and aged refuse all have the capable of oxidizing $CH_4$[9-12].Before this study, the effect of methane oxidation of 3 bio-covers(sewage sludge modified by coal ash、aged refuse and soil) was studied through simulation columns experiment. The results showed the methane oxidation capacity of sewage sludge is better than aged refuse and soil. The identification of an acceptable process for the modification of sewage sludge may provide a solution to the shortage of landfill cover material, at the same time, it is also an environmentally sustainable sludge treatment and disposal methods for the increasing volume of sludge being produced by an ever-larger number of sewage treatment plants. Oxidation rate of $CH_4$ depends on physical properties and environmental conditions, such as moisture content, organic content, temperature, cover material characteristics and composition, pH, cover thickness and oxygen concentrations [13-15]. This experimental choose sewage sludge modified by coal ash as landfill bio-cover. The maximum efficiency of $CH_4$ oxidation and $V(CH_4)$ can be found under the effects of mixed ratio, moisture content, nutrient addition, and cover thickness. The development trend and impact of each parameter in landfill bio-cover also examined.

## MATERIALS AND METHODS

### Experimental materials

Sewage sludge from the Liede sewerage treatment plant in Guangzhou, and coal ash provided by the Huangpu power plant in Guangzhou. The digested dehydrated sludge had the physical properties; pH 7.05, 73.32% of water content, 24.72% of organic content, and electric conductivity 1024μs/cm.

**Experimental design**

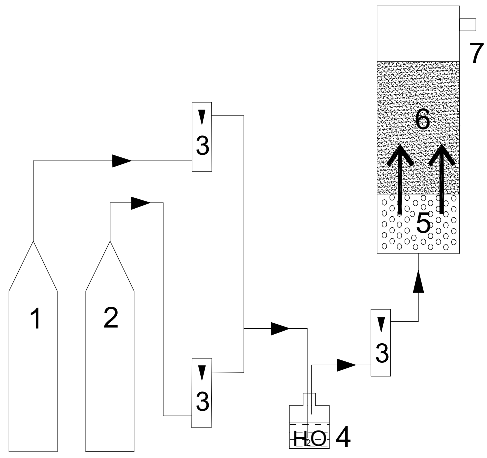
The capacity of the cover layer to oxidize methane depends on both the physical and the chemical properties of the bio-cover material. The experimental runs were designed as a four-factor three-level factorial (Table 1).All four parameters chosen were tested at three levels, low middle and high. The engineering requirements of osmotic coefficient and compressive strength for cover material of landfill was less than $10^{-4}$cm/s and stronger than 50 kPa. The osmotic coefficient and compressive strength of coal ash and sewage sludge in various mixing ratios were determined, the resulted showed that when the mixed ratio of coal ash and sewage sludge are 1:1～1.5:1,the engineering requirements of osmotic coefficient and compressive strength for cover material of landfill site was satisfied. So the mixed ratio of coal ash and sewage sludge was studied at the levels of 1:1, 1.25:1 and 1.50:1. One of the important factors influencing methane oxidation was the water content of cover material, so the water content was chosen as second parameters in this study and three levels were selected to verify the range reported in the literature [16-17].The levels were 20%, 30% and 40%. A number of researchers have investigated the methanotrophic bacteria which presented in the landfill cover materials can help convert methane to carbon dioxide [18]. The NMS nutrient solution will accelerate the growth of these methanotrophic bacteria, so NMS nutrient was chosen as the third parameter in this experiment. A liter NMS nutrient solution includes 0.85g $NaNO_3$, 0.53g $KH_2PO_4$, 2.17g$Na_2HPO_4$, 0.037g $MgSO_4 \cdot 7H_2O$, 0.17g $K_2SO_4$,0.007g $CaCl_2 \cdot 2H_2O$, 0.5mL 1mol/L $H_2SO_4$, 11.2 mg $FeSO_4 \cdot 7H_2O$, 2.5 mg $CuSO_4 \cdot 5H_2O$ and 2mL microelement solution. A liter microelement solution includes 0.204g $ZnSO_4 \cdot 7H_2O$, 0.223g $MnSO_4 \cdot 4H_2O$, 0.062g $H_3BO_3$, 0.048g $Na_2MoO_4 \cdot 2H_2O$, 0.048g $CoCl_2 \cdot 6H_2O$ and 0.083g KI. The concentration of nutrients was also studied at three levels: no nutrient added, 0.5mL of nutrient solution/kg of bio-cover and 1.0mL/kg.For the last factor scrutinized, the bio-cover layer thicknesses were: 200mm thickness, 300mm and 400mm respectively. The experiment resulted in examining nine combinations of these four factors across the three levels of each.

**Table 1.$3^4$orthogonal table**

| Factor | Mixed ratio | Moisture content (%) | Nutrient addition(mL/g) | Cover thickness(mm) |
|---|---|---|---|---|
| 1 | 1:1 | 20 | 0 | 200 |
| 2 | 1.25:1 | 30 | 0.05 | 300 |
| 3 | 1.50:1 | 40 | 0.10 | 400 |

**Experiment equipment**

The development of methane oxidation potential of bio-cover was investigated in laboratory-scale PVC columns. The experiment setup was showed in the figure 1.The PVC column was 1000 mm in length and 150 mm in diameter. Each PVC column had two layers: a lower layer which consisted of 200 mm of crushed gravel (20 mm in diameter) as a gas dispersion layer, in turn, an upper layer which consisted of bio-cover. The perforated plate (10mm in aperture) and geotextile placed over the crushed gravel layer which prevents bio-cover to jam gas dispersion.




*1.$CH_4$ 2.$CO_2$ 3. rotor flow meter 4. humidifier 5. crushed gravel layer 6.bio-cover 7.outlet*

**Fig.1 Apparatus for the experiments**

**Table 2. The chemical and physical properties of each material**

| Experimental number | moisture content (%) | organic content (%) | pH | electrode potential (mV) | Electric conductivity (μs/cm) | Loading density (g/mL) |
|---|---|---|---|---|---|---|
| 1 | 20.07 | 10.99 | 7.82 | -52 | 1124 | 1.24 |
| 2 | 29.55 | 14.85 | 8.31 | -83 | 1003 | 1.15 |
| 3 | 41.66 | 13.88 | 7.85 | -66 | 995 | 1.21 |
| 4 | 21.23 | 10.82 | 7.77 | -55 | 1062 | 1.01 |
| 5 | 30.75 | 12.88 | 8.19 | -80 | 1022 | 0.99 |
| 6 | 41.15 | 13.61 | 8.23 | -79 | 944 | 1.04 |
| 7 | 19.40 | 11.92 | 7.95 | -64 | 1088 | 1.05 |
| 8 | 30.64 | 13.92 | 8.30 | -84 | 1155 | 1.02 |
| 9 | 39.53 | 10.51 | 8.67 | -98 | 1083 | 1.03 |

## Experimental methods

Sewage sludge modified by coal ash is packed in each column according to factorial $3^4$.The $CH_4$ and $CO_2$ are supplied from two gas cylinder containing 99.9% pure gas and 99.5% pure gas. They were mixed in a ratio of 1:1 using rotor flow meter. After increasing their humidity by a humidifier, the gas mixture is injected in each column through the inlet port at a rate of 20mL/min for 60 min, and then the column inlet was tightly closed and never opened again through the entire experimental period. The concentration of headspace gas was monitored over time by taking samples from the outlet, using a gas tight 1.0 $cm^3$ syringe. The $CH_4$ and $CO_2$ concentration was direct determined using GC-6890N gas chromatograph with hydrogen flame ionization detector. The gasification chamber temperature is 100℃ and the detector temperature is 150℃.The oven temperature is initially kept at 70℃ and gradually increased to 80℃ at the speed of 2.5 ℃/min. The runtime is 5min. Standard gas mixtures having known concentration of $CH_4$ and $CO_2$ are used for standard curve.

Sewage sludge modified by coal ash initial moisture contents was tested, and determined at 105℃ for constant weight by electrothermal blowing dry box (101A-2E, from Shanghai AnTing). The moisture content of each bio-cover sample was adjusted to the level of the experimental design. Organic content was tested at 600℃ for constant weight by muffle (SX3-3-10,Hangzhou ZhuoChi). The pH and electrode potential of each bio-cover were test by pH meter (Phs-25,Shanghai YingGe). The electric conductivity was also determined by conductivity meter(DDB-303A,Shanghai LeiCi). The chemical and physical properties of each material are showed in the figure 2.

## RESULTS AND DISCUSSION

### The result of orthogonal test

Table 3 shows the maximum $CH_4$ oxidation efficiency and V($CH_4$) of landfill bio-cover under different environmental parameters. This would indicate that there was different in methane oxidation from the materials as a result of varying chemical and physical properties. The maximum $CH_4$ oxidation efficiency was 81.88% for experimental runs No.3, where mixed ratio was 1:1, 0.10 mL/g nutrients were added to 400 mm thickness landfill bio-cover that contained 40% moisture. However the max V($CH_4$) was 1.02 mmol/(kg•d) for experimental runs No.9, where mixed ratio was 1.50:1, 0.05 mL/g nutrients were added to 200 mm thickness landfill bio-cover that contained 40% moisture. All factors definitely influence methane oxidation ability but the degree of influence is the issue. By comparing R of maximum $CH_4$ oxidation efficiency, the degree of influence is mixed ratio>nutrient addition>cover thickness>moisture content. The optimal conditions were $A_1C_2D_3B_3$ where mixed ratio was 1:1, 0.05 mL/g nutrients were added to 400 mm thickness landfill bio-cover that contained 40% moisture. However, by comparing R of V($CH_4$), the degree of influence is cover thickness>mixed ratio>nutrient addition>moisture content. The optimal conditions were $D_1A_1C_2B_3$ where mixed ratio was 1:1, 0.05 mL/g nutrients were added to 200 mm thickness landfill bio-cover that contained 40% moisture. Because the importance of each target was different, each parameter had various effects on each target, accordingly optimal condition was different.

**Table 3. $L_9(3^4)$ orthogonal experimental runs and the resulting amylase measurements**

| Run no. | ixed atio | Moisture content (%) | Nutrient addition (mL/g) | Cover thickness (mm) | Maximum $CH_4$ oxidation efficiency (%)[a] | V($CH_4$)[b] mmol/(kg•d) |
|---|---|---|---|---|---|---|
| 1 | 1:1 | 20 | 0 | 200 | 68.1 | 0.90 |
| 2 | 1:1 | 30 | 0.05 | 300 | 77.3 | 0.79 |
| 3 | 1:1 | 40 | 0.10 | 400 | 81.9 | 0.58 |
| 4 | 1.25:1 | 20 | 0.05 | 400 | 56.4 | 0.49 |

| | | | | | | |
|---|---|---|---|---|---|---|
| 5 | 1.25:1 | 30 | 0.10 | 200 | 37.6 | 0.66 |
| 6 | 1.25:1 | 40 | 0 | 300 | 40.2 | 0.39 |
| 7 | 1.50:1 | 20 | 0.10 | 300 | 49.4 | 0.54 |
| 8 | 1.50:1 | 30 | 0 | 400 | 56.2 | 0.45 |
| 9 | 1.50:1 | 40 | 0.05 | 200 | 63.0 | 1.02 |

| Maximum $CH_4$ oxidation efficiency | | | | | $V(CH_4)$ | | | | |
|---|---|---|---|---|---|---|---|---|---|
| $K_1$ | 227.3 | 173.9 | 164.5 | 168.7 | $K_1$ | 2.27 | 1.93 | 1.74 | 2.58 |
| $K_2$ | 134.2 | 171.1 | 196.7 | 166.9 | $K_2$ | 1.54 | 1.90 | 2.30 | 1.72 |
| $K_3$ | 168.6 | 185.1 | 168.9 | 194.5 | $K_3$ | 2.01 | 1.99 | 1.78 | 1.52 |
| $k_1$ | 75.8 | 58.0 | 54.8 | 56.2 | $k_1$ | 0.76 | 0.64 | 0.58 | 0.86 |
| $k_2$ | 44.7 | 57.0 | 65.6 | 55.6 | $k_2$ | 0.51 | 0.63 | 0.77 | 0.57 |
| $k_3$ | 56.2 | 61.7 | 56.3 | 64.8 | $k_3$ | 0.67 | 0.66 | 0.59 | 0.51 |
| R | 31.1 | 4.7 | 10.8 | 9.2 | R | 0.25 | 0.03 | 0.19 | 0.35 |

[a]*Maximum $CH_4$ oxidation efficiency=* $\frac{(C_{CH_4})_{t,0}-(C_{CH_4})_{t,i}}{(C_{CH_4})_{t,0}}$ . $(C_{CH_4})_{t,0}$ *is the $CH_4$ concentration(%v/v) at the beginning of the experiment,* $(C_{CH_4})_{t,i}$ *is the $CH_4$ concentration (%v/v) at the end of the experiment.*

[b]$V_{CH4}$= $\frac{n_{CH_4}}{d\square m}$ . $n_{CH_4}$ *is the amount of substance of $CH_4$ consumption, d is the days of experiment, m is bio-cover weight.*

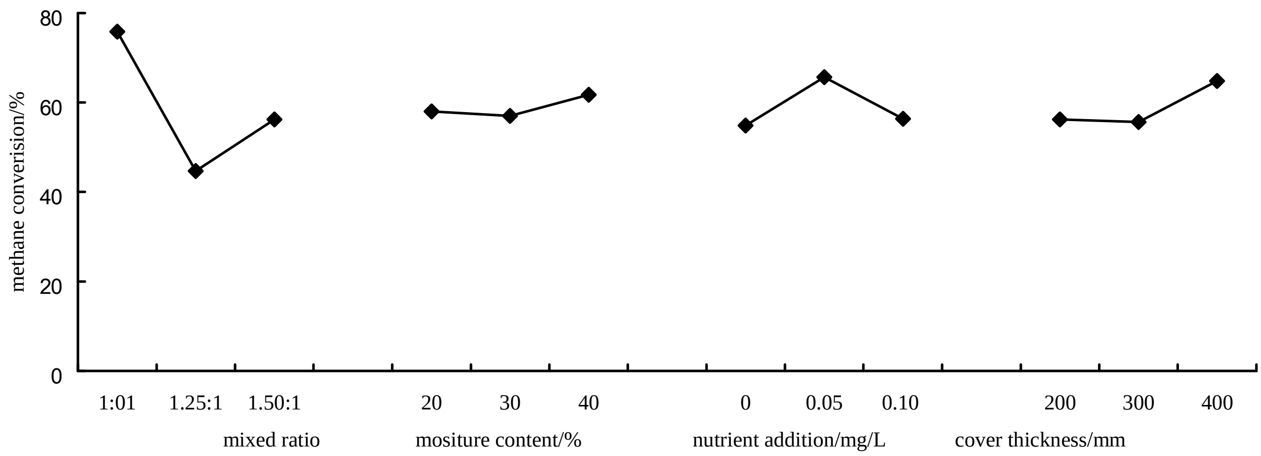



**Figure1. The effect of each factor on $CH_4$ oxidation efficiency**

**The effect of each factor on $CH_4$ oxidation ability**

As showed in Table 3, R of mixed ratio is 31.1 which indicated that the mixed ratio of coal ash and sewage sludge was a critical physical parameter affecting the $CH_4$ oxidation ability. The best mixed ratio of coal ash and sewage sludge is 1:1(Fig.1 and 2). There are a number of possible reasons for these results. On the one hand, the mixed ratio determine grain diameter which influence the gas vertical speed. It was studied that using the method of sieving when the mixed ratio of coal ash and sewage sludge is 1:1, grain diameter which greater than 0.90mm was 70.1%. The mixed ratio is 1.50:1, grain diameter which greater than 0.90mm was 72.0%.But grain diameter which greater than 0.90mm was only 52.1% when the mixed ratio is 1.25:1.The larger grain diameter of material, the faster vertical speed of gas, then it may be enhance methane oxidation efficiency. On the other hand, it was well known that sewage sludge is rich in microorganism but coal ash is only inert substance, the more sewage sludge contained in bio-cover, the more microorganisms in material. It was clear that increasing microbial activity can improve methane oxidation efficiency.

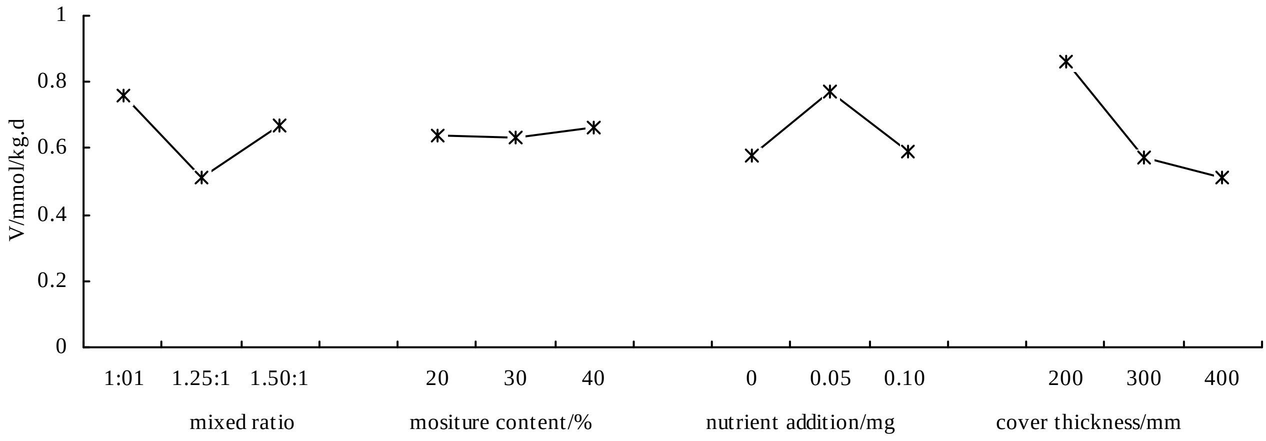



**Figure2. The effect of each factor on V($CH_4$)**

Results from the R of moisture content (Table 3) shows that a minor effect of bio-cover at various moisture contents and the wetter the material got the higher methane oxidation (Fig.1 and 2).It was hypothesized that when the moisture content was low, which led to osmotic pressure that caused the water from the bacterial cells to flow out and eventually the death of the microbial population [5]. But when the moisture content was high, compressive strength of material was low. The engineering requirement of compressive strength for cover material of landfill was stronger than 50 kPa, so the moisture content should be under 40%. And higher moisture affects the movement of gas through the landfill and the microbial growth. So the best moisture content is 40% in this study.

After reviewing the effect of nutrient on $CH_4$ oxidation ability (Fig.1 and 2), it was clear that adding nutrients positively affected the $CH_4$ oxidation ability, but it was not the more the better. The $CH_4$ oxidation ability was largest when 0.05 mL/g nutrients were added in landfill; however 0.10 mL/g nutrients were added in landfill, the $CH_4$ oxidation ability dropped. Considering the largest $CH_4$ oxidation ability and the lowest cost, the best nutrient addition was 0.05 mL/g in this study.

Fig.1 and 2 also illustrate the $CH_4$ oxidation ability for the different layer thickness. It was indicated that the effect of cover thickness on the maximum $CH_4$ oxidation efficiency and V($CH_4$) followed the different trend. The 400mm layer thickness had the higher maximum oxidation efficiency than 300mm and 200mm layer thickness, but it had crosscurrent on V($CH_4$). Zhao[19] reported that the landfill had a larger volume of bio-cover, larger population of methanotrophic bacteria and thus greater bacterial activities, resulting in higher $CH_4$ oxidation efficiency values. However the higher thickness must occupy more space and cost of landfill. The cover thickness should meet economic benefit and engineering requirements. This study suggests selecting 200mm as daily cover and 400mm as intermediate cover.

**Methane oxidation efficiency in the landfill bio-cover under optimal conditions**

From the results of $L_9(3^4)$ orthogonal experimental, the optimal conditions was 1:1 mixed ratio added 0.05 mL/g nutrients to 400 mm thickness in landfill bio-cover which made moisture reached 40%. Figure 3 depicts the changes in $CH_4$, $CO_2$ and $O_2$ concentrations with times under optimal conditions. Results in Fig.3 illustrate that the $CH_4$ concentration in the headspace gas dropped from around 43.9% to 5.0% in 25d and the $CO_2$ concentration increased from 26.6% to 31.4%.The $CH_4$ oxidation efficiency was up to 88.6%, which higher than $L_9(3^4)$ orthogonal experimental results. This indicates that the conditions from $L_9(3^4)$ orthogonal experimental were optimal for methane oxidation. The decrease in the $CH_4$ concentration and the increase in $CO_2$ concentration in the headspace gas were clear indication that there was $CH_4$ oxidation process. Hilger and Humer[6] reported that methanotrophs consum $CH_4$ and oxidize it to $CO_2$ and water for energy yield.

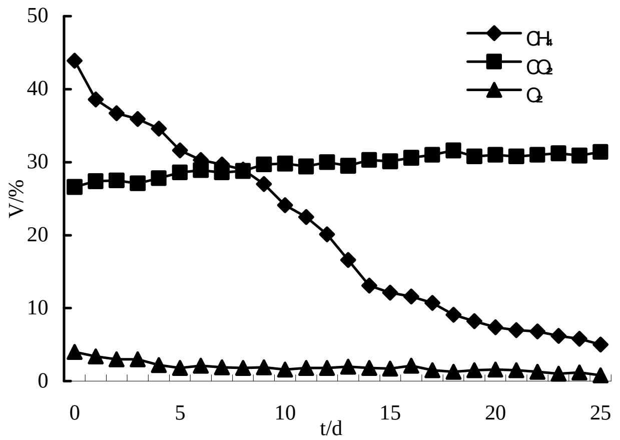



**Fig.3 Changes in $CH_4$(%v/v),$CO_2$(%v/v) and $O_2$(%v/v) concentrations with times under optimal conditions.**

## CONCLUSION

The amount of methane released at the top of the waste fill can be reduced on its way through bio-cover sewage sludge modified by coal ash. In this study, the $CH_4$ oxidation efficiency was different under different physical and chemical of material and environmental factors. The mixed ratio of coal ash and sewage sludge, moisture content, NMS nutrient addition and cover thickness of material definitely influence methane oxidation ability. The mixed ratio, NMS nutrient addition and cover thickness play a significant role in methane oxidation; nevertheless moisture content is a minor physical parameter affecting the methane oxidation ability. Considering the methane oxidation ability, project requirements and economic benefits of waste landfill, the optimal conditions was 1:1 mixed ratio of coal ash and sewage sludge, added 0.05 mL/g NMS nutrients to 400 mm thickness in landfill bio-cover which made moisture content of material reached 40%. The maximum $CH_4$ oxidation efficiency and V($CH_4$) were 88.6% and

0.75 mmol/(kg•d) under this optimal conditions. The results confirmed the observations from the simulation experimental program indicating that bio-cover should consider physical and chemical of materials even environmental factors through improved landfill cover design in order to enhanced methane oxidation ability to realize the maximum economic benefit.

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