Toluene-styrene secondary acclimation improved the styrene removal ability of biotrickling filter

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ABSTRACT
In this work, ceramic pellets were used as packing material to establish a biotrickling filter (BTF) with acclimated sludge being inoculated on the surface of the packing to purify waste gas containing styrene. A method of toluene-styrene secondary acclimation was applied to achieve rapid formation of biological films. Results showed that the total time of start-up was 48 days and the removal efficiency (RE) of styrene reached up to 95%. The suitable empty bed residence time (EBRT) was obtained that is 57 s for higher RE of styrene with the inlet loading rates of 6.7–271.6 g/m²/h. The pH and moisture content showed small effect on styrene removal indicating that the operation of BTF was stable. Biomass accumulation was normal and its rising velocity under the condition of short EBRT was faster than that of long EBRT.

1. Introduction
The environmental awareness of general public was rising gradually with development of the world [1]. The releasing of volatile organic compounds (VOCs) has been a serious environmental and health concern because of its contribution to global environmental effects [2]. A wide range of VOCs was released because organic solvents are used as raw materials in pharmaceutical industries [3]. Especially, Styrene is an important organic chemical raw material and it is commonly used in the synthesis of plastics, resins, synthetic rubber, insulation materials and soon [4]. Due to the mismanagement in the processes of production, transportation, use, storage and others, large quantity of low concentration of styrene have been leaked into the atmosphere, which resulted in the deterioration of air quality [5]. Styrene has a potential harm to human health and environment because of its strong volatility and toxicity [6]. The treatment of styrene waste gas has drawn much research attention globally [7–11].

Biological treatments are effective and economical for VOCs removal. Several studies showed that BTFs with ceramic pellets had the high removal efficiency (RE). Wu et al. [15] have recently investigated the removal of methyl acrylate by ceramic-packed BTF and showed that the ceramic-packed BTF exhibited excellent RE. The gaseous thioanisole was removed using a twin BTFs in the study of Li et al. [16] and the results showed that the BTF with packing material had high RE and elimination capacity (EC). In addition, hydrophobic VOC removal in biofilters is affected by many factors including VOC mass transfer, microbial populations, packing media and moisture [17].

The biomass accumulation requires regulation for stable performance, and pressure drop value is a critical indicator of biomass accumulation during the operation period [18,19]. Excess accumulation of biomass within gas phase biofilters often result in operational problems such as clogging, channeling, and excessive head loss within biofilter beds, and consequently, the deterioration of performance [20]. In this work, the solution of excess accumulation of biomass is washing with nutrient solution [21].

Styrene has been widely investigated both in biofilters and in BTFs packed with several kinds of media even in industrial scale [7,8,22,23]. However, there are lacking researches and investigations on the methods of improving the start-up of BTFs. The hydrophobicity and toxicity of styrene is the main causes of affecting film-forming time and quality. In order to improving them, toluene

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2. Materials and methods

2.1. Experimental equipment

A BTF was used in the present experiment which is presented in Figure 1 and it has four segments. The BTF was made of plexiglass with diameter of 10 cm and height of 80 cm, and a packing material volume of 6280 cm³. The BTF was operated in a countercurrent flow mode, i.e. with the gas flowing upward and the recirculation liquid flowing downward. The spray liquid was raised to the top of BTF, and a water distributor was placed at the top of the column to enable liquid redistribution. The styrene-contaminated stream was introduced through the bottom of the column of the BTF. The styrene loading could be controlled over an appropriate range by varying the ratio of the gas flow rate of the two rotameters. The tests were carried out under atmospheric pressure at 25 ± 2 °C, and the inlet gas flow was 0.2–0.8 m³/h, which corresponds to the empty bed retention time of 28–113 s, and the inlet concentration was 195.2–2112.3 mg/m³.

2.2. Packing material and microbial sludge

Modified ceramic pellets were chosen as the packing materials of the BTF. The basic properties of the ceramic pellets are showed in Table 1. The sludge was collected from an aeration tank of wastewater treatment plant in Sinopec Yangzi Petrochemical Company Ltd, Nanjing, Jiangsu province. The components of spray liquid can be found in a previous study [24].

2.3. Experimental procedures

First, the activated sludge was aerated for 48 h to consume nutrients. Then the activated sludge was poured into the BTF. Then, the BTF was bubbled into air the aeration time BTF was 24 h for microorganisms got a preliminary growth. The refresh rate of spray liquid was 1.7 L/d during the entire period and total volume of tank is about 10 L and the liquid flow rate was 10 L/h. The method of secondary acclimation was divided into three phases. Toluene was the sole carbon source at phase I. The mixture of toluene and styrene was the carbon source at phase II, with increasing the ratio of the concentration of styrene gradually. Styrene was the sole carbon source at phase III. The RE, thickness of biofilms, and pressure drop values was used to judge whether the start-up stage was successful [25]. In the steady state, the concentration of styrene gas increased gradually from 200 to 2000 mg/m³ under the empty bed residence time (EBRT) of 28, 38, 57, 113 s. Pressure drop values, inlet concentrations and outlet concentrations were detected during the whole period of operation of

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**Figure 1.** Schematic of biotrckling filter.

**Table 1.** Technological parameters of ceramic pellets.

| Material       | Particle diameter (mm) | Density (g/cm³) | Surface roughness (μm) | Main composition | Specific surface (m²/m³) |
|----------------|------------------------|-----------------|------------------------|-----------------|-------------------------|
| Ceramic pellets| 5–10                   | 2.9             | 15.2–22.5              | SiO₂            | 322.7                   |
the BTF. In addition, the pH value of BTF was adjusted by changing the pH value of spray liquid using the diluted NaOH or HCl. The EBRT was adjusted by changing the inlet flow rate [25]. For avoiding contamination, the gas for detection was collected quickly from the inlet and outlet. The culture solution from the BTF was imported into collection bottle directly using rubber hose.

2.4. Analytical methods

The styrene concentration was analyzed using a gas chromatograph (7890B, Agilent, USA) with flame ionization detector (FID). The packing humidity was determined by oven drying method as described by Sanchez et al. [26]. The pH of the spray liquid was detected with a pH meter (PHS-3C, Rex, China). Bacterial growth was observed using a scanning electron microscopy (SEM) (S3400 N, Hitachi, Japan). Fifteen milliliter culture solution from the BTF was added in 30 mL phosphate buffer glutaraldehyde solution after centrifugation (4500 r/min, 10 min, 4 °C) and it was washed 3 times using PBS. Then, the solution was dehydrated using different concentrations ethanol solution and each time spends 15 min. It was dried at the critical-point of CO2 after was replaced using isoamyl acetate. Finally, the bacteria were plated platinum to 10–20 nm by ion sputtering and were observed using S3400 N SEM. [27]

3. Results and discussion

3.1. Performance of BTF in the start-up period

In the start-up period, the variation of the RE of toluene and styrene were monitored during the start-up period at different phases at the EBRT of 57 s. The results are shown in Figure 2.

The start-up period was divided into three phases (phase I, phase II and phase III). In phase I (1–18 d), the toluene RE increased rapidly with the increased toluene inlet concentration. The maximum RE of toluene reached 98.5% at toluene inlet concentration of 4001.2 mg/m³ at day 18. This indicated a high ability of microbial metabolism to toluene. In phase II (19–38 d), when the styrene concentration increased from 200.8 to 700.9 mg/m³, the RE of styrene increased from 10.5 to 44.7%. Meanwhile the toluene inlet concentration dropped from 1200.4 to 300.88 mg/m³, the RE of toluene was still kept at around 98%. It indicated that styrene can be used gradually by microbes as carbon source, but toluene was easier to biological utilization. The low RE of styrene in the BTF might be caused by two reasons. Styrene was the new carbon source for microbes and its nature of degradation-resistant. At phase III (38–48 d), the RE of styrene rapidly increased from 44.7% (the maximum RE of phase II) to 64.2% during the first day at inlet concentration of about 700 mg/m³. Finally, the RE of styrene reached up to 95% at day 48 and the thicker ivory white biofilms were observed on the surface of the packing indicating that the start-up stage was successful [28]. In addition, the time needed would be 90 d to finish the starting up if the BTF was fed with the styrene as the sole carbon source (Figure 3) indicating that toluene-styrene secondary acclimation improved the start-up of the BTF. Some studies were reported about the starting up of bioreactor for relatively low concentration styrene removal. BTF treating styrene has been started-up without pretreatment and time such short as 7 days has been observed in the work of Pérez et al. [29]. Rene et al. [23] reported that the RE of styrene reached 90% using a fungal monolith bioreactor in the end of start-up period and it reached 99% when starting up was finish in the study of Song et al. [30]. According to comparison of the results with literature, although toluene-styrene secondary acclimation improved the styrene removal in BTFs, the time and RE of the start-up period did not reach the best value.

3.2. Performance of BTF in the steady state

3.2.1. Effect of inlet concentration and EBRT on styrene RE

When styrene was the sole carbon source in the BTF, inlet styrene would play a key role in normal microbial growth and metabolism. Empty bed retention time is also an important parameter to control during the operation of
the BTF. If the EBRT was too short, the mass transport is between the gas phase and the liquid phase was inadequate. On the other hand, when the EBRT was too long, it went against the efficiency of BTF.

As shown in Figure 4, when the EBRTs were 28, 38, 57 and 113 s and inlet concentration increased from 210.5, 208.4, 195.2 and 201.2–2009.5, 2010.3, 2001.5 and 2112.3 mg/m³ respectively, the RE decreased from 100% to 94.1, 90.2, 85.1 and 72.3%. At the same inlet concentration, less EBRT led to higher elimination capacity, therefore, to improve the operational efficiency of the BTF, the EBRT should be maintained at 57 s.

At the same EBRT, the RE of styrene decreased with the increasing of styrene inlet concentration. It may be because gas-liquid interface area was a fixed value in the same BTF, the contact probability of microbes and packing was also fixed. Perhaps, the RE of styrene decreased due to the toxicity of this compound on the microorganisms. Excessive concentration of styrene (>2009.5 mg/m³) would not be removed effectively in the BTF. In addition, the effect of EBRT for application of the BTF was accessed by the descent rate of RE with the inlet loading rate (ILR). As can be seen from Figure 5, the RE of \(m\)-dichlorobenzene removal decreased steadily and linearly with the ILRs of 6.7–271.6 g/m³/h. The slopes of the fitting line were \(-0.10, -0.09, -0.08\) and \(-0.09\) for EBRTs of 28, 38, 57 and 113 s, respectively, indicating that higher RE at same ILR is obtained under 57 s (EBRT).

### 3.2.2. Effect of pH on styrene RE

Under the conditions of EBRT of 57 s and styrene inlet concentration varying of 200–500 mg/m³, the effect of pH was studied on RE of the styrene. As shown in Figure 6, the RE of styrene decreased gradually from 100% to 96.7, 95.5, 93.2 and 86.1%, respectively with the decreasing various pH (pH = 2, 3, 4, 5). When the pH values were 5 and 4, respectively, the RE of the styrene was 95% approximately under the concentrations of about 500 mg/m³. Furthermore, under the extreme condition of the pH as low as 2, the RE of the styrene still was more than 85% under the inlet concentration of less than 500 mg/m³. These results showed that the operation of BTF can keep stable when pH appears decline due to the effect of microorganisms.

### 3.2.3. Effect of packing moisture content on styrene RE

The moisture content on the interval of packing material not only could make microbes maintain high activity, but also secure the long-term stable operation of the BTF system. The moisture content was fixed by changing the flow rate of spray liquid and it can be obtained formula as following:

\[
H = \frac{L}{(V/t - G)} \times 100\%
\]

where, \(H\) is the moisture content on the interval of packing material (%), \(V\) is the interval volume of packing material (L), \(t\) is the EBRT (s), \(L\) is the intervals liquid flow rate (L/s) and \(G\) is the intervals gas flow rate (L/s).

Figure 4. Effect of inlet concentration and EBRT on styrene removal efficiency.

Figure 5. RE vs. ILR for styrene removal under different EBRTs.

Figure 6. Effect of pH on styrene removal efficiency.

Figure 7. Effect of packing humidity on styrene removal efficiency.
3.3. Pressure drop values in a BTF

The value of pressure drop was recorded from the beginning to day 130 and the results are presented in Figure 9. As it can be seen, the pressure drop value was less than 50 pa with the increase of inlet concentration. The reason may be that the biomass accumulation was unfinished at phase I/II of the start-up periods. From day 36 to day 48, the pressure drop value was stable until the end of start-up periods. At the steady-state stage, the pressure drop grew relatively quickly as inlet concentration was raised. In addition, it can be found that empty bed retention time is an important parameter to pressure drop values in a BTF. If the EBRT was too short, the rising velocity of pressure drop values is more fast than long EBRT, This may be because that short EBRT got a higher ILR under the same concentration of styrene and more microorganisms were produced due to higher styrene feed, which may further minimize the external interspaces of the ceramic pellets and thus led to a higher growth rates of pressure drop across the BTF [31]. It is notable that the pressure drop increased extremely quickly and excessive biomass accumulation occurred from day 107 to day 110, and the excessive biomass accumulation is normal condition comparing other literature. For example, the excessive biomass accumulation appeared three times within 160 d in Wang et al. [28].

4. Conclusions

A method of the toluene-styrene secondary acclimation was applied in the operation of BTF, and the performance showed that it had abilities of shorting start-up time and improving the RE of styrene. In the steady state, higher RE at same ILR was obtained under EBRT of 57 s. The pH and moisture content showed small effect on styrene removal indicating the stability of operation. The normal biomass accumulation also showed the potential of the application of the method in operation of BTF.

Disclosure statement

No potential conflict of interest was reported by the authors.

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