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Mechanism of H_2S removal during landfill stabilization in waste biocover soil, an alterative landfill cover

Ruo He[a,*], Fang-Fang Xia[a], Yun Bai[a], Jing Wang[a,b], Dong-Sheng Shen[c]

[a] Department of Environmental Engineering, Zhejiang University, Hangzhou 310058, China
[b] Haiyuan Environmental Science & Technology Co., Ltd., Hangzhou 310052, China
[c] College of Environmental Science and Engineering, Zhejiang Gongshang University, Hangzhou 310012, China

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ABSTRACT

Hydrogen sulfide (H_2S) is one of the primary contributors to odors at landfills. The mechanism of waste biocover soil (WBS) for H_2S removal was investigated in simulated landfill systems with the contrast experiment of a landfill cover soil (LCS). The H_2S removal efficiency was higher than 90% regardless of the WBS or LCS covers. The input of landfill gas (LFG) could stimulate the growth of aerobic heterotrophic bacteria, actinomycete, sulfate-reducing bacteria (SRB) and sulfur-oxidizing bacteria (SOB) in the WBS cover, while that caused a decrease of 1–2 orders of magnitude in the populations of actinomycete and fungi in the bottom layer of the LCS cover. As H_2S inputted, the sulfide content in the WBS cover increased and reached the maximum on day 30. In the LCS cover, the highest soil sulfide content was exhibited in the bottom layer during the whole experiment. After exposure to LFG, the lower pH value and higher sulfate content were observed in the top layer of the WBS cover, while there was not a significant difference in different layers of the LCS cover. The results indicated a more rapid biotransformation between sulfide and sulfate occurred in the WBS cover compared to the LCS.

1. Introduction

Landfilling is the main disposal method of municipal solid waste (MSW), accounting for more than 80% of the total amount of treated waste in China [1]. Odors at landfills originate principally from the gaseous compound emissions that are formed during the biological and chemical processes of waste decomposition such as hydrogen sulfide (H_2S), methyl mercaptan and methyl sulfide, and are one of the primary complaints from residents living near landfills. Over 100 compounds have been identified as contributors to landfill odors [2]. H_2S has been identified as a major contributor to odors at landfills and is at a typical concentration of below 1% in landfill gas (LFG) [3,4]. At landfill sites that receive waste with high levels of sulfur (e.g. construction and demolition (C&D) debris), H_2S concentration can reach 50,000–100,000 ppm (5–10%) [5]. H_2S not only makes people feel disgusted, but also does harm to people and even leads to immediate fatality at the levels of 100–200 ppm [6–8].

A range of technologies have been developed to reduce H_2S emission, including adsorption of activated carbon, absorption of clean water scrubbers, photocatalytic oxidation, ozone oxidation, biofilters and activated sludge [9,10]. H_2S emission from landfills belongs to non-point source pollution. Due to the large area of landfills (usually landfill areas are above tens of acres) [11], the above technologies are difficult to apply for mitigating H_2S emission from landfills. In addition, the physical and chemical methods for H_2S removal are usually uneconomical because of the large flow rate of LFG and low concentration level of H_2S from landfills.

Landfill cover soil is the environmental interface between the deposited waste and the atmosphere and acts as a biofilter for LFG while LFG is escaping to the atmosphere. The effective use of cover materials can help control CH_4 emission from landfills [12]. Recent studies also demonstrate that effective use of cover materials at landfills, especially at C&D debris landfills, may provide a low-cost and effective technique for mitigating H_2S emission from landfills [5,13,14]. For example, Plaza and colleagues [5] demonstrated that the sandy soil amended with lime and the fine concrete had H_2S removal efficiencies greater than 99%, while the clayey and sandy soils, respectively, have average removal efficiencies of 65% and 30%. Based on the laboratory and field experiment, Xu et al. [14] reported that no H_2S emission was detected from cover materials consisting of selected waste products (compost and yard trash) and soils amended with quicklime and calcium carbonate at C&D debris landfills. The performance of each cover material for reducing H_2S is dependent on its physical and chemical characteristics [5,13,14].

Biocover soils such as compost, waste biocover soil (WBS), sewage sludge and garden waste are porous, coarse, and rich in

* Corresponding author. Tel.: +86 571 88982221; fax: +86 571 88982221.
E-mail address: heruo@zju.edu.cn (R. He).

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organic matter and have been reported to have high CH_4 oxidation capacity [12,15,16]. Recently, He and colleagues [17] show that WBS had the highest adsorption capacity of H_2S than landfill cover soil, mulberry soil and sand soil. However, few studies have been conducted to investigate the performance of biocover soil for attenuating H_2S during landfill stabilization. In this study, compared with a landfill cover soil (LCS) collected from Hangzhou Tianziling landfill cell, the capacity of waste biocover soil (WBS) for attenuating H_2S during landfill stabilization was evaluated in simulated landfill systems. The development of microbial populations and sulfur conversion was estimated in the two cover soils during landfill stabilization.

2. Materials and methods

2.1. Soil characteristics

Two kinds of soil were used in the experiment: WBS and LCS. The WBS was collected from an organic waste landfill bioreactor (2 m^3) with leachate recycle in a village located in Xindeng town, Zhejiang Province [18]. The LCS was taken from the top 30 cm of cover soil in Hangzhou Tianziling landfill cell, where MSW had been deposited for ~16 years. After removing large particles, such as stone, plastic, cellulose textile, both the two remaining soils were dried in a dim, well-ventilated room (air-dried) and then sieved through a 4-mm mesh for the experimental material. The physico-chemical properties of the two soils are shown in Table 1.

2.2. MSW

MSW was collected from Kaixuan waste transfer station in Hangzhou city, Zhejiang Province. Before loaded into the simulated landfill reactors, the MSW was shredded into 2–5 cm fragments. The composition of the MSW was as follows (by wet weight): kitchen waste, 60.0%; paper, 9.0%; plastic and rubber, 6.9%; wood, 0.5%; glass and chinaware, 0.2%, metal, 0.2%; other, 23.2%. The MSW contained: total nitrogen, 3.0 g kg dry weight (d.w.)$^{-1}$; total organic carbon, 104.0 g kg d.w.$^{-1}$. The moisture of the MSW was 60.9%.

2.3. Experimental set-up

Four experimental set-ups were used in this study, which consisted of two parts: simulated landfill reactor and soil cover system (Fig. 1). The simulated landfill reactor was constructed using a plastic cylinder, which had an inner diameter of 55 cm and a height of 80 cm. A polyethylene male adapter (~1 cm) was installed at the lid and bottom of each landfill reactor for gas outlet and leachate drainage, respectively. The soil cover system was made up of polyvinyl chloride (PVC) column, which had an inner diameter of 20 cm and a height of 40 cm. A polyethylene male adapter (~1 cm) was installed at the bottom of the cover soil column as a gas inlet. Three sampling ports (~4 cm) were set on one side of the column. The distances of the top, middle and bottom sampling ports, respectively, away from the cover of the column were 10 cm, 20 cm and 30 cm. A nitrogen inlet (~2 cm) was set at the distance of 5 cm away from the cover of the column.

Prior to being filled with MSW and soils, a gas leakage test of the experimental set-up was verified. Approximately 180 kg MSW was filled into each landfill reactor and a specific height of 80 cm and a density of ~0.95 t m^{-3} were attained. Approximately 11.5 kg air-dried WBS and LCS was placed into the experimental soil column system. Before added to the soil column, the water content of the WBS was adjusted to 45% (w/w), at which the WBS was reported to have the highest CH_4 oxidation rate and adsorption capacity of H_2S [17,18]. Because of the low water holding capacity (the saturated

Table 1
Physico-chemical properties of soils used in this study.

Soil	Granular composition (%)				pH	Organic matter (%)	Total nitrogen (g kg^{-1})	Al (g kg^{-1})	Ca (g kg^{-1})	Fe (g kg^{-1})	Cu (mg kg^{-1})	Zn (mg kg^{-1})
	2–4 mm	0.02–2 mm	0.002–0.02 mm	<0.002 mm								
WBS	61.2	33.3	4.4	1.2	7.91 ± 0.03[a]	3.1 ± 0.1	1.3 ± 0.0	17.1 ± 0.7	9.0 ± 0.2	10.4 ± 0.3	40.8 ± 0.0	1052.5 ± 122.8
LCS	35.0	14.1	28.1	22.8	7.39 ± 0.05	2.0 ± 0.0	0.3 ± 0.0	15.1 ± 0.5	3.1 ± 0.1	9.8 ± 0.5	12.7 ± 1.1	37.8 ± 12.3

[a] Mean ± standard deviation (n = 3).

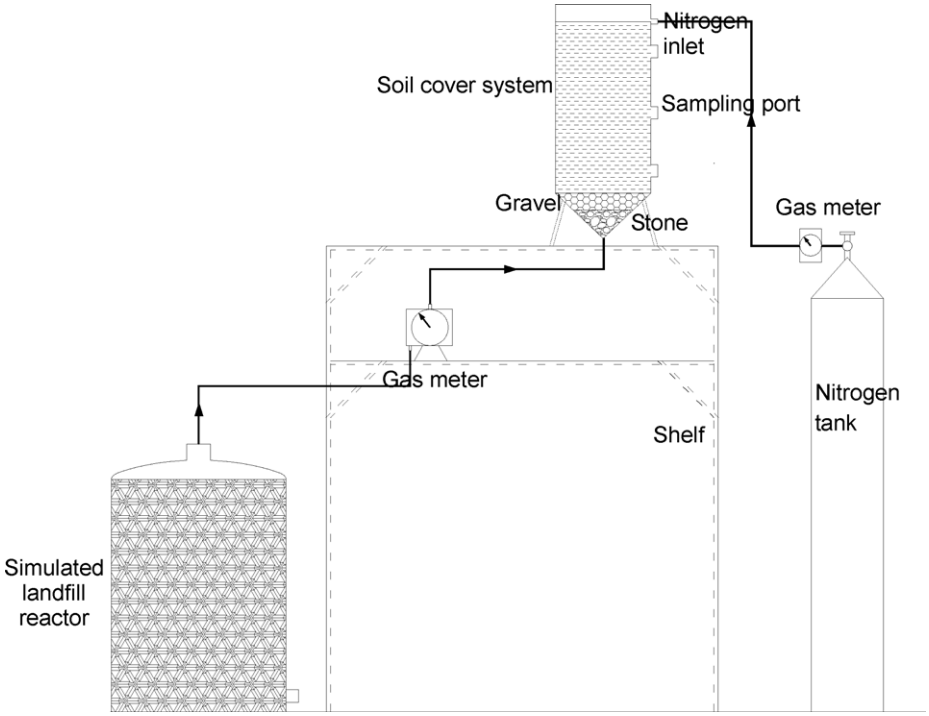

Fig. 1. The experimental set-up used in this study.

water holding capacity of 85%), it is impossible to adjust the LCS to the same water content as the WBS. So, the LCS was adjusted to a water content of 16% (w/w), i.e. the water content of LCS when collecting from Hangzhou Tianziling landfill cell. A 3–4 cm thickness of ~1 cm stone was placed at the bottom of each soil column and then 1–2 cm thickness of ~0.4 cm gravel was added to form a gas distribution layer. Then soil was filled into the columns and a specific height of 30 cm was attained. Each kind of soil was operated in duplicate systems including simulated landfill reactors and soil cover columns. It took 8 days to shred and put MSW into the landfill reactors and seal the whole system, including the simulated landfill reactors and the cover soil columns, with 791-N silicone sealant. The whole experiment systems were carried out at room temperature, which ranged from 20 to 37 °C. Based on the shift in soil water content, 5–10 ml water was dripped onto the soil surface to adjust the soils to the similar water contents to the original every 3–8 days over the course of the experiment. The whole experiment lasted 105 days.

2.4. Sampling and analytical methods

2.4.1. LFG composition and soil physico-chemical characteristics

LFG production rate from the landfill reactors was measured using a gas meter (model SQL, Shanghai, China) each day during the whole experiment. Gas samples were taken using a syringe from the LFG inlet tubes and three sampling ports of each soil column for gas component (CO_2 and CH_4 or O_2) analysis every 1–8 days. Gas concentrations were detected using gas chromatography (GC) equipped with thermal conductivity detector (TCD) and flame ionization detector (FID) [18]. Due to the complicated composition of LFG and the variation of gas pressure during the MSW stabilization, the concentrations of CH_4 and CO_2 were shown in the unit of mol m^{-3} in this study. H_2S in the LFG inlet tubes was absorbed with 3.75 mmol l^{-1} of cadmium hydroxide ammonium alcohol polyvinyl phosphate solution for 30–90 min every 3–13 days. Then sulfur concentration in the absorbed solution was measured by photometric method [19]. H_2S concentration in the LFG was calculated by Eq. (1):

$$C = \frac{22.4MT}{273 \times 34Vt} \quad (1)$$

where C is the H_2S concentration in the LFG, ppm (v/v); 22.4 is the standard volume of 1 mol of an ideal gas at standard temperature and pressure (273 K (0 °C) and one atmosphere pressure), l mol^{-1} K^{-1}; M is the absorbing amount of H_2S in the cadmium hydroxide ammonium alcohol polyvinyl phosphate solution, mg; 273 is the Kelvin of standard temperature (0 °C), K; 34 is the molar mass of H_2S, g mol^{-1}; V is the LFG production rate, m^3 d^{-1}; T is the experimental temperature, K; t is the absorbing time of H_2S by the absorbent, d.

Approximately 40 g soil samples were taken using a split-spoon type sampler from each sampling port every 15 days and immediately placed into plastic bags and homogenized. Approximately 10 g of the soil subsample in each bag was taken and processed for the measurements of microbial populations and sulfide content. Sulfide content of soil was determined by the method described by Qiu et al. [20]. Soil pH value and sulfate content were determined by the conventional methods [21]. The residual sample was used to monitor moisture content by measuring the loss of sample weight after drying in an oven at 105 °C for 16 h to a constant weight.

2.4.2. Measurement of microbial population

Soil subsample was used to form an inoculum for aerobic microbial enumeration as reported previously [22]. Aerobic heterotrophic bacteria, actinomycete and fungi were enumerated by the dilution agar-plate method. The culture media for aerobic heterotrophic bacteria, actinomycete and fungi were Beef-peptone medium, Gause's 1 medium with a K_2CrO_4 concentration of 0.1 g l^{-1} and Martin-Bengal medium with a streptomycin concentration of 0.3 g l^{-1}, respectively. The plates for aerobic heterotrophic bacteria, actinomycete and fungi enumeration were all incubated for 3 days at 30 °C. Sulfate-reducing bacteria (SRB) and sulfur-oxidizing bacteria (SOB) was enumerated by the most probable number (MPN)

method ($n=3$). The medium for SRB enumeration was ($g\,l^{-1}$): sodium lactate, 3.5; yeast extract, 1.0; Na_2SO_4, 0.5; NH_4Cl, 1.0; $CaCl_2$, 0.1; K_2SO_4, 0.5; $MgSO_4{\cdot}7H_2O$, 2.0; resazurin, 0.001. Sterile $(NH_4)_2Fe(SO_4)_2$ solution was added into the autoclaved SRB medium to a concentration of $0.12\,g\,l^{-1}$. The medium for SOB enumeration was ($g\,l^{-1}$): $(NH_4)_2SO_4$, 3; KCl, 0.1; K_2HPO_4, 0.5; $MgSO_4{\cdot}7H_2O$, 0.5; $Ca(NO_3)_2$, 0.01. The medium was adjusted to pH 4.5 with the pH indicator of bromophenol blue ($12\,mg\,l^{-1}$). After treated with ultraviolet light for 30 min, sulfur was immediately added to the autoclaved SOB medium to a concentration of $10\,g\,l^{-1}$. In each sample MPN experiment, three uninoculated tubes were used as controls. The tubes used for the MPN analysis were incubated at 30 °C for 14 days. The presence of SRB and SOB in the MPN dilution tubes, respectively, was evaluated by the formation of black FeS precipitate and the color change of the SOB medium from blue to yellow.

2.4.3. H_2S emission and removal efficiency

A cap with a polyethylene male adapter (~1 cm) as a gas outlet was used to cover the top of each column when measuring H_2S emission rate. Before measuring H_2S emission, N_2 (minimum purity 99.99%) was applied at the surface of the soil covers to avoid the accumulation of the LFG at the flow rate of $100\,ml\,min^{-1}$ for about 60 min. Effluent H_2S concentration from each column was detected as the same method for the measurement of H_2S concentration in the LFG and was absorbed with $3.75\,mmol\,l^{-1}$ of cadmium hydroxide ammonium alcohol polyvinyl phosphate solution for 30–90 min at the N_2 flow rate of $100\,ml\,min^{-1}$ to the surface of the soil covers. The H_2S emission rate and removal efficiency were calculated by Eqs. (2) and (3), respectively.

$$F = \frac{M}{St} \tag{2}$$

$$\rho = \frac{CV - 22.4FST/(34 \times 273)}{CV} \times 100 \tag{3}$$

where F is the H_2S emission from the soil cover, $mg\,m^{-2}\,d^{-1}$; S is the surface area of the soil cover, m^2; ρ is the removal efficiency, %; C is the H_2S concentration of the inlet gas for the soil cover, i.e. H_2S concentration in the LFG, ppm (v/v); V is the volume of the inlet gas for the soil cover, i.e. the LFG production rate, $m^3\,d^{-1}$.

3. Results

3.1. LFG production rate and composition

After the system was operated, a large amount of LFG ($98–99\,l\,d^{-1}$) was produced from the landfill reactors on day 1 (Fig. 2) (note the values present in the graphs are the average of the duplicate systems for each kind of soil). The LFG production rates from the landfill reactors increased quickly and reached the maximum values of $256–257\,l\,d^{-1}$ on day 5. After that, the LFG product rates decreased quickly and dropped to $30–32\,l\,d^{-1}$ on day 10, accounting for 11–12% of the maximum values. As the easily biodegradable organic waste was degraded by microorganisms within the landfill reactors, the LFG product rates decreased slowly from day 10. The average LFG product rates from the four landfill reactors (duplicate systems for each kind of soil) dropped from $30\,l\,d^{-1}$ on day 11 to $3\,l\,d^{-1}$ on day 59, and then kept stable at $0.1–1\,l\,d^{-1}$ until the end of the experiment.

During the process of waste degradation, landfills go through five phases: initial adjustment phase, transition phase, acid formation phase, CH_4 formation phase and maturation phase [23]. The composition of LFG changes with each of the five phases within landfills [23]. Among the measured three gases (e.g. CH_4, CO_2 and H_2S), H_2S and CO_2 were first detected in the LFG (Fig. 3). At the beginning of the experiment, the CO_2 concentrations in the LFG present a decreasing trend and dropped to 23–31 $mol\,m^{-3}$ on day 7. After that, the CO_2 concentrations increased and reached the maximum of 55–57 $mol\,m^{-3}$ between days 17 and 20, and then decreased and kept a stable fluctuation within 17–22 $mol\,m^{-3}$ between days 59 and 86.

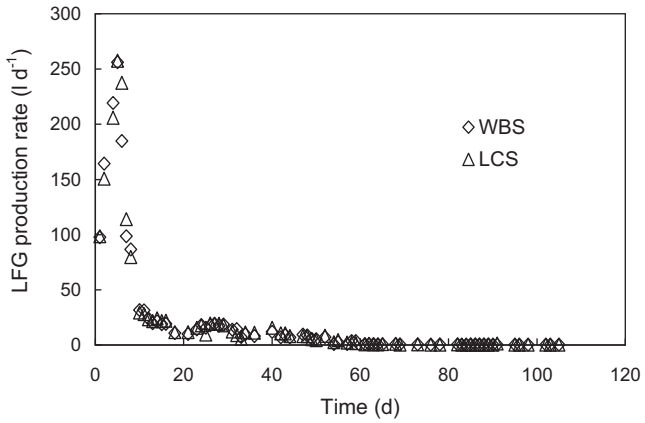

Fig. 2. Landfill gas (LFG) production rate from the landfill reactors over time.

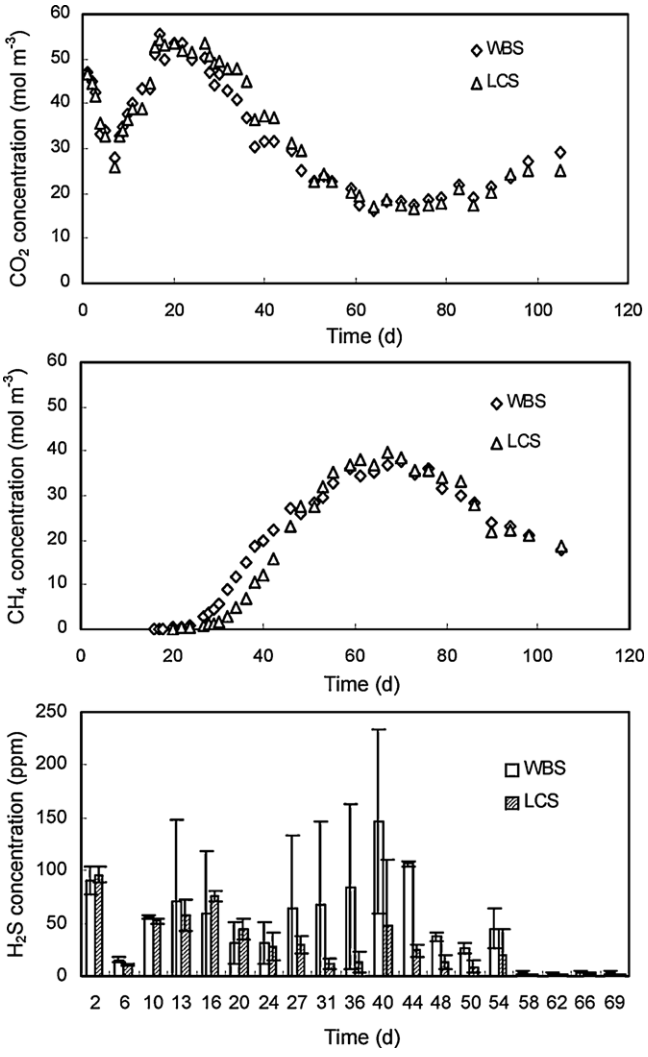

Fig. 3. CH_4, CO_2 and H_2S concentrations in the landfill gas (LFG) produced from the landfill reactors over time.

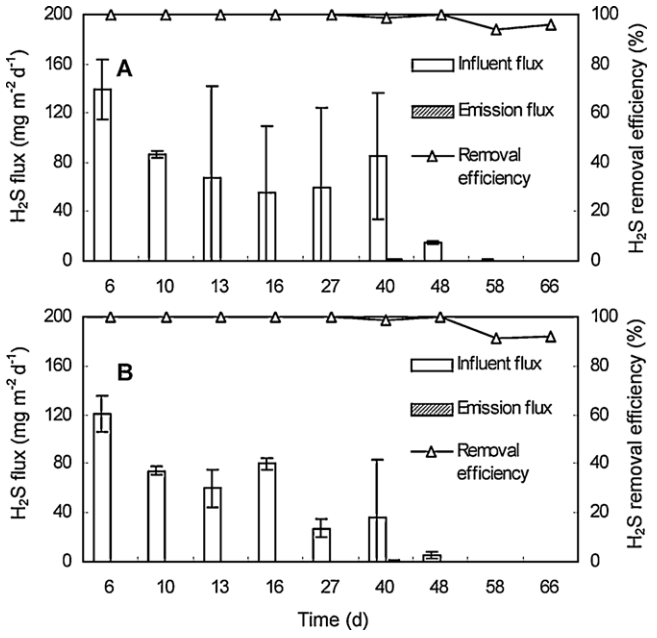

Fig. 4. H_2S influent and emission fluxes and H_2S removal efficiency for the landfill cover soil microcosms. (A) WBS and (B) LCS.

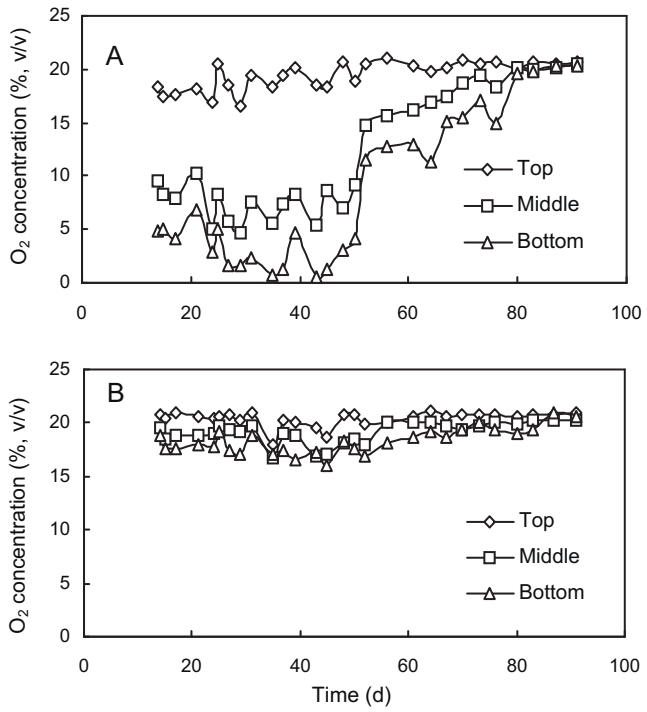

Fig. 5. Vertical profiles of O_2 concentrations in the landfill cover soil microcosms over time. (A) WBS and (B) LCS.

With the consumption of waste deposit of O_2 as buried waste in the landfill reactors, anoxic and anaerobic bacteria are active in the decomposition of buried waste. CH_4 was first measured in the LFG of the WBS and LCS landfill reactor on days 16 and 20, respectively. The CH_4 concentration in the LFG increased to above 30 mol m^{-3} between days 59 and 76 as methanogen grew and converted H_2/CO_2 into CH_4.

The H_2S concentrations in the LFG exhibited a significant difference in the four landfill reactors and fluctuated over time. The maximum measured H_2S concentration in the LFG was 234 ppm from the WBS landfill reactor. The H_2S concentration was below 4 ppm between days 58 and 69. After that, with the decrease of LFG production rates, H_2S concentration was lower than the detection limit (the detection limit of H_2S concentration in the absorbent is 0.01 mg l^{-1}).

3.2. H_2S removal and emission

Although the H_2S concentration in the LFG fluctuated over time during the whole experiment, the H_2S influent fluxes for the soil covers exhibited a decreasing trend over time (Fig. 4). The maximum measured H_2S influent fluxes for the covers were 121–139 mg m^{-2} d^{-1} on day 6. Due to the fluctuation of H_2S concentration in the LFG, the H_2S influent flux present a great difference in duplicate covers of each kind of soil, with the standard deviation of 0.1–65 mg m^{-2} d^{-1} for the WBS cover and 0.03–47 mg m^{-2} d^{-1} for the LCS cover, respectively. The H_2S emissions from the two soil covers were lower than 0.05 mg m^{-2} d^{-1}, except for the average of 0.9 and 0.5 mg m^{-2} d^{-1} for the WBS and LCS covers, respectively, on day 40. The H_2S removal efficiencies were both above 98% for the two kinds of soil covers between days 6 and 48. After that, the H_2S removal efficiencies of the two covers decreased a little as the H_2S influent flux dropped, but still kept above 90%.

3.3. Vertical profiles of O_2 concentration in the soil covers

O_2 concentration in landfill covers mainly relies on LFG emission rate, the consumption of biological metabolism and O_2 diffusion. The O_2 concentration in the WBS cover exhibited a great difference in different layers (Fig. 5). In the WBS cover, the highest O_2 concentration was observed in the top layer within the fluctuation of 16.8–20.9% over the course of the experiment. For the first 80 days, the O_2 concentrations varied with time in the middle and bottom layers of the WBS cover. The O_2 concentrations were low in the middle and bottom layers of the WBS cover between days 14 and 48, and even undetected in the bottom layer in one of the duplicate WBS covers on days 35 and 43. With the decrease of the LFG and CH_4 influent flux, the O_2 concentration in the WBS cover increased from day 48, and kept stable within 19.5–20.5% between days 80 and 91. The O_2 concentration in the LCS cover did not show so much variation as in the WBS cover, with the average O_2 concentrations of 18.3–20.5% in different layers over the course of the experiment. This might be due to the higher activity of aerobic methanotrophs in the WBS cover (data not shown), which consumed more O_2 than in the LCS cover.

3.4. Conversion of sulfide

To test the mechanisms of H_2S removal by the WBS and LCS covers, the sulfide contents of different layers in the two covers were measured. The sulfide contents of the original WBS and LCS were 12.6 ± 3.6 and 4.0 ± 1.9 mg kg d.w.$^{-1}$, respectively (Fig. 6). As H_2S inputted, the sulfide contents in the top, middle and bottom layers of the WBS cover increased and reached the maximum values (43.4–59.1 mg kg d.w.$^{-1}$), which were 2.4–3.7-fold higher than the original, on day 30. After that, the sulfide contents in the WBS cover decreased and present similar values in different layers. At the end of the experiment, the sulfide content of the WBS cover was 23.1–28.9 mg kg d.w.$^{-1}$, 1.8–2.3 times of that of the original. In the LCS cover, the highest sulfide content was observed in the bottom layer during the whole experiment, which was 3.4–6.1 times higher than the original. The sulfide contents in the top and middle layers of the LCS cover, respectively, increased to 8.8 and

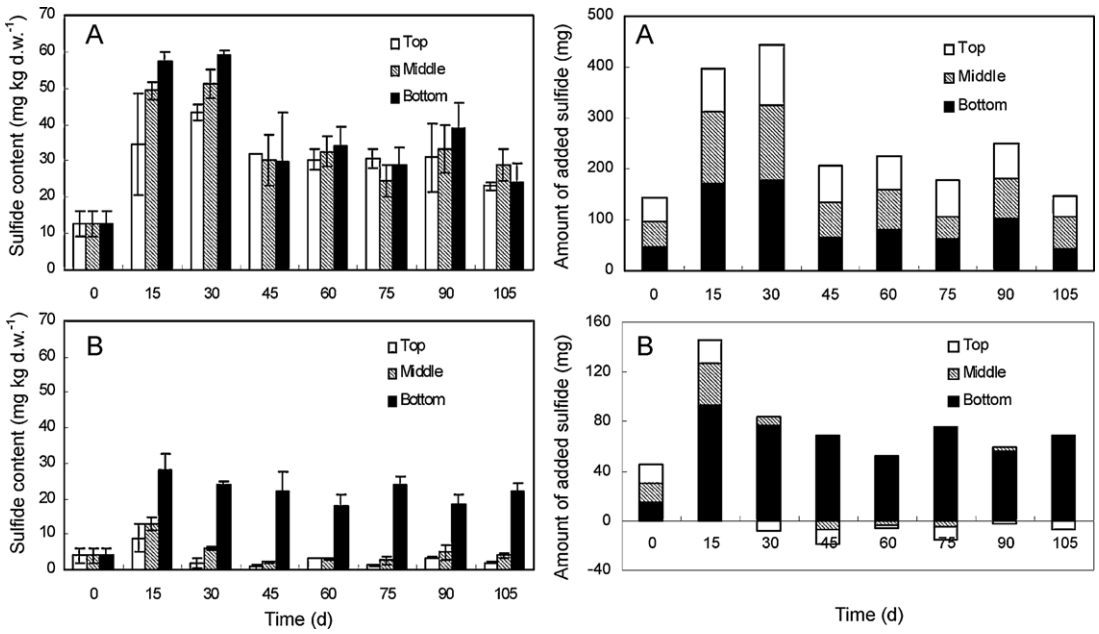

Fig. 6. Sulfide contents and amount of added sulfide in the landfill cover soil microcosms over time. (A) WBS and (B) LCS.

12.8 mg kg d.w.$^{-1}$ on day 15, and then decreased and kept at similar values to the original until the end of the experiment.

In the WBS cover, the amounts of the added sulfide (the value equaled the amount of the original soil sulfide subtracted from the total amount of the soil sulfide in different layers) were 395.4 and 444.1 mg, respectively, on days 15 and 30, which was 2.4 times of the accumulated amount of the sulfur input from H_2S in LFG, while it was near to the accumulated amount of the sulfur input from H_2S in the LCS cover, especially in the bottom layer, accounting for 57% of the accumulated amount of the sulfur input from H_2S on day 15 (Fig. 6). As the H_2S influent flux decreased (Fig. 4), the amounts of the added sulfide in the two soils both showed decreasing trends. In the LCS cover, the amount of the added sulfide was mainly at the bottom layer after day 30.

The sulfate contents of the original WBS and LCS were 3.91 ± 0.52 and 0.87 ± 0.49 g kg d.w.$^{-1}$, respectively (Fig. 7). After exposure to the LFG, the sulfate content in the WBS cover showed a significant difference between the top and middle and bottom layers. The highest sulfate content was observed in the top layer of the WBS cover, which had 0.5-fold higher than the original. The sulfate contents in the LCS cover did not present an obvious difference in different layers and all were below 0.7 ± 0.3 g kg d.w.$^{-1}$. At the end of the experiment, a decrease of pH was observed in the experimental soil covers. pH value in the top layer of the WBS cover was lower than the middle and bottom layer, while there was not a significant difference at the level of 5% in different layers of the LCS cover.

3.5. Microbial populations

The population of aerobic heterotrophic bacteria was 9.5×10^9 colony-forming units g dry weight^{-1} (cfu g d.w.$^{-1}$) in the original WBS (day 0), which was more than 2 order of magnitude higher than the original LCS (1.4×10^7 cfu g d.w.$^{-1}$) (Fig. 8A). The population of aerobic heterotrophic bacteria followed a similar trend in the top, middle and bottom layers of the WBS cover. The input of the LFG stimulated the growth of aerobic heterotrophic bacteria, and reached 3.0×10^{12}–3.3×10^{13} cfu g d.w.$^{-1}$ on days 15 and 30. From day 45, the population of aerobic heterotrophic bacteria in the WBS cover decreased and kept lower values than the original on days 90 and 105. The populations of aerobic heterotrophic bacteria increased to $\sim 2 \times 10^9$ cfu g d.w.$^{-1}$ in the top and middle layers of the LCS cover on day 15, and then decreased to a similar value of the original at the end of the experiment, while it did not show much change over time in the bottom layer of the LCS cover.

The populations of actinomycete were 7.9×10^7 and 9.6×10^4 cfu g d.w.$^{-1}$ in the original WBS and LCS, respectively (Fig. 8B). After exposure to the LFG, the population of actinomycete in the WBS cover increased to 1.9×10^9–6.6×10^9 cfu g d.w.$^{-1}$ on day 15. The population of actinomycete in the bottom

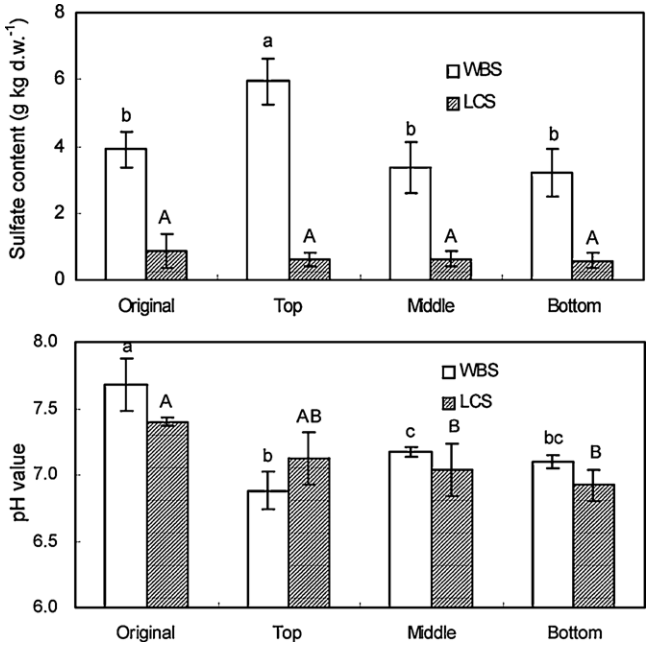

Fig. 7. Sulfate concentrations and pH values of soil in the landfill cover soil microcosms at the end of the experiment. Different letters within the graph (small letters in the WBS and capital letters in the LCS, respectively) refer to significant difference at 5% level based on Least Significant Difference (LSD) method.

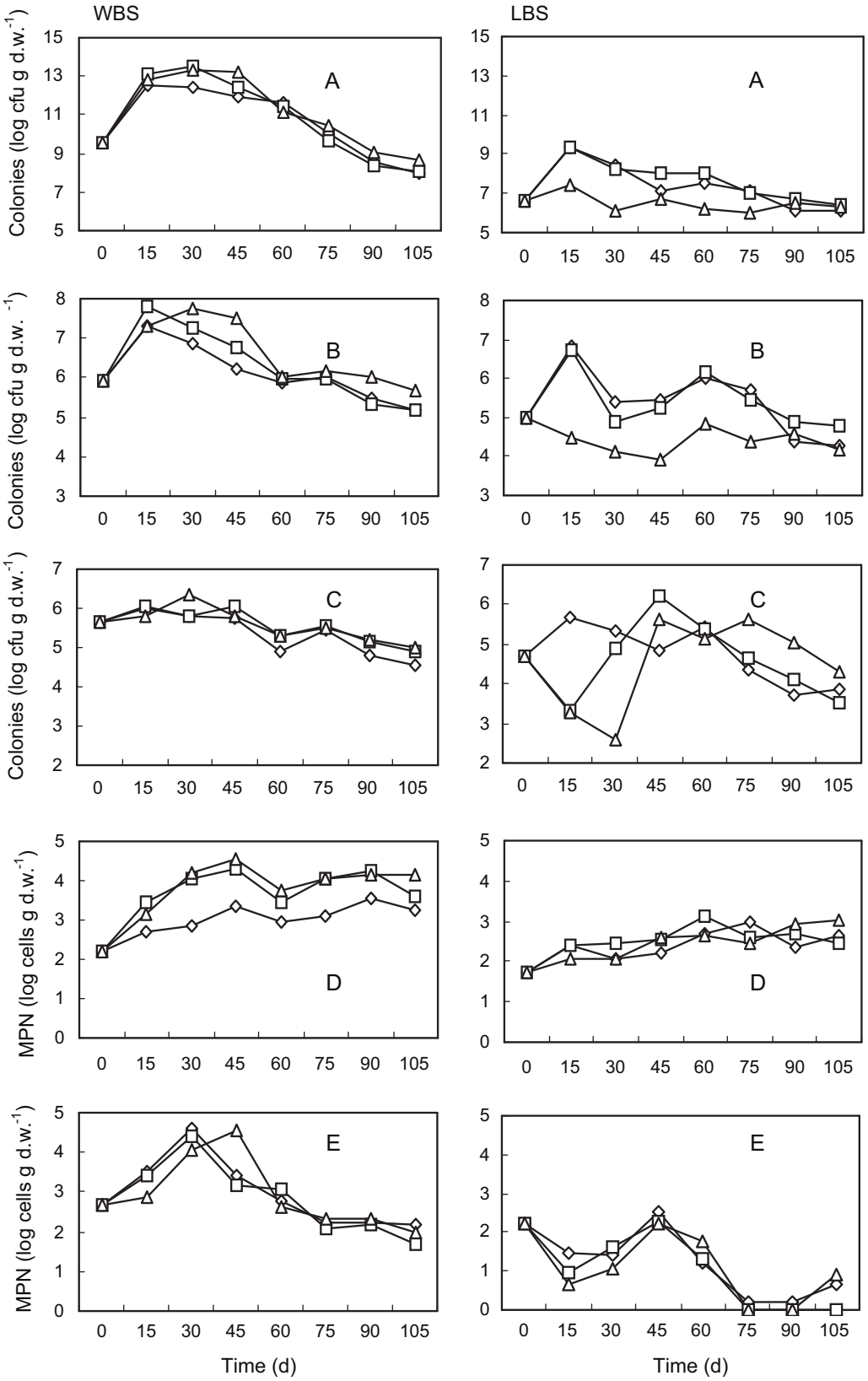

Fig. 8. Microbial populations in the landfill cover soil microcosms over time. (A) Aerobic heterotrophic bacteria; (B) actinomycete; (C) fungi; (D) sulfur-oxidizing bacteria (SOB) and (E) sulfate-reducing bacteria (SRB). Top layer (◊), middle layer (□), bottom (△).

layer increased to 5.8×10^9 cfu g d.w.$^{-1}$ on day 30 and then decreased to a similar value of the original. The population of fungi in the WBS cover showed a similar trend in different layers, increasing a little on days 15 and 30, and decreasing to $3.6–9.6 \times 10^4$ cfu g d.w.$^{-1}$ on day 105 (Fig. 8C). In the LCS cover, the populations of actinomycete in the top and middle layers increased to $5.2 \times 10^6–6.4 \times 10^6$ cfu g d.w.$^{-1}$ on day 15. However, in the bottom layer of the LCS cover, the input of the LFG caused a

decrease in the populations of actinomycete and fungi at the first 30 days (Fig. 8B and C).

The populations of SOB in the original WBS and LCS were low (51–161 cells g d.w.$^{-1}$) (Fig. 8D). The input of the LFG, including H_2S, stimulated the growth of SOB in the experimental WBS and LCS covers. The populations of SOB in the middle and bottom layers of the WBS cover increased to the maximum values of 2.1×10^4–3.5×10^4 cells g d.w.$^{-1}$ on day 45, and then dropped a little as the H_2S influent flux decreased. Over the course of the experiment, the population of SOB in the top layer of the WBS cover was one order of magnitude lower than the middle and bottom layers. In the LCS cover, the effect of LFG input on SOB was not evident. Although O_2 was present in each layer of the experimental soil cover (Fig. 5), SRB was measured and showed an increasing trend in the WBS cover between days 0 and 30 (Fig. 8E). The populations of SRB were 5–332 cells g d.w.$^{-1}$ in the LCS cover at the first stage and was near 0 (not to be measured) since day 75.

4. Discussion

In this study, the H_2S removal efficiency was higher than 90% regardless of the WBS or LCS covers over the course of the experiment (Fig. 4). The removal process of H_2S in landfill cover soils is similar to a biofiler and occurs in two phases: adsorption onto the liquid–solid phase, including H_2S adsorption to solid surfaces and dissolution into interstitial soil pore water adsorption, and biotransformation [17,24,25]. H_2S is a soluble weak acid gas. Although the particle size of the WBS was larger than that of LCS, the higher sulfide content was observed on the WBS, likely due to the high water content and metal contents of the WBS (Table 1), leading to a high adsorption capacity of H_2S on the WBS [17]. As H_2S inputted, the sulfide content in the WBS cover increased and presented higher values than the initial sulfide content at the end of the experiment, while the sulfide contents in the top and middle layers of the LCS cover decreased after day 30, even lower than the orignial (Fig. 6). This might be due to the high O_2 concentration and low water content in the LCS cover, which resulted in the form of sulfur dioxide while H_2S was escaping from landfills [17]. In the WBS cover, the amount of the added sulfide was ~2.4 times of the accumulated amount of the sulfur input from H_2S in LFG on days 15 and 30, while it was near to the accumulated amount of the sulfur input from H_2S in the LCS cover on day 15 (Fig. 6). The difference between the sulfide content of soil and the total amount of H_2S input to the WBS and LCS covers indicated H_2S was mainly removed by adsorption in the LCS cover at the beginning of the experiment, while in the WBS cover, except for the adsorption, the LFG also induced a rapid biotransformation between sulfide and sulfate.

In the bottom layer of the LCS cover, the input of the LFG caused a decrease in the populations of actinomycete and fungi at the first 30 days (Fig. 8B and C). This might be due to the toxic compounds in the LFG including benzene, trichloroethylene, dichlorobenzene, which killed some microorganisms when the LFG influent flux was high [26,27]. However, in the WBS cover, the effect of LFG on the fungi was not evident and the input of the LFG stimulated the growth of aerobic heterotrophic bacteria and actinomycete. The reason might be that these microorganisms in the WBS had been exposed in the LFG for several years and they were well acclimated to the exposure of LFG because the experimental WBS was collected from an organic waste landfill bioreactor.

The input of the LFG stimulated the growth of SRB and SOB in the WBS cover (Fig. 8D and E). SRB are traditionally considered as anaerobic microorganisms and are widespread in anoxic habitats [28]. However, in this study, large numbers of SRB were found in the soil covers where O_2 was measured, even in the top layer (Fig. 8E). Similar results of abundance and activity of SRB have been reported in the oxic zones of marine and fresh water sediment [29,30]. There are two main O_2 defense strategies for SRB to survive in the presence of O_2: behavioral strategies, including aerotaxis and aggregate formation, and molecular strategies to remove and protect themselves from harmful effects [31,32]. During sulfate reduction, sulfate and sulfur are converted to sulfide by SRB. Relatively stable sulfide content was exhibited in the WBS cover at the last stage. This might be due to the high metal contents in the WBS (Table 1), a part of sulfide produced might react with Fe, Cu and Zn to form FeS, ultimately pyrite (FeS_2), CuS and ZnS, which might sorb to the WBS.

The sulfide can be oxidized under oxic conditions by chemolithotrophic sulfur bacteria or under anoxic conditions by phototrophic sulfur bacteria [33]. In this study, the chemolithotrophic sulfur bacteria and phototrophic sulfur bacteria were not be distinguished in the measurement experiment of SOB population and both were named into SOB. The populations of SOB in the middle and bottom layers of the WBS cover were one order of magnitude higher than that of the top layer (Fig. 8D). However, the highest sulfate content was found in the top layer of the WBS cover, which was 1.5 times of that of the original (Fig. 7). This might be due to the coexistence of SOB and SRB in the WBS cover leading to the sulfur transfer. At last sulfur mainly appeared in the form of sulfate in the top layer of the WBS cover due to the higher concentration of O_2 which resulted in the higher activity of sulfide oxidation than sulfate reduction [34].

In the process of sulfide oxidation, H^+ is produced and can lead to a decrease of environmental pH value. This observation is in common with the studies of biofilters for H_2S removal [35,36]. In this study, except for the top layer of the LCS cover, a significant decrease of pH was observed in the experimental cover soils compared to the original WBS and LCS (Fig. 7), indicating that biological sulfide oxidation was a mechanism of H_2S removal in the two cover soils. Although biological sulfide oxidation occurred in the middle and bottom layer of the LCS cover, sulfide was found to be accumulated in the bottom layer and did not show much change over the course of the experiment (Fig. 6). However, a greater decrease of pH and a 0.5-fold higher sulfate content than the original was exhibited in the top layer of the WBS cover at the end of the experiment. These indicated that the higher activity of SOB occurred in the WBS cover than the LCS. Compared to the sulfate contents of the original WBS and LCS, the total sulfide amount of the LFG input in the form of H_2S was much lower, only accounting for 0.4% of the sulfate content of the original WBS and 1.4% of the original LCS, respectively. Due to the soil heterogeneity, it cannot be confirmed how much of H_2S were biotransformed into sulfate in the two cover soils.

In conclusion, this study indicated the WBS had a high adsorption removal capacity for H_2S. The input of the LFG could stimulate the growth of aerobic heterotrophic bacteria, actinomycete, SOB and SRB, leading to a more rapid biotransformation between sulfide and sulfate in the WBS cover than the LCS. These findings demonstrate that the WBS has a good capacity for attenuating H_2S and is a good alternative cover material for landfills to control odor problems.

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