Available online at www.sciencedirect.com
ScienceDirect
Journal of Environmental Sciences 20(2008) 1409–1414
JOURNAL OF ENVIRONMENTAL SCIENCES
ISSN 1001-0742
CN 11-2629/X
www.jesc.ac.cn

Performance of two biofilters with neutral and low pH treating off-gases

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Received 20 January 2008; revised 18 February 2008; accepted 4 March 2008

Abstract

Two different functional biofilters were carried out and compared for the treatment of off-gas containing multicomponent odors and volatile organic compounds (VOCs) in this study. The effects of pH values and the empty bed retention time (EBRT) on the performance of the bioreactors were studied; and the characteristics of microbial populations in the two biofilters were also determined. The experimental results indicated that the removal efficiencies of hydrophilic compounds such as butyric acid and ammonia were higher in the neutral pH biofilter (NPB) than those in the low pH biofilter (LPB). In contrast, the removal efficiencies of the compounds with poor water solubility such as styrene and ethyl mercaptan were higher in the LPB than those in the NPB. The characteristics of microbial population in the two biofilters revealed that the heterotrophic bacteria, nonacidophilic thiobacteria, ammonia oxidizing bacteria, and nitrite oxidizing bacteria were major microorganisms in the NPB, whereas acidophilic thiobacteria and fungi were dominant in the LPB. Therefore, the performance of the biofilter depended on the characteristics of the compound being treated and the type of microorganisms.

Key words: waste gas treatment; biofiltration; VOCs and odors; bacteria; fungi

Introduction

Biofiltration is a kind of cost-effective technology for the treatment of odors and waste gases containing low concentration volatile organic compounds (VOCs) compared with other air pollution control technologies (Devinny *et al*., 1999). It has been successfully applied to the removal of different pollutants as individual compound or mixtures (Kennes and Thalasso, 1998; Williams and Miller, 1992). Bacteria and fungi are two main groups of microorganisms in the biofilter. A conventional biofilter with dominant microorganisms of bacteria can degrade compounds with high water solubility quickly and efficiently (Devinny *et al*., 1999). However, the biofilter with bacteria faces problems in eliminating hydrophobic compounds, which are poorly absorbed by the bacterial biofilms, and its operational stability is often hampered by acidification and drying out of the filter bed. To solve these problems, a biofilter with fungi has been developed (Van Groenestijn *et al*., 2001). The fungi can take up hydrophobic compounds faster than bacteria due to their aerial mycelia that form a very large surface area and may contact directly with the gas flowing through the bioreactor (Zhu and Liu, 2005). Moreover, fungi are more tolerant to dry conditions and acidification than bacteria. There were several reports of successfully treating hydrophobic compounds from waste gases base on the biofilter containing fungi to date (Zhu and Liu, 2004; Van Groenestijn and Liu, 2002).

In fact, the off-gases discharged by industry, manufacture, or wastewater treatment plant are often a complex mixture of odors and VOCs. The major compounds in composting facilities are sulfide hydrogen, ammonia, amine, fatty acids. Hexane, benzene, toluene, xylene, and 1,2,4-trimethylbenzene are often found in exhaust from petroleum refinery (Williams and Miller, 1992; Rao *et al*., 2005). A two-stage biofilter with a low pH stage and a neutral pH stage (Chitwood *et al*., 1999) and a combined bioreactor with bacteria and fungi (Li and Liu, 2006) had been innovated to remove off-gases with complex components. The biofilters have the potential for effective coremoval of hydrogen sulfide, ammonia, and VOCs since they can host complex, mixed microbial populations, which are presumably capable of simultaneously treating a variety of pollutants (Deshusses, 1997). Most previous studies have focused primarily on the operational characteristics of individual low pH stage or neutral pH stage for off-gases treatment. However, less was known about the difference of performance and microbial community of the two parallel stages under the same operational condition.

In this work, two biofilters were operated at two pH values (4.0 and 7.0) under the same inoculum condition and operation mode for off-gas treatment. Their performances were investigated and compared to understand the effective factors on their performances and the characteristics of microbes in the process.

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1 Materials and methods

1.1 Artificial off-gas

The artificial off-gas used in this experiment was generated as follows. Hydrogen sulfide was introduced by passing the air stream into the dilute sulfuric acid solution in which sodium sulfide solution was dripped. A small stream of air was bubbled through vessels containing hydrogen sulfide, ammonia, ethyl mercaptan, butyric acid, and styrene. Then, it was mixed with a large gas stream, resulting in an inlet gas with average concentrations of 20, 20, 20, 20, 80 mg/m^3 for hydrogen sulfide, ammonia, butyric acid, ethyl mercaptan, and styrene, respectively. The desired concentrations in the influent air stream were maintained by adjusting the ratio of two airflows.

1.2 Biofilters setup and operation

Two laboratory-scale biofilters were setup for the off-gas treatment (Fig.1). Each biofilter was a single-stage Plexiglas column of 9.0 cm in diameter and 40.0 cm in height and was packed with porous polyurethane foam cubes for the growth of microorganisms. The bulk porosity polyurethane foam cubes was 97.0%, and packed bed density was 29.2 mg/cm^3.

Both biofilters were operated under upflow mode. The artificial off-gas stream was introduced into the biofilter from the bottom. During the experimental period, the empty bed retention time (EBRT) was varied from 20 to 180 s, and the flow rate was varied from 0.5 to 4.5 L/min. The pH values of the two biofilters were 7.0 for the neutral pH biofilter (NPB) and 4.0 for the low pH biofilter (LPB), and were maintained by adding the nutrient solution periodically from the top of the biofilters. The nutrient solution contained (g/L): KH_2PO_4 0.54, NaCl 1, $MgSO_4$ 0.025, $CaCl_2$ 0.02, $FeSO_4{\cdot}4H_2O$ 0.005, $MnSO_4{\cdot}H_2O$ 0.000088, and $K_2HPO_4{\cdot}3H_2O$ 1.38 (for NPB), KH_2PO_4 1.25 (for LPB). The pH adjustment of the nutrient solution was realized by adding acid or alkali. The experiment was carried out in a laboratory, with seasonal temperature changed from 18 to 38°C.

The removal efficiency (R) (%) of the pollutants in the off-gas and elimination capacity (EC) (mg/(m^3·h)) of the biofilters were calculated as follows:

$$R = (1 - \frac{C_{out}}{C_{in}}) \times 100\% \quad (1)$$

$$EC = (C_{in} - C_{out}) \times Q/1000V \quad (2)$$

where, C_{in} (mg/m^3) is inlet gas concentration; C_{out} (mg/m^3) is outlet gas concentration; Q (m^3/h) is gas flow rate, and V (m^3) is the volume of the packing bed considered.

1.3 Inoculum

Both the biofilters were inoculated with 2.0 L of the activated sludge supernatant, which was obtained from a wastewater treatment plant in Beijing.

After inoculation, the artificial off-gas with low concentration pollutants was introduced to the biofilters for acclimation. Two liters of nutrient solution was added into the packing beds once every three days to maintain optimum moisture and supply nutrients for the growth of microorganisms. The acclimation time was determined by actual treatment efficiency.

1.4 Analytical methods

1.4.1 Gas samples

In this experiment, ammonia was transferred in aqueous solution by bubbling the gas in a solution of 5.0 mmol/L sulfuric acid for 10 min in which the NH_4^+ concentration was analyzed by a standard analysis method (NSCEP, 1995). The H_2S, ethyl mercaptan, butyric acid, and styrene gases were collected from the biofilter using 1.0 ml gas-tight syringes and injected immediately into a gas chromatography (GC) (6890 N, Agilent, USA) unit for concentration determination. For the analysis of H_2S and ethyl mercaptan, a flame photometric detector (FPD) and HP-5 capillary column (30 m × 0.32 mm × 0.25 μm, Hewlett Packard, USA) was used. The GC oven temperature was programmed from 30 to 45°C in increments of 6°C/min with a hold of 0.5 min at 30°C and 1 min at 45°C. The injection and the detector temperatures were set at 100 and 200°C, respectively. Air, nitrogen, and hydrogen flow rates were 50, 65.6, and 60.0 ml/min, with a column head of 85 kPa. The analysis of butyric acid

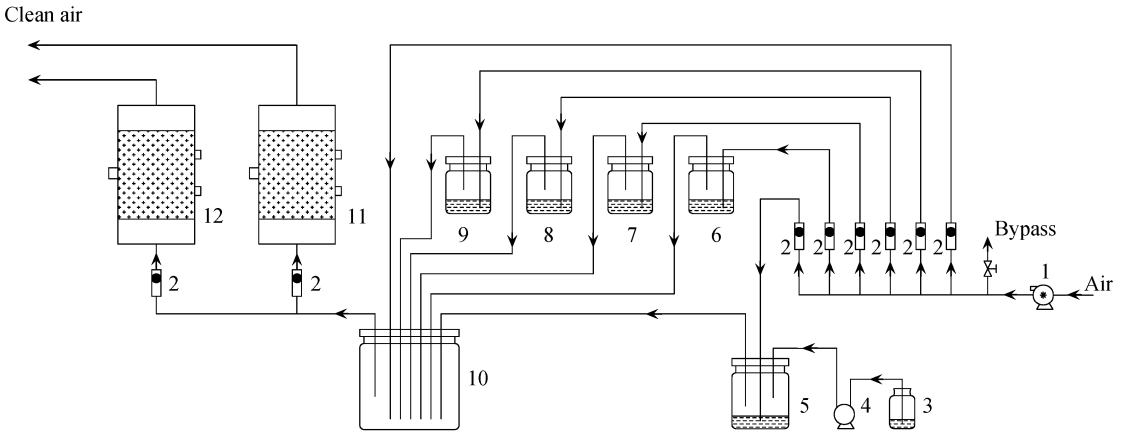

Fig. 1 Schematic representation of the experimental setup. (1) air compressor; (2) rotameter; (3) sodium sulfide solution; (4) peristaltic pump; (5) dilute H_2SO_4 solution; (6) pure ammonial solution; (7) pure ethyl mercaptan solution; (8) pure butyric acid solution; (9) pure styrene solution; (10) mixing chamber; (11) neutral pH biofilter; (12) low pH biofilter.

was performed using a flame ionization detector (FID) and DB-FFAP capillary column (30 m × 0.25 mm × 0.25 μm, Hewlett Packard, USA). The GC oven temperature was programmed from 100 to 180°C in increments of 8°C/min with a hold of 1 min at 100°C and 1 min at 180°C. The injection and the detector temperatures were set at 200 and 240°C, respectively. Air, nitrogen, and hydrogen flow rates were 300, 15.1, and 30 ml/min, with a column head of 80 kPa. The concentration of styrene was determined using a FID and a capillary column (HP-5, 30 m × 0.32 mm × 0.25 μm, Hewlett Packard, USA). The temperatures of the injector, the oven, and the detector were 250, 200, and 250°C, respectively. Flow rates of air, nitrogen, and hydrogen were 400, 45, and 40 ml/min, with a column head of 87.6 kPa.

Series of H_2S, ethyl mercaptan, butyric acid, and styrene concentrations were used for the calibration.

1.4.2 Microbial analysis agitated

For microbial enumeration, 1.0 g moist polyurethane foam cubes were taken from each sampling ports when the biofilters were in steady-state. Then, they were mixed with 100 ml sterile water and agitated for 10 min. The cell numbers of heterotrophic bacteria, fungi, and thiobacteria were enumerated by traditional plate-counting method. Heterotrophic bacteria were cultured using nutrient agar at 37°C for 2 d, and fungi were cultured using rose bengal agar at 28°C for 5 d. The thiosulfate agar and the modified Waksman agar were used to culture nonacidophilic thiobacteria and acidophilic thiobacteria for 15 d at 28°C, respectively (Cho *et al*., 1991). Inoculation was performed in triplicate, and the average value for each sample was taken. The number of the microorganisms was expressed as colony forming units per gram dry packing medium (CFU/g).

Ammonia oxidizing bacteria and nitrite oxidizing bacteria were counted using the method of most probable number (MPN)-Griess. Samples were incubated for 30 d at 28°C in the dark. The counts of ammonia oxidizing bacteria and nitrite oxidizing bacteria were expressed as MPN per gram dry packing medium (MPN/g).

1.4.3 Liquid samples

To measure the pH value of the media, 5.0 g packing media was mixed with 100.0 ml distilled water and then the mixture was agitated for 5.0 min. A PHS-3C Digital pH-meter (Shanghai Rex Instrument Factory, China) was used to determine the pH value of the solution.

2 Results and discussion

2.1 Performances of two biofilters

The two biofilters were initially inoculated with the activated sludge supernatant from a wastewater treatment plant. The off-gas with hydrogen sulfide, ammonia, ethyl mercaptan, butyric acid, and styrene were introduced continuously into the NPB and LPB. The performances of the two biofilters for multicomponent VOCs and odors treatment were examined for more than 290 d by gradually decreasing the EBRT from 180 to 20 s. The results are presented in Fig.2.

In the startup stage (the first 60 d), the removal efficiencies of all compounds increased slowly in both biofilters. Removal efficiencies of more than 90% were obtained for all compounds with the exception of styrene in this period. On day 100 over 90% styrene could be removed in the LPB, whereas the removal efficiency of styrene in the NPB was still lower than 70%. During the day 150 to 240, when EBRT decreased from 90 to 40 s, the removal efficiencies of ammonia, butyric acid, and styrene decreased accordingly in both biofilters. The removal of ethyl mercaptan decreased apparently in the NPB and maintained to a relatively stable level in the LPB. Unlike other compounds, the removal of hydrogen sulfide was not distinctly affected by EBRT either in the LPB or NPB. When the EBRT was under 40 s, the removal efficiencies of all compounds in both biofilters decreased quickly. At the same EBRT, the removal efficiency of hydrophobic styrene in the LPB was always higher than that in the NPB, and the highest removal efficiency of over 90% was obtained in the LPB. These results indicated that the removal efficiencies of various compounds in the LPB were very different from that in the NPB.

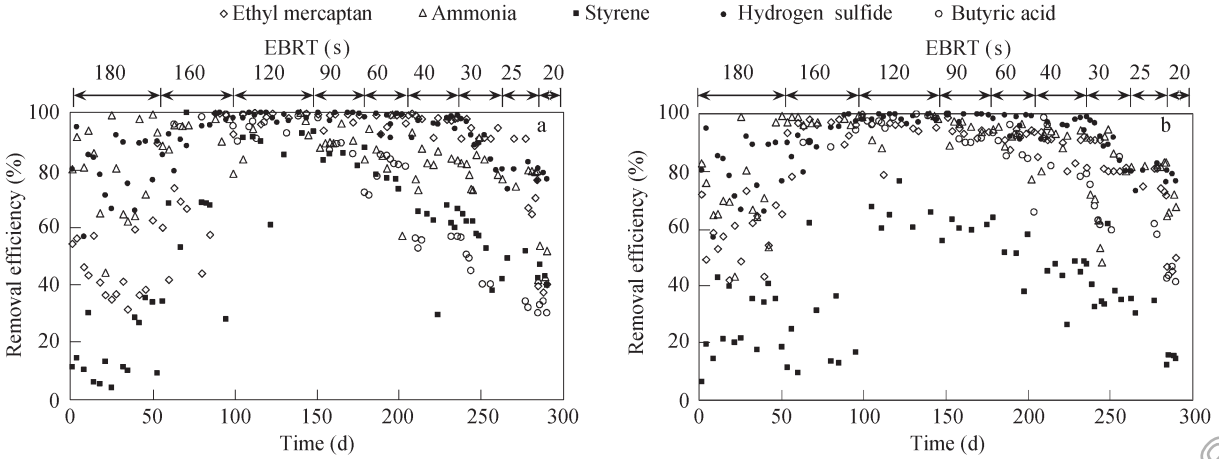

Fig. 2 Overall performance of the low pH biofilter (LPB) (a) and neutral pH biofilter (NPB) (b) during 290 d operation. EBRT: empty bed retention time.

2.2 Elimination capacities of two biofilters

Elimination capacity is an important parameter, which can display the biofilter performance. It is usually interrelated with the inlet gas loading of the biofilter. Fig.3 shows the elimination capacities of the compounds as a function of inlet loading in the LPB and NPB. The corresponding removal efficiency at the same inlet gas loading is shown in Fig.4

The elimination capacities increased with inlet loading rate. At lower inlet loading range (<1.0 g/(m^3·h)), almost all compounds could be totally removed in both biofilters. With further increase of the inlet loading rate, the elimination capacities tended to increase slowly and approach a plateau (Fig.3). Maximum elimination capacities were reached for all pollutants after 200 d of operation in both biofilters. The maximum elimination capacities of hydrogen sulfide, ethyl mercaptan, ammonia, styrene, and butyric acid in the LPB were 3.1, 2.3, 1.7, 2.6, 1.3 g/(m^3·h), respectively, and in the NPB were 3.0, 1.6, 2.1, 1.8, and 1.9 g/(m^3·h), respectively. These results were lower compared with other reports (Jang *et al*., 2005; Djeribi *et al*., 2005), which might be due to the multisubstrate inhibitions or cross-substrate interactions in the LPB and NPB.

The maximum elimination capacity of compounds in the LPB was as the order of hydrogen sulfide > styrene > ethyl mercaptan > ammonia > butyric acid. Whereas in the NPB, the order was hydrogen sulfide > ammonia > butyric acid > styrene > ethyl mercaptan.

To obtain an expected removal efficiency, the inlet loadings of all compounds should be controlled to a certain range (Fig.4). The inlet loadings of five compounds corresponding to the removal efficiency of 90% and their Henry's law constant (Genium database, 1999) are listed in Table 1. It could be found that high inlet loadings for styrene, ethyl mercaptan, and hydrogen sulfide corresponding to removal efficiency of 90% could be obtained in the LPB than that in the NPB. Whereas a contrary result was obtained for ammonia. As to butyric acid, the results were similar for the two biofilters. The water solubilities of styrene, ethyl mercaptan, and hydrogen sulfide were very low. Whereas ammonia and butyric were remarkably soluble in water. It clearly showed that higher elimination capacities of hydrophobic compounds were obtained in the LPB and most ammonia could be eliminated in the NPB due to its high water solubility. However, water-miscible butyric acid had low elimination capacities in both biofilters. This phenomenon might be related to the

Table 1 Inlet loadings of the compounds corresponding to 90% removal efficiency and their Henry's law constant

Compounds	Inlet loading (g/(m^3·h))		Henry's law constant
	LPB	NPB	
Butyric acid	0.75	0.74	5.35×10^{-7}
Styrene	2.62	0	2.75×10^{3}
Ammonia	0.93	1.75	0.76
Ethyl mercaptan	1.90	1.23	4.5×10^{3}
Hydrogen sulfide	3.15	2.78	5.5×10^{2}

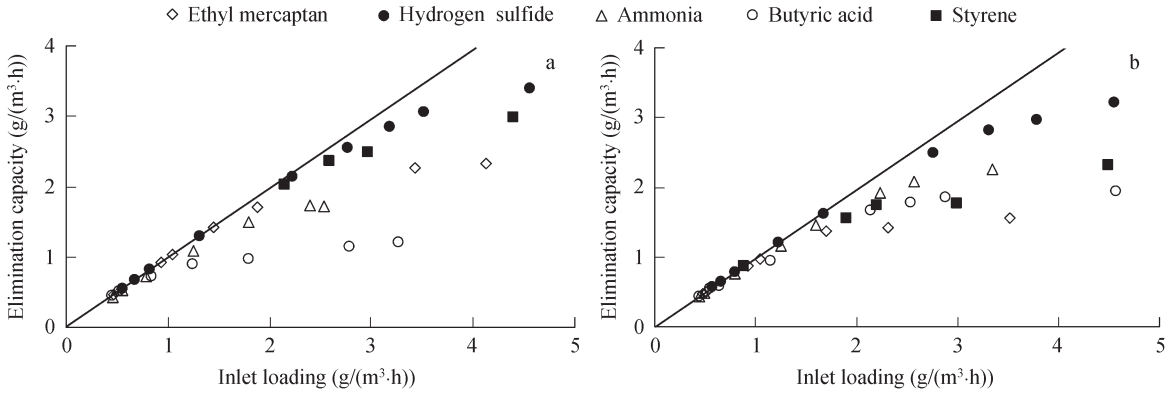

Fig. 3 Elimination capacity as a function of inlet loading in LPB (a) and NPB (b). The straight line represents 100% removal.

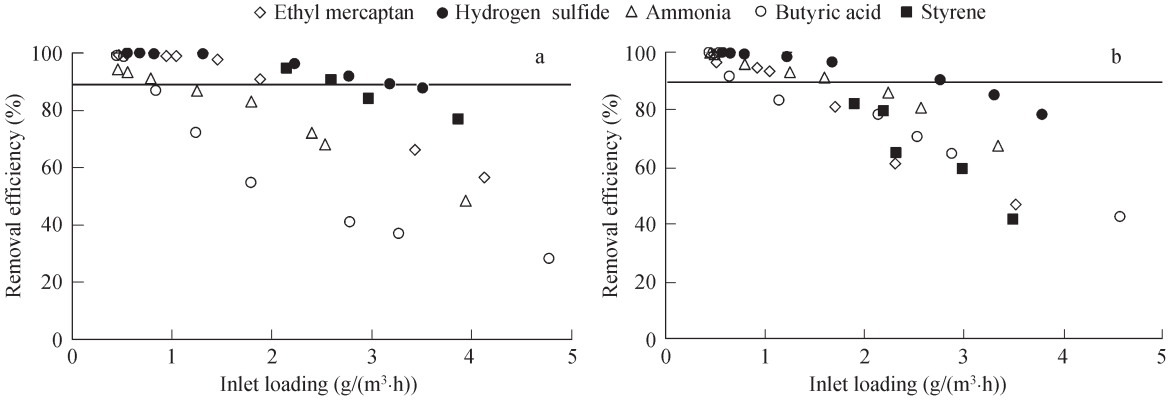

Fig. 4 Removal efficiency as a function of inlet loading in LPB (a) and NPB (b). The straight line represents 90% removal.

different microorganisms developed in the LPB and NPB.

2.3 Characterization of microbial populations in the two biofilters

In the biofilters, it was the microorganisms which could transform pollutants in off-gas into harmless products. The result obtained in this study demonstrated that there was a significant difference of the elimination capacities for different pollutants between the LPB and NPB under the same inoculum and operation conditions. Such discrepancies were most likely due to different microbial communities developed in two biofilters. Fig.5 presents the number of microbial populations presented on the packing medium in the NPB and LPB during the 250 d biofilter operation. The types of microbial populations investigated included heterotrophic bacteria, fungi, acidophilic thiobacteria, nonacidophilic thiobacteria, ammonia oxidizing bacteria, and nitrite oxidizing bacteria.

It can be observed from Fig.5 that different microbial communities developed in the NPB and LPB, although the initial inoculum condition was the same. Heterotrophic bacteria, nonacidophilic thiobacteria, ammonia oxidizing bacteria, and nitrite oxidizing bacteria developed quickly in the NPB, whereas fungi and acidophilic thiobacteria developed rapidly in the LPB after an acclimation period. Microbial amount on the packing medium in the biofilters was determined at the steady state, and their average viable counts are listed in Table 2.

The results in Table 2 indicate that the dominant microorganisms in LPB were fungi, and acidophilic thiobacteria and heterotrophic bacteria were the secondary dominant microorganisms. In the NPB, heterotrophic bacteria were the main microorganisms, and the secondary dominant species were nonacidophilic thiobacteria. Ammonia oxidizing bacteria and nitrite oxidizing bacteria existed only in the NPB. For the thiobacteria, there were mainly acidophilic ones in the LPB and nonacidophilic ones in the NPB.

2.4 Function of microbial community in the biofilters

By comparing the results in Table 1 and Table 2, it could be found that the elimination capacities of the LPB and NPB to each pollutant in off-gases were related with the characteristic of the substrates and microbial community in the biofilters. Fungi and heterotrophic bacteria were the dominant microorganisms in the NPB and LPB, respectively.

Much more styrene and ethyl mercaptan with poor water solubility could be removed in LPB than that in NPB as fungi could take up hydrophobic compounds faster than the bacteria. The elimination capacity of ammonia in the NPB was much higher than that in the LPB due to the function of ammonia oxidizing bacteria and nitrite oxidizing bacteria. However, in LPB, ammonia may be mainly removed by a neutralization reaction with acidic substances, and hence, its removal was limited.

The results also indicated that hydrogen sulfide could be degraded by acidophilic thiobacteria and nonacidophilic thiobacteria in the biofilters. Therefore, both the NPB and LPB had higher elimination capacities in the removal of hydrogen sulfide. The elimination capacity of butyric acid in the NPB was as high as that of the LPB (Fig.3), which might be the function of heterotrophic bacteria or fungi developed in the two biofilters.

Table 2 Microbial amount on the packing medium at the steady operation state

Bacteria	LPB	NPB
Heterotrophic bacteria (CFU/g)	1.2×10^7	2.69×10^8
Fungi (CFU/g)	3.86×10^8	5×10^5
Acidophilic thiobacteria (CFU/g)	2.23×10^7	7×10^5
Nonacidophilic thiobacteria (CFU/g)	4.6×10^5	3.14×10^7
Ammonia oxidizing bacteria (MPN/g)	0	1.97×10^7
Nitrite oxidizing bacteria (MPN/g)	0	1.24×10^7

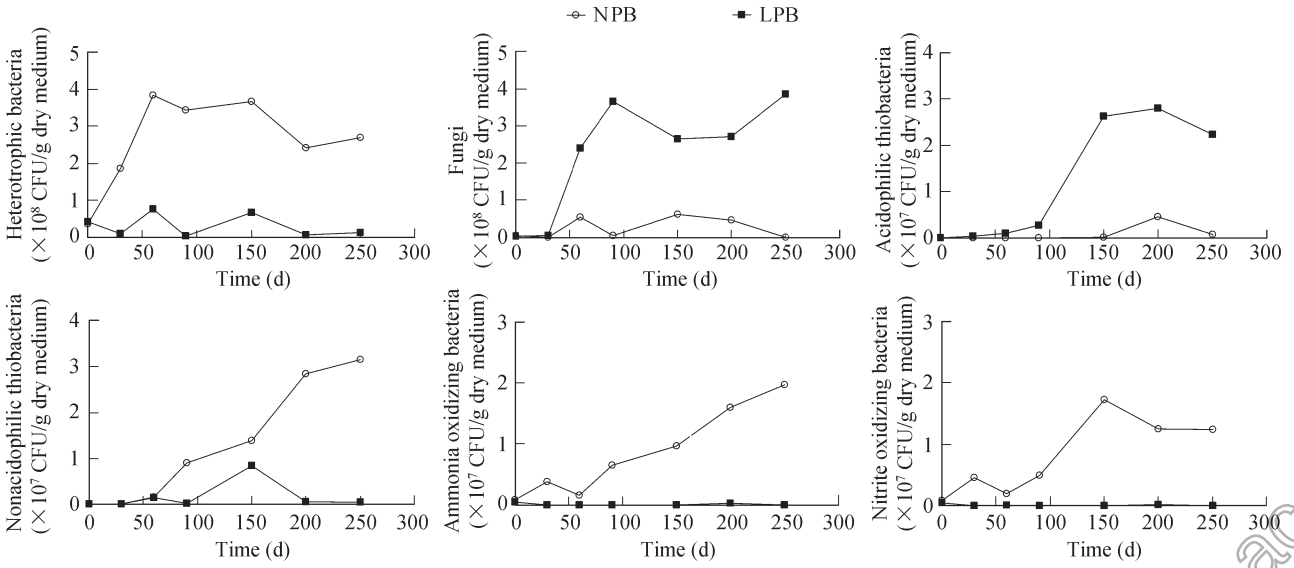

Fig. 5 Microbial populations changes on the packing medium in the NPB and LPB.

3 Conclusions

The NPB and LPB had different performances in the treatment of same VOCs and odors. For removal of the hydrophobic or poor water-solubility compounds, e.g., styrene and ethyl mercaptan, the LPB had higher elimination capacity than the NPB. For the removal of hydrophilic compounds, e.g., ammonia and butyric acid, the elimination capacity of the NPB was higher than that of LPB. Both biofilters had high elimination capacities in the elimination of hydrogen sulfide due to the function of acidophilic thiobacteria and nonacidophilic thiobacteria.

The microbial communities in the NPB and LPB were different, although they were operated under the same inoculation and EBRT conditions. Fungi were the dominant microorganisms, and acidophilic thiobacteria and heterotrophic bacteria were the secondary dominant ones in the LPB. The dominant microorganisms in the NPB were heterotrophic bacteria and secondary species were nonacidophilic thiobacteria. Ammonia oxidizing bacteria and nitrite oxidizing bacteria only existed in the NPB.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (No. 50621804).

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