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Comparative study of the eliminating of waste gas containing toluene in twin biotrickling filters packed with molecular sieve and polyurethane foam

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ABSTRACT

Two kinds of packing materials, molecular sieve (MS) and polyurethane foam (PUF), were loaded into two identical biotrickling filters respectively to compare the microbial removal efficiency of waste gas containing toluene by seeding with same bacteria. The affecting parameters of the removal performance, such as gas flow rates, inlet toluene concentrations, periods of starvation, were investigated in detail in biotrickling filters. The results demonstrated that both of the packing materials exhibited high toluene degradation efficiency when the gas flow rates ranged from 100 L h^{-1} to 600 L h^{-1}. For MS, the total maximum removal efficiency (RE) of toluene maintained 100% when the gas flow rates increased from 100 L h^{-1} to 200 L h^{-1} accompanied with the decrease of empty bed residence time (EBRT) from 266 s to 133 s. However, as for PUF, merely 97.64% RE was obtained at the gas flow rate of 100 L h^{-1} and the EBRT of 266 s. With further increasing the gas flow rates (to 600 L h^{-1}) and decreasing the EBRTs (to 44 s), both the total REs of toluene for MS and PUF decreased to 70.68% and 63.18%, respectively. When varying the inlet toluene concentrations, the REs for MS are able to maintain nearly 100% at the inlet concentration of 9.19 mg L^{-1} or below, and with the maximum elimination capacity (EC) of 373.24 g m^{-3} h^{-1} (RE = 100%) at the inlet concentration of 9.19 mg L^{-1}. Contrastively, the maximum EC of PUF was only 119.41 g m^{-3} h^{-1} (RE = 56.66%) at the inlet concentration of 5.19 mg L^{-1}. As illustrated by different starvation period (2, 10 and 60 days), MS possessed shorter recovery time (9 h for 2 days, 17 h for 10 days and 324 h for 60 days starvation, respectively) than PUF (14 h for 2 days, 24 h for 10 days and 324 h for 60 days starvation, respectively). Based on its higher removal capacity of toluene and shorter recovery time, MS would be a better choice than PUF for packing material used for biotrickling filter.

1. Introduction

In the past few decades, human being has been suffering increasingly from severe industrial air pollutions [1], Notably, volatile organic compounds (VOCs), which are by-products of the production and application of pesticides, varnish, adhesives, and so on, have imposed a crucial adverse effect on the healthy and environmental problems [2]. Benzene, toluene, ethyl benzene and xylene (BTEX) is one group of the most typical VOCs from these emission sources [3]. Thus, the Clean Air Act Amendments proposed in 1990 by the US Environmental Protection Agency pays special attention to the manufacture, usage and treatment of BTEX which are among the 188 hazardous air pollutants regulated in this recognized Act. Both of the liquid and gaseous states of these compounds in the environment are considered as not only odor nuisance, but also toxic and carcinogenic characteristics which pose a significant threat to human health and the environment [3]. Therefore, to release the threat of BTEX, various treatment methods have been developed globally, most of which are based on the physical or chemical properties of BTEX. The most conventionally used technologies are adsorption, condensation and thermal incineration [4], and they have been proved to be effective in many ways. However they all have certain limitation for further applications. For example, molecular-level destructions of organic pollutants are unavailable for absorption and adsorption methods, which also may suffer certain defects in treating VOCs with low molecular weight [5]. Furthermore, the high cost of space, energy and expenses to manufacture, operate and maintain for condensa-

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tion and combustion equipment may inevitably confine their broad applications.

Quite recently, biological waste gas treatment technologies have attracted considerable attentions due to their advantages of being environment friendly, highly adaptive, efficient and cost-effective [6,7]. Among them, using biofilter and biotrickling filter are the most promising biotechnologies for the removal of airborne pollutants [8]. Biofilter is a substantially compost bed through which the waste gases can pass and simultaneously be absorbed then degraded by the microorganism immobilized on the packing materials [9]. The biotrickling filter operated in a similar way to biofilter, except that nutrimental solution, which contains essential inorganic nutrients such as nitrogen, phosphorous, potassium, and some microelements, is continuously trickled on the packing materials [10]. And biotrickling filter is much easier to control the operational conditions. So biotrickling filter has received increasing attention due to its outstanding capability to eliminate various organic pollutants, such as toluene [11], xylene [12], 1,4-dioxane [13], mono-chlorobenzene [14], mixture of chlorobenzene and 1,2-dichlorobenzene [15] and other odorous compounds [16]. Most of previous research mainly focused on the investigation of kinetics of different waste gases which could be degraded in biotrickling filter and the improvement of various dominant microorganism [17–20].

However, the packing materials were expected to be one of the most important parameters in a biotrickling filter, and the selection of cost-effective packing materials may give us a new choice to solve the drawback of biotrickling filter which is not successfully applied to high-concentrated VOCs treatment. Different packing materials such as ceramic pellets, Pall ring, lava rock or compost (woodchips mixtures) are usually made of natural and inert materials [21]. But the dependence of the pores structure of the packing materials on the removal efficiency of biotrickling filter is rarely reported. Molecular sieve (MS) is a kind of typical microporous material, which was widely used in the field of waste gas and water treatment because of its high absorption capacity [22,23], while polyurethane foam (PUF) belongs to a kind of typical macroporous material, which was also found as an efficient carrier to immobilize microorganism in the field of wastewater treatment [24]. Thus, in this paper, in order to find out one high efficient packing material suited for biotrickling filter for toluene degradation, two different porous packing materials, i.e. microporous MS and macroporous PUF, were loaded into two identical biotrickling filters respectively to compare the eliminating of waste gas containing toluene. Furthermore, some key influencing factors affecting the degradation efficiencies of toluene in the biotrickling filters, such as the gas flow rates, the inlet toluene concentrations and the starvation mode (without liquid recycle and without airflow) were also optimized in detail.

2. Materials and methods

2.1. Description of the packing materials and the microorganism

The packing materials and their physical–chemical characteristics were listed in Table 1. MS Bead with a dimension of 1.9–2.0 mm and the opening Porosity of 50%, was used for this experiment. While the PUF Cube with a dimension of 10.0 mm and the opening Porosity of 96%, was comparably selected for the corresponding packing material. It was also clearly shown that the average aperture of PUF (0.12 mm) was 10^5 times larger than that of MS (10^{-6} mm), while the specific surface area (770–900 $m^2\,g^{-1}$) and bulk density (0.65 $g\,m^{-3}$) of MS were much higher than that of PUF (80–120 $m^2\,g^{-1}$ and 0.024 $g\,m^{-3}$). Optical microscope photographs were employed to observe the microscopical surface structures of MS and PUF. As illustrated in Fig. 1(A), the surface of MS was zoomed in 100 times, it can be seen that the surface was lacking of pores and only some irregular bulges were observed on it. It is because that MS is a kind of microporous material whose average aperture was merely near 1 nm, thus the pores on the surface can not be found with 100 times magnification. In contrast, uniform macropores with the mean pore size of 0.12 mm can be found easily in Fig. 1(B) inside of PUF with the same magnification.

Table 1
The physical–chemical characteristics of the packing materials used in this study.

Packing materials	Molecular sieve	Polyurethane foam
Main composition	Aluminosilicate	Polyurethane
Shape	Bead	Cube
Dimension (mm)	1.9–2.0	10.0
Average aperture (mm)	1.0×10^{-6}	0.12
Specific surface area ($m^2\,g^{-1}$)	770–900	80–120
Porosity (%)	50%	96%
Bulk density ($g\,m^{-3}$)	0.65	0.024
Supplier	Guangzhou Zhonghua trade Co. Ltd., China	Baiyin Yinguang Chemical Co. Ltd., China

The seeded bacterium is *Bacillus cereus* S1, which was originally obtained from a wastewater treatment facility of Guangzhou Petrochemical Corporation. And this strain has been found possessing high removal capacity of toluene and can rapidly recover to its full performance after the starvation [20].

2.2. Description and operation of biotrickling filter

A home-made twin biotrickling filter was employed in this experiment and the schematic diagram is shown in our previous published work [20]. What is different from the former experiment is that the packing materials (MS or PUF) we used to fill each biotrickling filter bed were 480 mm high totally. The *Bacillus cereus* S1 was inoculated into two biotrickling filters after two different packing materials were loaded successfully. 150 mL nutrient medium was sprinkled from the top of each bed every 1.5 h by a rotary distributor in order to provide the necessary nutrients and maintain adequate humidity. The composition of the nutrient medium was the same as in the former published work [20]. The nutrient medium was collected in the lower water tank, then pumped to the upper water tank and cycled by the peristaltic pumps. Two air streams were pumped during the experiment, one of which was used to sparge the toluene from liquid phase to vapor in the liquid bottle and the other was used to dilute and blend the toluene vapor. The toluene vapors with determinate concentrations in the mixed streams were controlled by adjusting the gas flow rate of the former stream. The above mentioned pumps and rotary distributor were all coordinated by microcomputers.

Prior to the experiment, sterile distilled water was passed through the biotrickling filter with sterilized packing materials installed. In order to shorten the start-up stage of the experiment, 1 $mg\,L^{-1}$ liquid phase toluene was added to the cycled nutrient medium and 0.5 $mg\,L^{-1}$ gaseous toluene was blew into the biotrickling filter at the same time. The biofilm on the packing materials of MS was completely formed after 12 days cultivation, while 20 days were required for the packing materials of PUF. Fig. 2(A and B) demonstrates the biofilm morphologies of MS (×250 magnification) and PUF (×200 magnification), respectively. As can be seen from Fig. 2, the MS biofilm appeared full of microorganism colonies, while much less *Bacillus cereus* S1 were observed on PUF. It further confirmed that PUF needs more time to form the biofilm than MS in the start-up period. This maybe explained by the fact that the pores inside of PUF are much larger than that of MS, which is not beneficial to the holding of nutrient medium and the growth of microorganisms. Moreover, the microorganism can also grow inside hole of

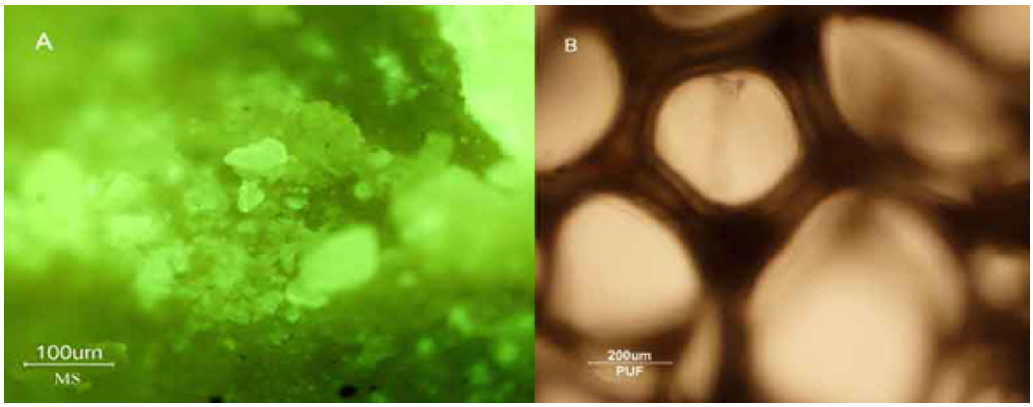

Fig. 1. Optical micrograph: (A) Surface of molecular sieve (100×); (B) surface of polyurethane foam (100×).

the PUF as well as the surface of PUF and MS, thus less bacteria may observe at the surface of PUF than that of MS when the same amounts of bacteria was inoculate.

2.3. Analytical methods

With an airtight syringe, a 200 μL of the toluene sample was collected from the inlet, outlets on the biotrickling filter at regular time intervals, and then toluene concentration was determined by using an HP 6890 gas chromatograph equipped with the FID detector. A DB-5MS (30 m × 0.25 mm × 0.25 μm) capillary column was used for chromatographic separation. The column temperature was programmed to hold at 40 °C for 2 min, increase from 40 °C to 80 °C with 5 °C min^{-1}, followed by an increase to 200 °C with 25 °C min^{-1} (held for 1 min). The carrier gas was ultra-high purity nitrogen at a constant flow rate of 2.2 mL min^{-1}. The temperature of injector was 230 °C and the temperature of detector was 250 °C.

3. Results and discussion

The performance of the biotrickling filter was evaluated in terms of the removal efficiency (RE, %), the total elimination capacity (EC, g m^{-3} h^{-1}) and empty bed residence time (EBRT, s) of the two biotrickling filters, which were calculated by the following equations:

Removal efficiency,

$$RE = \frac{C_{in} - C_{out}}{C_{in}} \times 100\%$$

Elimination capacity,

$$EC = \frac{(C_{in} - C_{out})Q}{1000V}$$

Empty bed residence time,

$$EBRT = \frac{V}{Q}$$

where Q is the gas flow rate (L h^{-1}), V is the volume of the packing materials in the biotrickling filter (m^3), C_{in} and C_{out} are the inlet and outlet gaseous toluene concentrations (mg L^{-1}), respectively.

3.1. Effects of the gas flow rates

The effects of the gas flow rates on the toluene REs of *Bacillus cereus* S1 seeded onto different packing materials (MS and PUF) in the biotrickling filter were compared at a fixed inlet concentration of around 2.0 mg L^{-1} toluene, with the gas flow rates were changed between 100 L h^{-1} and 600 L h^{-1}. Fig. 3 shows the influence of the gas flow rates on the REs of toluene. Lower gas flow rates generally led to higher REs for both packing materials. However, MS and PUF exhibited different trends for toluene degradation. For the MS, the maximum total RE maintained 100% when the gas flow rate increased from 100 L h^{-1} to 200 L h^{-1} with the decrease of EBRT from 266 s to 133 s correspondingly (Table 2). Notably, at 266 s of EBRT, the toluene could be thoroughly removed when the gas passed through the third layer of the biotrickling filter with the removal rate of 81.57% at the first layer, and 15.92% at the second

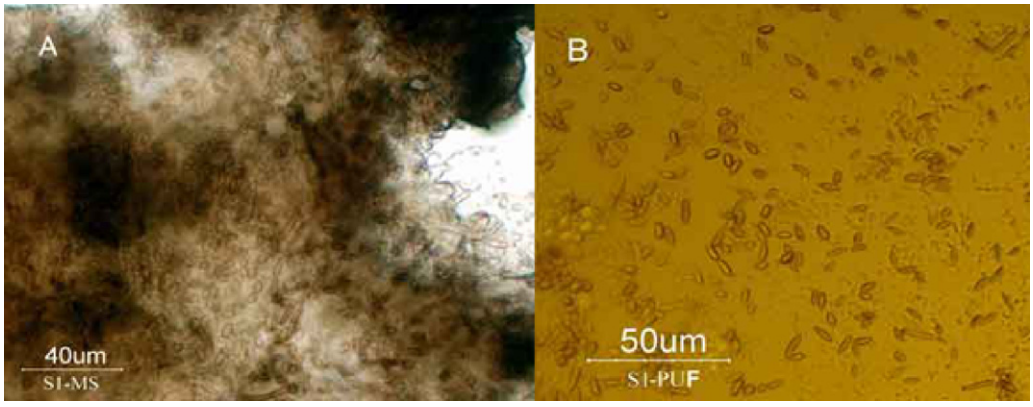

Fig. 2. Optical micrograph: (A) Microorganisms immobilized on molecular sieve (250×), (B) Microorganisms immobilized on polyurethane foam (200×).

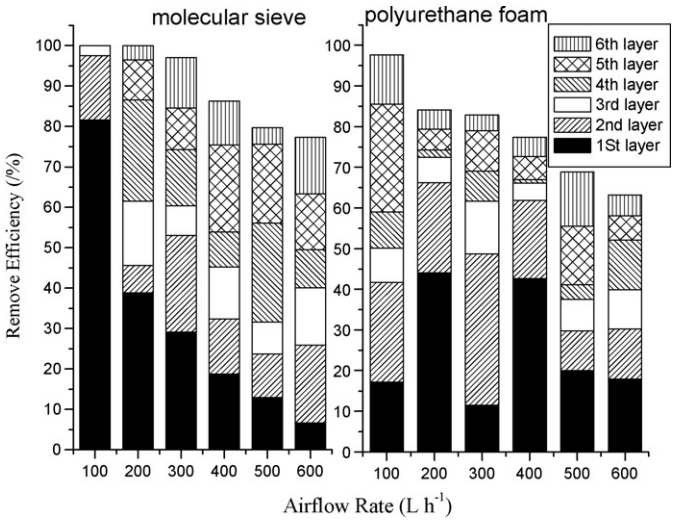

Fig. 3. Removal efficiency comparison of the biotrickling filters loaded with molecular sieve and polyurethane foam at different gas flow rates: the inlet toluene concentration: 2.0 mg L^{-1}.

layer. Obviously, large quantity of toluene (97.49%) was degraded at the first two layers. However, with the decrease of EBRT to 133 s, 100% RE could not be obtained until the gas reached the sixth layer. With further increasing the gas flow rate and decreasing the EBRT, the total toluene REs decreased slightly to 71% with the gas flow rate at 600 L h^{-1} and corresponding EBRT at 44 s. Unlike the change trend of REs, the total EC showed reverse trend. With the falling of EBRT from 266 s to 44 s, EC increased from 27.88 g m^{-3} h^{-1} to 111.16 g m^{-3} h^{-1} (Table 2) for MS material.

Comparatively, PUF possessed much lower RE and EC than MS. Total toluene RE maximized at 97.64% with the EBRT of 266 s (100 L h^{-1}) and decreased sharply to 84.11% with the EBRT of 133 s (200 L h^{-1}). Further increasing the gas flow rate from 300 L h^{-1} to 600 L h^{-1}, the RE dropped monotonously to 63.18% (Table 2). The total EC for PUF showed the similar trend as MS. The longer the EBRT is, the lower the total EC is. The reason why we got this trend was that the removal efficiencies were mainly controlled by mass transfer of toluene from the air to the biofilm and gas phase boundary layer, which were in fact controlled by the EBRT of the biotrickling filter. The lower the gas flow rate, the longer the gas contact time between toluene and microorganisms was, facilitating enough time for microbes to biodegrade toluene completely. At the same inlet toluene gas rates and the same inlet gas concentration range, the ECs were 1.5 or 80 times higher than those reported for other bacterial systems [25,26].

It is also noteworthy that, when gas flow rates were not higher than 300 L h^{-1}, a high and steady RE could be obtained for both MS and PUF packing materials. Therefore, in all further experiments, 300 L h^{-1} was chosen as the optimum gas flow rate for both reactors to remove the toluene. Known from the above results, it could be concluded that the MS packing material has a higher and more stable removal capacity than PUF when the same bacteria, *Bacillus cereus* S1 was seeded. It maybe explained by the fact that in the biotrickling filter, the bacteria were immobilized onto the surface rather than inside hole of MS and PUF. After the microorganisms were incubated for a certain time, the biofilms were formed and immobilized onto the surface of carriers. And thus the biodegradation of organic pollutants occurred at the surface of biofilms rather than inside hole of MS and PUF. Thus, the perfect immobilized microorganism carrier with higher BET, for example MS, may have much wonderful holding effect than that of with small BET, for example PUF, for organic waste gas. Thus these adsorption and degradation cycle procedures will prolong the contacted time between the organic waste gas and the biofilms coated onto the surface of with high BET carrier, resulting in the enhancement the degradation efficiencies of waste gas.

3.2. Effects of inlet toluene concentrations

The gas flow rate was set at 300 L h^{-1} with the corresponding EBRT at 88 s when the effect of inlet toluene concentrations was optimized in this paper. The inlet toluene concentration varied from 1.10 mg L^{-1} to 12.96 mg L^{-1} for MS and from 1.08 to 5.19 mg L^{-1} for PUF. The effect of inlet toluene concentration was determined by regularly analyzing the outlet toluene concentrations of each layer of the biotrickling filter. The system was stabilized first for 24 h for good equilibrium after two different inlet toluene concentrations were adjusted. The ECs of MS and PUF in total and each layer at different inlet toluene concentrations were plotted in Fig. 4. Initially, the total EC of biotrickling filter packed with MS increased rapidly from 44.62 g m^{-3} h^{-1} to a maximum value of 373.24 g m^{-3} h^{-1} at an inlet toluene concentration of 9.19 mg L^{-1}, and then slightly decreased to 315.86 g m^{-3} h^{-1} as the inlet gas concentration increased up to 12.96 mg L^{-1}. It is also worth pointing out that the total RE does not show remarkable decrease with the rapid increase of the inlet gas concentration (Table 3). The REs steadily maintained at about 100% when the inlet toluene concentration was below 9.19 mg L^{-1}, while with further increasing the toluene concentration, the REs would decrease gradually to 60.02% at the inlet toluene concentration of 12.96 mg L^{-1}. The same changing trend was also observed for the ECs of the biotrickling filter. The results indicated that when the inlet toluene concentrations increased to a relative high level, the performance of the biotrickling filter would decrease remarkably. In other words, there existed a maximum tolerant concentration of inlet toluene. It was noticeable that, at the same maximum inlet toluene concentration, the ECs were twice as high as the previous research [27], and much higher than previous publications for toluene degradation in biotrickling filters [28].

For PUF packing material, with the increase of the inlet toluene concentration, the total EC increased slowly, and the RE also decreased gradually. The maximum total RE was only 84.9% (Table 3) at an inlet toluene concentration of 1.08 mg L^{-1} with the total EC of 37.14 g m^{-3} h^{-1}. A slight decrease in the total RE (82.83%)

Table 2
The removal efficiency at different gas flow rate as a function of EBRT.

Gas flow rate (L h^{-1})	EBRT (s)	Molecular sieve		Polyurethane foam	
		RE (%)	EC (g m^{-3} h^{-1})	RE (%)	EC (g m^{-3} h^{-1})
100	265.87	100	27.88	97.64	26.53
200	132.96	100	51.39	84.11	47.62
300	88.64	97.05	78.21	82.83	72.36
400	66.48	86.30	99.08	77.40	81.48
500	53.17	79.69	107.32	68.82	92.16
600	44.32	70.68	111.16	63.18	109.62

The inlet toluene concentration: 2.0 mg L^{-1}.

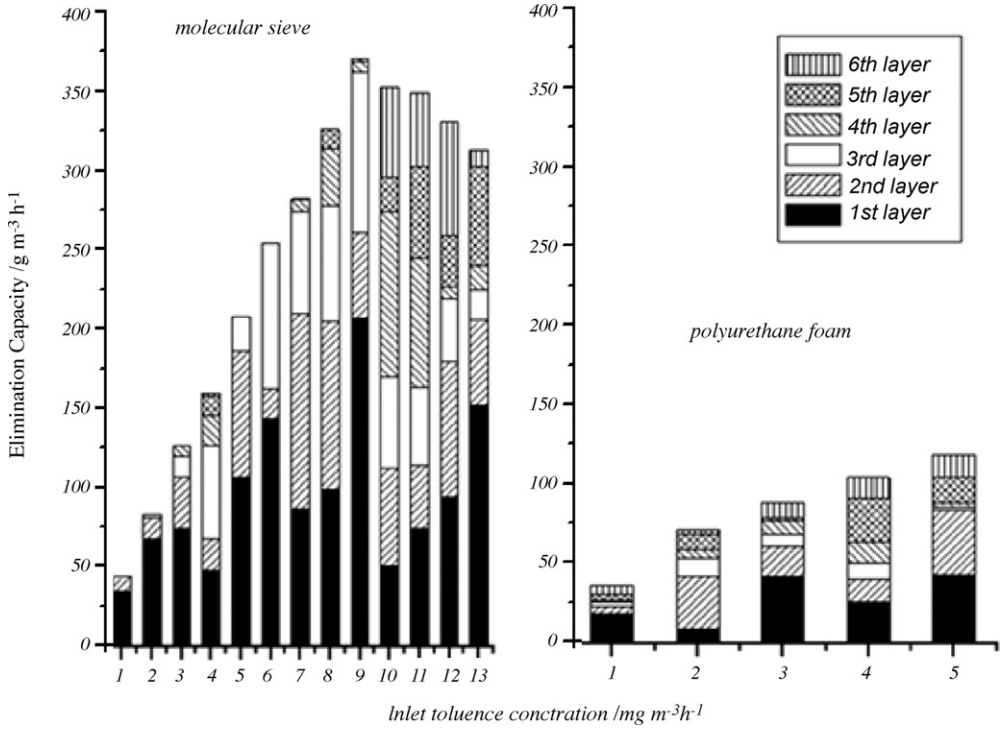

Fig. 4. Elimination capacities comparison of the biotrickling filters loaded with molecular sieve and polyurethane foam at different inlet toluene concentrations: the gas flow rate: 300 L h^{-1}. *Molecular sieve*: 1: 1.10 mg L^{-1}; 2: 2.06 mg L^{-1}; 3: 3.15 mg L^{-1}; 4: 3.97 mg L^{-1}; 5: 5.16 mg L^{-1}; 6: 6.33 mg L^{-1}; 7: 7.02 mg L^{-1}; 8: 8.09 mg L^{-1}; 9: 9.19 mg L^{-1}; 10: 10.18 mg L^{-1}; 11: 11.21 mg L^{-1}; 12: 12.20 mg L^{-1}; 13: 12.96 mg L^{-1}; *Polyurethane foam*: 1: 1.08 mg L^{-1}; 2: 1.94 mg L^{-1}; 3: 3.02 mg L^{-1}; 4: 4.09 mg L^{-1}; 5: 5.19 mg L^{-1}.

and steep increase in the total EC (72.36 g m^{-3} h^{-1}) were observed when the inlet toluene concentration was increased to 1.94 mg L^{-1}. As further increasing the inlet toluene concentration, the total RE decreased sharply, and the total EC increased slowly. And the maximum EC was peaked at 119.41 g m^{-3} h^{-1} with the corresponding RE of 56.66% at the highest inlet gas concentration of 5.19 mg L^{-1}. (Table 3; Fig. 4.)

Obviously, both of the EC and RE of PUF were much lower than those of MS at the approximately equivalent inlet toluene concentration. Moreover, the biotrickling filter packed with MS appeared much steadier (an average toluene EC of 248.28 g m^{-3} h^{-1} and RE of 91.60% at all studied toluene concentrations) than that packed with PUF (an average toluene EC of 82.37 g m^{-3} h^{-1} and RE of 72.07%) at an EBRT of 66.48 s. It was also worthwhile to mention that, an optimized point (inlet concentration = 9.19 mg L^{-1}, RE = 100%, EC = 373.24 g m^{-3} h^{-1}) could be observed for the performance of MS-packed biotrickling filter, while the EC of PUF-packed biotrickling filter increased monotonously to the maximum value at last as the increase of inlet toluene concentration. This can be interpreted that MS is a kind of microporous carrier and the pores on the surface are smaller than 2 nm, and the size of toluene molecule (*ca.* 0.6 nm) was close to the pores sizes of MS, thus the toluene molecule could pass through the liquid film and be hold into the inside and outside of micropores and then be biodegraded by the bacteria loaded onto the MS. In contrast, PUF is full of macropores with the average diameter of 0.12 mm (much larger than that of toluene molecule), thus toluene molecule was much smaller than the pore sizes of PUF (200 times to the size of toluene), thus the toluene molecule can easily pass through the macropores of PUF without any holding effect inside and outside of PUF material.

Table 3
The removal efficiency of molecular sieve and polyurethane foam at different initial concentrations of toluene.

Molecular sieve			Polyurethane foam		
Concentration (mg L^{-1})	Total RE (%)	Total EC (g m^{-3} h^{-1})	Concentration (mg L^{-1})	Total RE (%)	Total EC (g m^{-3} h^{-1})
1.10	100	44.62	1.08	84.90	37.14
2.06	100	83.59	1.94	82.83	72.36
3.15	100	127.81	3.02	72.70	89.22
3.97	100	161.31	4.09	63.28	105
5.16	100	209.41	5.19	56.66	119.41
6.33	100	256.83			
7.02	100	284.89			
8.09	100	328.51			
9.19	100	373.24			
10.18	86.03	355.69			
11.21	77.35	351.91			
12.20	67.40	333.98			
12.96	60.02	315.86			
Average	91.60	248.28		72.07	82.37

The gas flow rate: 300 L h^{-1}.

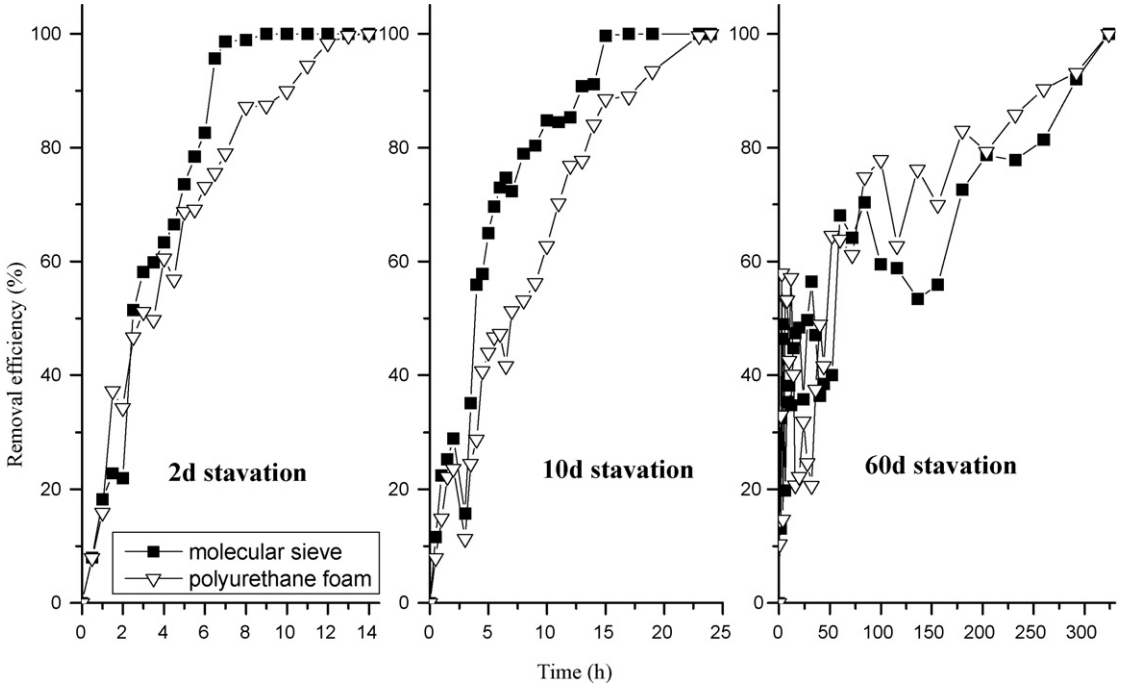

Fig. 5. Re-acclimation period after starvation: the inlet toluene concentration: 2.0 mg L^{-1}; the gas flow rate: 300 L h^{-1}.

3.3. Biotrickling filter starvation

The performance of biotrickling filters is usually studied under relatively ideal situations, such as steady-state and well-supply operation in laboratory systems [29]. However, operational problems undetected in the laboratory may burst out when the pilot scale biotrickling filter was operated in industrial settings [30]. Therefore, it is meaningful to investigate the test of the recovery of the performance of the biotrickling filter after a certain starvation period. The starvation period may be caused by the interruptions in the plant operation, such as weekend shutdown, holiday breaks and equipment up-gradations, which can often lead to temporary lack of the feed of waste gas or nutrient medium in the real industrial operation. Therefore, in the present experiment, the bacteria loaded onto different packing materials (MS and PUF, respectively) were compared for their recovery from the starvation without toluene and nutrient medium for a pre-regulated period in order to mimic practical shutdown. For each of the biotrickling filters, the standard operation was selected in the experiments. The concentration of toluene was 2.0 mg L^{-1} and the flow rate was 300 L h^{-1}, with the corresponding EBRT of 88.64 s was conducted after starvation for 2, 10, and 60 days, respectively. The effect of starvation was determined by comparing the REs of the biotrickling filters before and after the different starvation intervals, and the re-acclimation profiles were demonstrated in Fig. 5. It could be seen that, for both kinds of packing materials, relative high RE appeared shortly after the restart when compared with the starvation phase, and then a sudden decline in REs could be observed in 2 h and 3 h respectively after 2 and 10 days of starvation. Subsequently, the toluene degradation capability recovered gradually and reached a RE of 100% finally within 13 h and 23 h. But after the starvation for 60 days, the values of REs fluctuated obviously. Two possible reasons may explain the experimental results. One reason is that a significant decrease in microbial population may occur during starvation resulted from biomass death and lysis [30]. Nutrients were released by biomass death and lysis, and then employed by the primary degraders after resuming toluene and mineral medium supply. So the REs were higher than before starvation periods initially. The high loading carbon source and mineral medium supply may exceed the tolerance of those primary degraders later, the direct results of this step are metabolism and re-acclimation, because some of the microorganisms could not endure the high concentration of nutrient they die, the other adapted themselves to this condition and then survived and propagated. As the re-acclimation continued, more bacteria with higher adaptability were propagated and thus the RE was recovered. The other reason is that the starvation period may result in the decrease of the thickness of biofilm and an increase in gas-biofilm interfacial area, which may lead to higher performance at the beginning of the re-acclimation. In the starvation period, the liquid film on the biofilm was gradually thinner and when the reactor recover from the starvation, the mineral salt medium was besprinkled on the surface of the biofilm periodically that should make the liquid film thicker. The starvation occurred on the biofilm, the thinner liquid film can shorten the diffusion distance of toluene, therefore the toluene degradation by bacteria is easier and the process is shorter. After a period of time, the liquid film became thicker and thicker, the diffusion of toluene from gas phase to liquid film and then to biofilm becomes more difficult, and then some declines of REs appeared. Finally, the microorganisms adapted well to the change of the circumstance in the biotrickling filter, and the REs began to recover.

Generally, the MS-packed biotrickling filter possesses higher degradation capacity than PUF-packed one. After starvation for 2 days, only 9 h was required for 100% RE recovery for MS-packed bed while the corresponding time for PUF-packed bed was 14 h. The very similar recovery trends were also observed for 10 days starvation, as shown in Fig. 5, which exhibited a sudden fall in the toluene REs first and a quick recovery subsequently. The recovery times were 17 h (RE = 100%) and 24 h (RE = 100%) for MS and PUF, respectively. It should be noted that the REs of MS-packed bed are higher than the maximum REs of PUF-packed bed in the relevant starvation period. After starvation for 60 days, the REs for both kinds of packing materials fluctuated from about 20% to 60% in the re-acclimation period of 24 h. Interestingly, before the recovery of 72 h, the RE of MS is higher than that of PUF, but in the following period, PUF appeared more effectively in the recovery of degrada-

tion capability than MS. The REs increase gradually and smoothly to 100% after 136 h recovery for MS and 204 h for PUF. The total re-acclimation period lasted 324 h (13.5 days) for both kinds of packing materials. One thing also worth mentioning is that PUF appeared more effective in the recovery of degradation efficiencies than MS after 60 days of starvation. The reason for this is that the biofilm on the surface of MS could not survive for such a long time, but the bacteria attached into the holes of PUF may get support from the water and nutrition holding by the packing material in the longer starvation period, so more bacteria could survive on PUF rather than MS.

To the best of our knowledge, the re-acclimation times for both kinds of packing materials were found to be much shorter than previous reports [14], which further confirmed that the biotrickling filter could be effectively used to treat toluene emitted from the systems with weekend shutdown (2 days), holiday breaks (10 days) or equipment up-gradations (60 days). It also could be concluded that MS-packed biotrickling filter possesses not only a higher toluene removal capacity but also a shorter recovery time than PUF-packed one in the current experiments.

4. Conclusions

Two kinds of packing materials were employed for comparison of toluene degradation abilities in a twin biotrickling filters. The removal capability of toluene in the biotrickling filter strongly depended on the packing materials, inlet gas flow rate (EBRT) and gas concentration. Under the same treatment conditions, with the decrease of EBRTs from 266 s to 44 s, the RE fell from 100% to 70.68% for MS, and from 97.64% to 63.18% for PUF, respectively. MS-packed bed maintained a RE of 100% at the EBRTs of 133 s and 266 s. The effect of the inlet toluene concentrations on the performance of the two kinds of the packing materials at fixed EBRT also varied dramatically. However, MS-packed bed had higher ECs and REs than PUF-packed one at the same inlet toluene concentration. The maximum total ECs for MS and PUF-packed beds were 373.24 $g\,m^{-3}\,h^{-1}$ and 119.41 $g\,m^{-3}\,h^{-1}$ at the inlet toluene concentrations of 9.19 $mg\,L^{-1}$ and 5.19 $mg\,L^{-1}$, respectively. The biotrickling filter packed with MS was capable of recovering to its full performance rapidly after different periods of starvation. By comparison, it took longer time for the PUF-packed biotrickling filter to fully recovery. Conclusively, MS packing material is superior to PUF packing material for the removal of gaseous toluene based on their removal capacity and starvation recovery time.

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References

[1] N.D. Nevers (Ed.), Air Pollution Control Engineering, second ed., McGraw-Hill Companies, Inc., New York, 2000.
[2] W.L. Lau, L.Y. Chan, Commuter exposure to aromatic VOCs in public transportation modes in Hong Kong, Sci. Total Environ. 308 (1–3) (2003) 143–155.
[3] C.T. Chang, B.Y. Chen, Toxicity assessment of volatile organic compounds and polycyclic aromatic hydrocarbons in motorcycle exhaust, J. Hazard. Mater. 153 (3) (2007) 1262–1269.
[4] J.S. Devinny, M.A. Deshusses, T.S. Webster (Eds.), Biofiltration for Air Pollution Control, Lewis Publishers, Boca Raton, 1999.
[5] H.H.J. Cox, M.A. Deshusses (Eds.), Biotrickling Filters for Air Pollution Control, John Wiley, New York, 2002.
[6] M.C. Delhomenie, M. Heitz, Biofiltration of air: a review, Crit. Rev. Biotechnol. 25 (1–2) (2005) 53–72.
[7] H.H.J. Cox, M.A. Deshusses, Biological waste air treatment in biotrickling filters, Curr. Opin. Biotechnol. 9 (3) (1998) 256–262.
[8] C. Kennes, M.C. Veiga (Eds.), Bioreactors for Waste Gas Treatment, Kluwer Academic Publishers, Dordrecht, The Netherlands, 2001.
[9] M.C. Delhomenie, L. Bibeau, N. Bredin, S. Roy, S. Broussau, R. Brzezinski, J.L. Kugelmass, M. Heitz, Biofiltration of air contaminated with toluene on a compost-based bed, Adv. Environ. Res. 6 (3) (2002) 239–254.
[10] V. Alopaeus, K. Hynynen, J. Aittamaa, M. Manninen, Modeling of gas–liquid packed-bed reactors with momentum equations and local interaction closures, Ind. Eng. Chem. Res. 45 (24) (2006) 8189–8198.
[11] H.H.J. Cox, T.T. Nguyen, M.A. Deshusses, Toluene degradation in the recycle liquid of biotrickling filters for air pollution control, Appl. Microbiol. Biotechnol. 54 (2000) 133–137.
[12] Q. Liu, A.E. Babajide, P. Zhu, L.P. Zou, Removal of xylene from waste gases using biotrickling filters, Chem. Eng. Technol. 29 (3) (2006) 320–325.
[13] M.J. Zenker, R.C. Borden, M.A. Barlaz, Biodegradation of 1,4-dioxane using trickling filter, J. Environ. Eng. ASCE 130 (9) (2004) 926–931.
[14] A.K. Mathur, J. Sundaramurthy, C. Balomajumder, Kinetics of the removal of mono-chlorobenzene vapour from waste gases using a trickle bed air biofilter, J. Hazard. Mater. 137 (3) (2006) 1560–1568.
[15] C. Seignez, N. Adler, C. Thoeni, M. Stettler, P. Peringer, C. Holliger, Steady-state and transient-state performance of a biotrickling filter treating chlorobenzene-containing waste gas, Appl. Microbiol. Biotechnol. 65 (1) (2004) 33–37.
[16] E. Smet, P. Lens, H. Van Langenhove, Treatment of waste gases contaminated with odorous sulfur compounds, Crit. Rev. Environ. Sci. Technol. 28 (1) (1998) 89–117.
[17] Q. Liao, X. Tian, X. Zhu, R. Chen, Y.Z. Wang, Measurements and modeling of heat generation in a trickling biofilter for biodegradation of a low concentration volatile organic compound (VOC), Chem. Eng. J. 140 (1–3) (2008) 221–234.
[18] P. Jacobs, I. De Bo, K. Demeestere, W. Verstraete, H. Van Langenhove, Toluene removal from waste air using a flat composite membrane bioreactor, Biotechnol. Bioeng. 85 (1) (2004) 68–77.
[19] S.H. Yeom, A.J. Daugulis, Development of a novel bioreactor system for treatment of gaseous benzene, Biotechnol. Bioeng. 72 (2) (2001) 156–165.
[20] Z. He, G.Y. Li, T.C. An, X.Y. Zeng, G.Y. Sheng, J.M. Fu, Comparative study of the elimination of toluene vapours in twin biotrickling filters using two microorganisms Bacillus cereus S1 and S2, J. Chem. Technol. Biotechnol. 83 (2008) 1019–1026.
[21] S. Kim, M.A. Deshusses, Determination of mass transfer coefficients for packing materials used in biofilters and biotrickling filters for air pollution control. 1. Experimental results, Chem. Eng. Sci. 63 (4) (2008) 841–855.
[22] K.R. Kim, M.S. Lee, S. Paek, S.P. Yim, D.H. Ahn, H. Chung, Adsorption tests of water vapor on synthetic zeolites for an atmospheric detritiation dryer, Radiat. Phys. Chem. 76 (8–9) (2007) 1493–1496.
[23] B. Soontornworajit, L. Wannatong, P. Hiamtup, S. Niamlang, D. Chotpattananont, A. Sirivat, J. Schwank, Induced interaction between polypyrrole and SO2 via molecular sieve 13X, Mater. Sci. Eng. B 136 (1) (2007) 78–86.
[24] Z.F. Ye, L.L. Wen, A.G.L. Borthwick, J.R. Ni, Aerobic Biological Fluidized Bed Technology Treatment of Sulfur and High Ammonia-nitrogen Wastewater in a Petroleum Refinery, J. Basic Sci. Eng. 13 (4) (2005) 345–357.
[25] A.R. Pedersen, E. Arvin, Effect of biofilm growth on the gas-liquid mass transfer in a trickling filter for waste gas treatment, Water Res. 31 (8) (1997) 1963–1968.
[26] S. Peishi, Y. Xianwan, H. Ruohua, H. Bing, Y. Ping, A new approach to kinetics of purifying waste gases containing volatile organic compounds (VOC) in low concentration by using the biological method, J. Clean. Prod. 12 (1) (2004) 95–100.
[27] H.T. Znad, K. Katoh, Y. Kawase, High loading toluene treatment in a compost based biofilter using up-flow and down-flow swing operation, J. Hazard. Mater. 141 (3) (2007) 745–752.
[28] H.H.J. Cox, M.A. Deshusses (Eds.), Biotrickling Filters, Kluwer Academic Publisher, Norwell, USA, 2001.
[29] H.H.J. Cox, M.A. Deshusses, Effect of starvation on the performance and re-acclimation of biotrickling filters for air pollution control, Environ. Sci. Technol. 36 (14) (2002) 3069–3073.
[30] T.S. Webster, H.H.J. Cox, M.A. Deshusses, Resolving operational and performance problems encountered in the use of a pilot/full-scale biotrickling fiber reactor, Environ. Prog. 18 (3) (1999) 162–172.