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Study on the removal of indoor VOCs using biotechnology

Yang Lu, Jing Liu*, Bingnan Lu, Anxi Jiang, Chunli Wan

State Key Lab of Urban Water Resource and Environment (SKLUWRE), School of Municipal and Environmental Engineering, Harbin Institute of Technology, China

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ABSTRACT

With the improvement of living standard and civil building innovation, large numbers of building materials and decoration are being used. The emission of gaseous organic pollutants such as formaldehyde, benzene, toluene and xylene from these materials may trigger immediate or persistent potential harm to human health. In this study, with the combination of bake-out exhaust, biological treatment was applied to deal with volatile organic compounds (VOCs). Four bacterial strains were isolated from the biotrickling filter and were identified according to physiological and biochemical tests as well as bacterial fatty acids. As a result, they were characterized as *Pseudomonas* sp., *Kocuria* sp., *Arthrobacter* sp. and *Bacillus* sp. Under the conditions of gaseous flow rate of 600 L/h, surface liquid velocity of 3.14 m/h, pH 6–7 and temperature of 30 °C, VOCs could be degraded by using biological method before they were exhausted to the environment. For formaldehyde, benzene, toluene and xylene in the air stream with the concentration of 0–6.5 mg/m^3, 2.2–46.7 mg/m^3, 0.5–28.2 mg/m^3 and 4.1–59.0 mg/m^3, VOCs removal efficiencies of biotrickling filter ranged in about 100%, 65–70%, 93% and 85–90%, respectively.

1. Introduction

It has been well known that majority of people spend approximately 80% of their time in the indoor environments such as residences, public buildings and offices. The levels of indoor air pollutants can be several hundred times higher than that of outdoor ones [1,2]. Thus, indoor air quality has significant impact on the human health. Since the recent decade, the prevalence of sick building syndrome (SBS), building related illness (BRI) or multiple chemical sensitivity (MCS) has been reported considerably [3–5]. Many studies have shown that VOCs are among the major air pollutants, and impact human health substantially [6–12]. In China, indoor air quality (IAQ) research began in the late 1970s and comprehensive IAQ studies started to appear in the 1980s. However, IAQ became one of the leading issues since the rapid increase in the number of airtight buildings equipped with air-conditioning systems, and commonly usage of indoor decorating and remodeling using synthetic materials. According to indoor air sample investigations conducted by Chinese Consumer Union in 2001, 73.3% and 43.3% of formaldehyde and VOCs concentrations exceed the standard levels [13].

Currently, there are various methods such as source control, ventilation, and air cleaning to control indoor VOCs. Source control needs to characterize the complicate VOCs emission, which is often inapplicable by occupant level. Ventilation is commonly considered as the most efficient manner because it can remove indoor air pollutants directly, but the disadvantage is the dependence on building air-tightness and the corresponding increase of energy consumption [14]. Therefore, air purification remains to be one of the most promising options to improve the indoor air quality. Of the air-cleaning methods, adsorption by activated carbon, which is known as a traditional pollution control method, merely transfers pollutants from gaseous phase to solid phase [15]. Photocatalytic oxidation (PCO) seems to be a promising technology for VOCs removal. However, this technology has been found effective only when VOCs concentrations are at relatively high levels. Extrapolation of the oxidation data collected at concentrations much higher than the intended application may be invalid [16]. Mo et al. carried out the photocatalytic oxidation of toluene in a plate-type continuous reactor under the indoor condition. PTR-MS investigations indicated that the contaminations with mass 44, 58 and 106 were the main intermediates in the gas phase. They may be acetaldehyde, propionaldehyde and benzaldehyde. However, how to remove the harmful by-products, is still issues needed to solve for PCO technology [17].

Biotechnology represents a fairly new manner for the application of bioprocess engineering in water management. The use of biotechnology for the treatment of VOCs was ever reported for the first time in the United States. Since the late 1980s, Germany and the Netherlands had applied this technology to control VOCs pollution successfully [18]. Additionally, in the last two decades, much research on biological treatment has been carried out in order to

* Corresponding author at: School of Municipal and Environmental Engineering, Harbin Institute of Technology, Box 2651, 73 Haihe Street, Harbin 150090, China. Tel.: +86 451 86282123; fax: +86 451 86282123.
E-mail address: liujinghit0@163.com (J. Liu).

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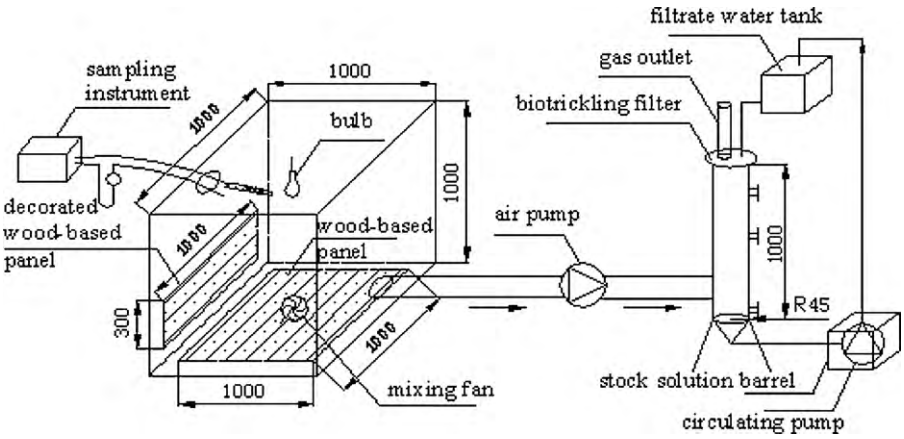

Fig. 1. Schematic diagram of the set-up for the experiments (left: chamber for studying bake-out exhaust; right: biological equipments).

develop an important alternative to many physical and chemical techniques for the treatment of VOCs [19,20]. The advantages of this technology over the above-mentioned air-cleaning methods include (1) the by-products of biodegradation are innocuous and (2) biological processes are readily accepted as an environment-friendly process.

Typical biotechnology has frequently been used for industrial pollutants removal and there have been few reports to treat indoor VOCs. The main objective of this study is to investigate the treatability of indoor VOCs using biotechnology with the combination of bake-out exhaust. The effect of air stream temperature and VOCs concentrations on the biofiltration performance was studied. And the high-efficient bacteria were isolated and identified.

2. Materials and methods

2.1. Experimental apparatus

The experimental apparatus consisted of one test chamber and the biological management installment. The test chamber was used to be a representative of a newly renovated room. The biological management installment was one biotrickling filter with the inside diameter of 9 cm and height of 100 cm (shown in Fig. 1). Because the indoor VOCs concentrations are commonly at low levels, the building material should be baked out to accelerate pollutant volatilization firstly. Bake-out exhaust method can be used to significantly accelerate the release of VOCs from building materials [21]. The research on the effect of bake-out has been well studied in Ref. [22]. Then, the toxic air was introduced into the biotrickling filter by an air pump. After that, purified air was exhausted outside. It is possible to use this air as recirculated air to the room. The remove effect of biotrickling filter was studied. Nourishing cream was put into filtrate water tank, and flowed down biotrickling filter at certain speed of flow, provided the nutrients for microorganism growth in the biotrickling filter. One connecting pipe was set in the lower part of the biotrickling filter. The nourishing cream effluent would enter the stock solution barrel, in which the circulating pump was set. At a fixed time, the nourishing cream was recirculated to the filtrate water tank. Biotrickling filter included the padding where biofilm developed. The microorganisms were taken from the sludge in a municipal sewage treatment plant in Harbin. Based on the previous studies [22,23], the gaseous flow rate, surface liquid velocity and pH were determined at 600 L/h, 3.14 m/h and 6–7, respectively.

2.2. Padding selection for biotrickling filter

The padding was the key component of biotrickling filter, which was used to support the biofilm growth. This experiment utilized pottery piece to make the biotrickling filter padding. The pottery piece was made up of the raw material like shale, the clay, the pulverized coal ash, the industry waste residue. Its hole diameter was 0.5–1 micron approximately, with the large relative surface to accumulation and the strong adsorptive capacity. In addition, the material was light and hard, and had widespread source, which made it become the ideal microorganism padding.

2.3. Humidity condition of padding

The padding humidity was the most important operation parameter for the biotrickling filter. If the padding humidity was too low, it could cause the microorganism death, and the padding could also shrink to burst and produce the gas short flow. On the other hand, if padding humidity was too high, then it not only resulted in compaction for reducing porosity and leading to high back-pressure, but also caused insufficient oxygen and anaerobic condition, which would produce the fetid odor and accelerate the reduction of biodegradation.

2.4. Analysis

Adsorption tubes containing special activated charcoal were used to take 10-L VOCs air samples and 5-mL re-distilled water was used to absorb formaldehyde. A spectrometer was used to analyze absorbency of formaldehyde. After comparing with demarcated curve about absorbency, concentration of formaldehyde was determined. VOCs were extracted from activated carbon with 2-mL CS_2 and quantitatively analyzed by gas chromatography/mass spectrometry (GC/MS). FID was used to detect benzene, toluene and xylene. All measurements were carried out according to national indoor air quality standard methods (GB/T 18883—2002).

2.5. Bacteria isolation and identification

Bacterium was isolated and stored by three different kinds of culture mediums. Table 1 shows the compositions of mediums for identification.

In sterile lab, 10 g padding was taken from the biotrickling filter and diluted by 90 mL sterilized water in 250 mL Erlenmeyer flask with glass beads. After being mixed for 20 min in a rotary shaker at 120 rpm, 1 mL mixture was taken and diluted with 9 mL sterilized water to be a fresh mixture. 1 mL of the new mixture was taken and

Table 1
Compositions of mediums.

Medium	Component (1000 ml)				
(1) Basal medium	Agar (18 g)	Peptone (10 g)	Beef broth (5 g)	NaCl (5 g)	pH (7.0)
(2) Selective mediums (4 kinds)	Agar (18 g)	$MgCl_2{\cdot}6H_2O$ (3.34 g)	NH_4Cl (2 g)	NaH_2PO_4 (1 g)	pH (7.0)
	$FeSO_4{\cdot}7H_2O$ (0.012 g)	$MnSO_4{\cdot}7H_2O$ (0.003 g)	$ZnSO_4{\cdot}7H_2O$ (0.003 g)	$CoSO_4{\cdot}7H_2O$ (0.001 g)	
	After autoclaved at 121 °C, formaldehyde, benzene, toluene or xylene was supplied.				
(3) Enrichment mediums (4 kinds)	NaCl (5 g)	$MgCl_2{\cdot}6H_2O$ (3.34 g)	KH_2PO_4 (1 g)	$(NH_4)_2SO_4$ (1 g)	pH (7.0)
	$ZnSO_4{\cdot}7H_2O$ (0.003 g)	$CoSO_4{\cdot}7H_2O$ (0.001 g)	$FeSO_4{\cdot}7H_2O$ (0.012 g)	$MnSO_4{\cdot}7H_2O$ (0.003 g)	
	After autoclaved at 121 °C, formaldehyde, benzene, toluene or xylene was supplied.				

diluted once again. With such repeating procedures, the filling was diluted to 10^{-6} fold.

0.1 mL dilution was taken from the Erlenmeyer flask and placed on the plate with basal medium, which was cultured in an incubator. Then the bacteria were transferred from basal medium to selective medium with one of formaldehyde, benzene, toluene or xylene. Because the pollutant was the sole carbon source of the selective medium, the bacteria that could grow on the culture medium were the ones able to biodegrade the pollutant.

Each bacterium that could grow on the selective medium was then transferred to the enrichment medium. The bacteria that are capable of making a maximum decrease of pollutant concentration in the plates were the optimum strain. In the case of formaldehyde, the bacteria that made the maximum formaldehyde concentration change in the plate were defined as the best strain L1. The other three high-degrading bacteria were also obtained by this approach. The results were given for benzene, L2; for xylene, L3; and for toluene, L4.

L1, L2, L3 and L4 were identified according to the following two methods.

2.6. Bacteria identification

L1, L2, L3 and L4 were isolated and identified by the physiological and biochemical experimental methods which are: (1) oxidase test; (2) catalase test; (3) glucide ferment and oxidation test; (4) hydrolysis of starch test; (5) methyl red test; (6) Voges-Proskauer test; (7) nitrate deoxidize test.

Each isolated bacterium was inoculated on the plate medium with four quadrant separate parts. For the optimum analysis of the concentration, bacterial cells were taken from the third quadrant among four quadrant separate parts of the plate after their growing up and they were identified by gas chromatography (GC).

2.7. Removal efficiency

Both the inlet and outlet of VOC concentrations were measured to estimate the removal efficiency of biotrickling filter, as given by Eq. (1).

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

where η is the removal efficiency of biotrickling filter (%), C_{out} the outlet air concentration (mg/m^3) and C_{in} is the inlet air concentration (mg/m^3).

3. Results and discussion

3.1. Strain identification results

Different bacterial strains have different pathways of metabolism, which results in different degradation of certain carbon and nitrogen compounds. The results of physiological and biochemical experiments are shown in Table 2. Using gas chromatography of bacterial fatty acids with the MIDI Sherlock Microbial Identification System, L1–L4's fatty acids are presented in Fig. 2. Combined identification results of physiological and biochemical experiments, the bacterium was confirmed that L1 is *Pseudomonas* sp., L2 is *Kocuria* sp., L3 is *Arthrobacter* sp., and L4 is *Bacillus* sp.

3.2. Effect of temperature

Temperature is an important ecological factor for biosystem. According to the method proposed in this study, the air stream

Table 2
Main physiological and biochemical characteristics of bacteria.

Physiological and biochemical	L1	L2	L3	L4
Oxidase	+	+	–	+
Catalase	+	–	+	+
Glucide ferment and oxidation	Oxidation + ferment –	Oxidation + ferment +	Oxidation + ferment +	Oxidation + ferment +
Hydrolysis of starch	–	–	–	–
Methyl red test	–	+	+	–
Voges-Proskauer	–	–	–	–
Nitrate deoxidize	+	–	–	+
Identification	*Pseudomonas* sp.	*Kocuria* sp.	*Arthrobacter* sp.	*Bacillus* sp.

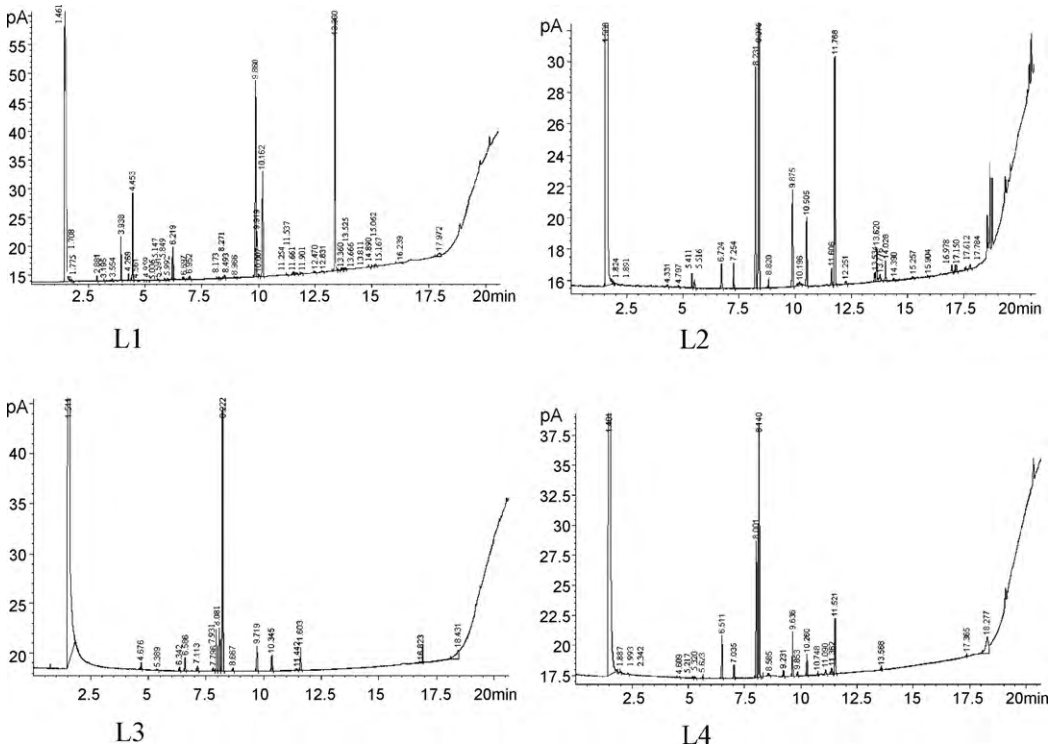

Fig. 2. Chromatograms of L1–L4 for bacterial fatty acids.

should be baked out before biological treatment. Therefore 30 °C and 40 °C were selected to illustrate the effects of different bake-out temperatures on biofiltration performance. Removal efficiencies of indoor decoration noxious air by the biotrickling filter processing at 30 °C and 40 °C are shown in Figs. 3 and 4.

It can be seen that the removal efficiency of benzene was 65–70% when bake-out temperature is kept at 30 °C, while the removal efficiencies of toluene and xylene reached about 93% and 85%, respectively. Nevertheless, when temperature was raised to 40 °C, the removal efficiencies of benzene dropped to 48.9–73%, while

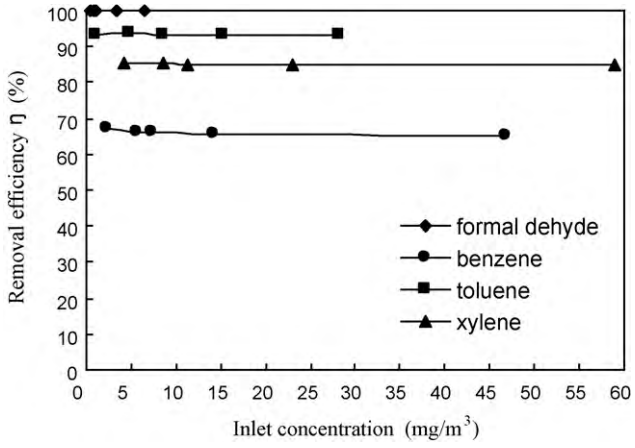

Fig. 3. Removal efficiencies vs. as function of inlet VOCs concentrations at 30 °C.

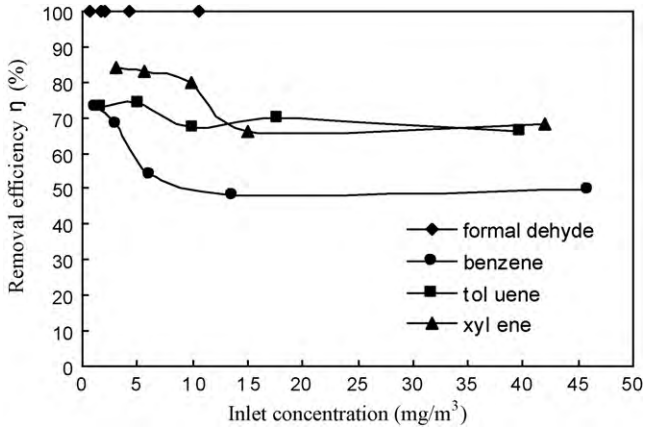

Fig. 4. Removal efficiencies vs. as function of inlet VOCs concentrations at 40 °C.

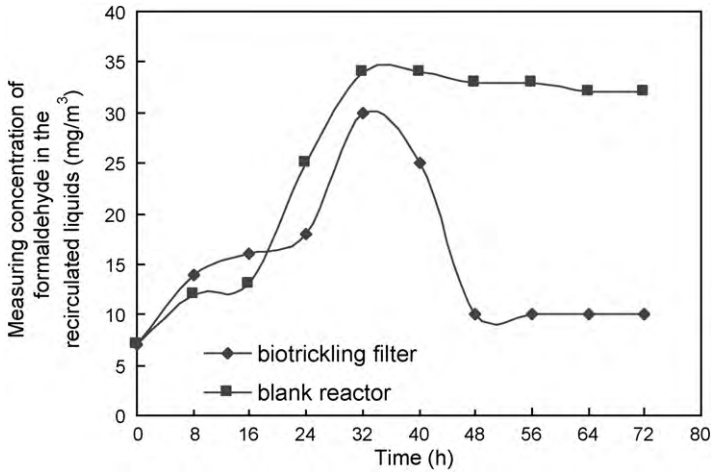

Fig. 6. Contrast experiment results of formaldehyde degradation.

the removal efficiencies of toluene and xylene dropped to 66.2–75% and 66.3–84%, respectively. Removal efficiencies at 30 °C are higher than that at 40 °C. The most likely reason for this difference is that, the *Pseudomonas* is the superiority bacteria in biotrickling filter, its proper temperature range for the growth is 1–37 °C, and the most suitable temperature for bio-activity is about 26 °C [24].

3.3. Effect of initial VOCs concentration in the air stream

The emission rates and corresponding VOCs concentrations are determined by bake-out effects. In this study, the highest concentrations of formaldehyde, benzene, toluene and xylene in the air stream were 6.578, 46.733, 28.254 and 59.008 mg/m^3, respectively at 30 °C, which were about 5 times of the actual indoor VOCs concentrations in Harbin without bake-out [25]. The relationship between removal efficiencies and initial VOCs concentrations in the air stream is given in Fig. 5.

It can be seen that removal efficiencies were over the range of 65–70%, 93% and 85–90% when the concentrations of benzene, toluene and xylene in the air stream were fixed at 2.2–46.7 mg/m^3, 0.5–28.2 mg/m^3 and 4.1–59.0 mg/m^3, respectively. On the other hand, formaldehyde can be completely removed when its concentration in the air stream was lower than 6.5 mg/m^3. This could be explained by the fact that the formaldehyde is one of the highly soluble pollutants, especially easy to dissolve in the water under the normal temperature. Its highest aqueous-solution concentration can achieve up to 55% [26]. That formaldehyde released from indoor decoration is not only decomposed by biodegradation, but also absorbed by liquid which is sprayed into the biotrickling filter.

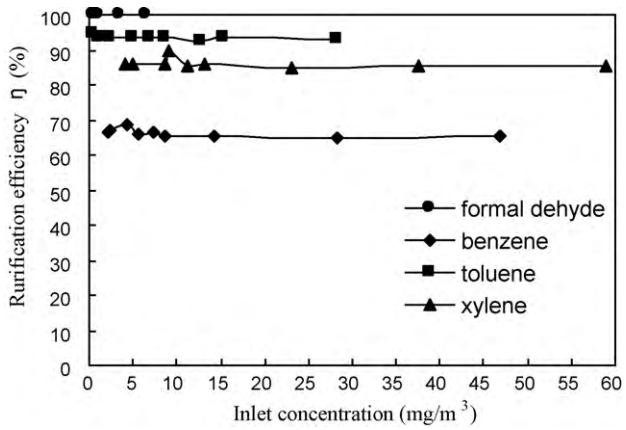

Fig. 5. Removal efficiencies vs. as function of inlet VOCs concentrations.

To verify the removal of formaldehyde, the carriers without biofilm development were placed in the blank reactor that was operated under the same conditions as the biotrickling filter. The roles of microbial metabolisms during pollutant degradation were investigated by measuring concentration of formaldehyde in the recirculated liquids of the different reactors at a given time interval. The results were shown in Fig. 6. At the initial stage of the experiment, the biotrickling filter had the same performance to the blank reactor. The concentration of formaldehyde in the recirculated liquid varied with time, reaching its maximum for the two reactors after 32 h. Thereafter, the formaldehyde concentration in the biotrickling filter began to decrease at a rate being faster than that in the blank reactor. This can be demonstrated by stable concentration of formaldehyde in the biotrickling filter as compared with no change for the blank reactor after 48 h. Hence, the degradation of formaldehyde should be a result of microbial metabolisms of biofilm in the biotrickling filter.

4. Conclusions

(1) Four bacterial strains were isolated and screened from the biotrickling filter for the biodegradation of formaldehyde, benzene, toluene and xylene. By means of physiological and biochemical experiments and the resulting bacterial fatty acids, four strains are identified to be *Pseudomonas* sp., *Kocuria* sp., *Arthrobacter* sp. and *Bacillus* sp.

(2) Under gas flow rate of 600 L/h, surface liquid velocity of 3.14 m/h, pH of 6–7 and temperature of 30 °C, for formaldehyde, benzene, toluene and xylene in the air stream with the concentration of 0–6.5 mg/m^3, 2.2–46.7 mg/m^3, 0.5–28.2 mg/m^3 and 4.1–59.0 mg/m^3, VOCs removal efficiencies of biotrickling filter ranged in about 100%, 65–70%, 93% and 85–90%, respectively.

(3) As verified by experimental data presented herein, the biological treatment could be effective as a manner for removing indoor VOCs. It is recommended to bake-out prior to treatment, as it could achieve a high VOC level required for bioremediation. Further research will focus on the evaluation of this strategy in real VOC-emission buildings and then develop the guidelines for field application.

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