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# Effect of presence of hydrophilic volatile organic compounds on removal of hydrophobic n-hexane in biotrickling filters



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# HIGHLIGHTS

- Hydrophilic VOCs improve BTF performance for n-hexane at low EBRTs and temperatures.
- Both toluene and 4-methyl-2pentanone promote the degradation of n-hexane in BTFs.
- Mass of biofilms in BTFs increased at the presence of each of the hydrophobic VOCs.

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# G R A P H I C A L A B S T R A C T



# ABSTRACT

Hydrophilic VOCs (volatile organic compounds) were applied to explore their positive influence on the elimination of the single hydrophobic VOC in biotrickling filters (BTFs). Comparison experiments were carried to evaluate the effect of 4-methyl-2-pentanone and toluene on the performance of BTFs for n-hexane removal. The results showed that the existence of 4-methyl-2-pentanone improved the removal performance of BTFs at short gas empty bed contact time (EBRT) of 15 s and low temperature of 10 °C. The degradation of n-hexane in the presence of 4-methyl-2-pentanone was slightly enhanced with a loading ratio of 6:1. When the mixing ratio was greater than 4, toluene significantly promoted the biodegradation of n-hexane with toluene loading rate less than 10 g m<sup>-3</sup> h<sup>-1</sup>. Additionally, The promotion effect was not only reflected in the contents of proteins and polysaccharides, but also in the growth rates of microorganisms in biofilms. This work discussed the detailed effect between n-hexane and hydrophilic VOCs in BTFs, which would contribute to develop a more economical method to improve the removal performance of hydrophobic VOCs in BTFs.

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# 1. Introduction

In recent years, due to the harm caused by air pollution to humans and the environment, governments have imposed more restrictions and requirements on exhaust emissions of various enterprises (Barbusinski et al., 2017; Li et al., 2018). Therefore, the emission of hazardous air pollutants, particularly volatile organic compounds (VOCs), has been a main issue worldwide (Bordoloi et al., 2019; Yang et al., 2009). In response to the rising concern about the problem, numerous technologies for the elimination of VOCs were developed recently. Physical, chemical and biological methods were utilized as traditional pathways for the treatment of VOCs (Kasperczyk et al., 2019). Among them, biological techniques such as biofilter, bio-trickling filter (BTF), and bio-scrubber have been widely used, owing to their advantages of cost-effectiveness and environmental-friendliness (Yang et al., 2011). Meanwhile, BTF has long been considered as a promising method for the removal of VOCs due to its superiorities of treating pollutants in a wide range and strong ability to withstand pollution loading rate (LR) fluctuations (Eregowda et al., 2019).

However, there were challenges in applying BTF to deal with VOCs. In addition to the fact that changes in experimental conditions were likely to affect the performance of BTF, their low degradation efficiency for hydrophobic VOCs was the most challenging problem (Cheng et al., 2016a). Hydrophobic VOCs possessed high Henry's law constant, which limited their mass transfer rate between gas, liquid and biofilm phase, and the performance of BTF would be greatly affected due to the poor solubility of hydrophobic VOCs in liquid phase. Thus, reducing the mass transfer resistance of hydrophobic VOCs in three phases and improving their bioavailability are the keys to improving the performance of BTF.

Some progresses for improving the degradation efficiency of hydrophobic VOCs in BTFs have been made by researchers. Previous studies mainly focused on the following aspects: application of surfactants (Yang et al., 2010a), catalysis of fungal organisms (Alberto et al., 2010), innovation of bioreactors (Yang et al., 2008), as well as combination of biological and physical or chemical methods (Wang et al., 2009; Hinojosa-Reyes and Arriaga, 2012). Despite some drawbacks in term of cost and operation, these pathways did help to enhance the degradation efficiency of hydrophobic VOCs in BTFs (Tu et al., 2015). Nevertheless, the above approaches might not be optimal for transferring biological methods from laboratory scale to factory scale. For example, the toxic effects of surfactants on microorganisms and the environmental pollution problems caused by their degradation products (Abhinayaa et al., 2019; Song et al., 2012). Innovative bioreactors or bio-chemical/physical methods were likely to bring cost issues, and the extraction of fungal microorganisms made the experimental conditions difficult to operate and control (Yang et al., 2003a).

Therefore, a more economically viable solution needs to be proposed. There have been large number of publications on the removal of single-component VOC in bioreactors. For instance, nhexane, hydrocarbons (Aly Hassan and Sorial, 2011; Xi et al., 2015) and alcohols/ketones, which have significant differences in bioavailability. In general, contaminated air streams from municipal facilities and industrial processes are complicated and often comprised multiple VOCs (Rene et al., 2018). When dealing with mixtures, the interaction of pollutants played an important role in the mass transfer and biodegradation of the biological process, which might lead to the increase or decrease of the degradation efficiency of target pollutants (Chheda and Sorial, 2017). Several studies showed that the addition of hydrophilic VOCs could stimulate the degradation of hydrophobic VOCs in bioreactors (Yao et al., 2019). A previous study showed that the removal of nhexane was significantly promoted by methanol, especially when the LR of n-hexane was less than 13.2 g m<sup>-3</sup> h<sup>-1</sup> (Zehraoui et al., 2012). There are relatively few studies on the interaction of multi-component VOCs, especially those with different hydrophilic properties, in the bioreactor.

N-hexane, 4-methyl-2-pentanone and toluene, the main emission factors of rubber waste gas from tire factory (Gagol et al., 2015). were used as target pollutants for the experiment. The three VOCs are all recognized as typical hazardous air contaminants; among them, n-hexane is known for its low biodegradability and high hydrophobicity, which leads to high mass transfer resistance in the bioreactors (Saucedo-Lucero et al., 2014). Many other investigators have used n-hexane as the target contaminant in biofiltration studies (Volckaert et al., 2016). However, low removal rate of nhexane was obtained or a short running cycle was assessed which might not meet the prescribed emission levels as well as the applications in industrial production (Amin et al., 2017). In contrast, 4methyl-2-pentanone and toluene could be easily biodegraded in BTFs due to their higher hydrophilicity, with the former higher (Kim et al., 2007; Saingam et al., 2018). The addition of hydrophilic VOCs might have positive, negative or neutral impact on n-hexane depending on LRs, biomass control strategies, temperature et al. (Yang et al., 2018).

Introducing a mixture of hydrophilic VOCs and n-hexane had the potential to expose the biofilm to increased n-hexane LRs which might weaken the mass transfer resistance between phases (Zehraoui et al., 2012). Therefore, this study aims to evaluate the performance of BTFs for the efficient removal of hydrophobic VOC (n-hexane) in the presence of hydrophilic VOCs (4-methyl-2pentanone or toluene). Two equally biofilters, BTF A and BTF B, were operated in parallel to remove hydrophilic and hydrophobic volatile organic contaminants from the exhaust stream. As a control unit, the sole carbon source of n-hexane was degraded in BTF A. The removal of a mixture of hydrophilic VOCs (4-methyl-2pentanonetoluene or toluene) and hydrophobic n-hexane occurred in BTF B. Effect of hydrophilic VOCs on the performance of BTFs for n-hexane removal was investigated under various experimental conditions, and the biomass characteristics at different filtering layers in BTFs were evaluated. The mechanism about the interaction between the hydrophobic and hydrophilic VOCs was also discussed.

# 2. Materials and methods

# 2.1. Packing material

Due to its high porosity, good mechanical strength, as well as low density, polyurethane sponges (Shenzhen Jiechun Filter Material, Guangdong, China) were used as packing material in the study. The polyurethane sponges have a size of 10 cm  $\times$  10 cm, a porosity of 95.3%, and an apparent density of 28 kg/m<sup>3</sup>. The characteristic parameters of the module polyurethane sponge tube are listed in Table S1.

#### 2.2. Inoculation

Activated sludge was obtained from aerobic tank at Changsha Kaifu Wastewater Treatment Co. Ltd., Hunan, China and used for inoculation of BTF. The polyurethane sponges were immersed in the activated sludge for 24 h to acclimate to the biofilm, and the packing material was placed in the plexiglass column for the capture and biodegradation of volatile organic pollutants.

## 2.3. Chemicals

Three different types of VOCs were used as target pollutants in this study. n-hexane ( $C_6H_{14}$ , >99%), 4-methyl-2-pentanone ( $C_6H_{12}O$ , >99%), and toluene ( $C_7H_8$ , >99%) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). The chemicals used in the nutrient solution were listed in Table 1. All chemicals mentioned above were analytical grade.

#### 2.4. Analytical methods

Gas phase samples were extracted with gas-tight syringes from top, middle, and bottom gas sampling ports. The VOCs concentration was monitored daily by gas chromatograph (Agilent 7890 N, Series II, California, USA) equipped with a flame ionization detector (FID). The capillary column equipped in the experiment was HP-VOC ( $60 \text{ m} \times 320 \text{ }\mu\text{m} \times 1.8 \text{ }\mu\text{m}$ ), whose maximum operating temperature was 280 °C. The inlet and outlet CO<sub>2</sub> concentration during the operation was measured by gas chromatography (SP7820, Hongtu, China) equipped with a thermal conductivity detector (TCD). TC (total carbon) was determined by TOC tester (Shimadzu, Japan).

The biofilm on the surface of polyester sponges was removed for EPS analysis. EPS was extracted by the thermal extraction method mentioned in the previous study (Qian et al., 2018). The determination of volatile suspended solids (VSS) was performed according to standard methods (APHA, 1998). The content of proteins and polysaccharides were detected by Coomassie brilliant blue staining method and the anthrone–sulfuric acid colorimetry method, respectively (Chen et al., 2018). Microbial cell counts were determined by taking 1 g of biofilm samples taken from different layers of filter medium. Each biofilm sample was added with 9 mL of distilled water containing 0.9% NaCl. This solution was shaken vigorously and serially diluted and then inoculated into nutrient agar media. The plates were incubated for 3 d at 30 °C before counting the colonies.

Variations in pressure drop was estimated by monitoring the differential pressure gauge readings connected to both ends of the BTFs. The temperature of the biofilter bed was regulated by an indoor air-conditioner and measured by a glass thermometer.

# 2.5. Biotrickling filters

## 2.5.1. Biotrickling filter system

A schematic diagram of the BTF was shown in Fig. 1. Biofilter consist of transparent plexiglass tube, nutrient solution distribution system, and gas distribution system (Wang et al., 2013). Plexiglas column had an internal diameter of 10 cm and a total bed height of 78 cm which was divided into four parts. Each part was filled with 10 cm  $\times$  10 cm polyester sponge filler. A void space of 9 cm was set up at the bottom of plexiglass tube for leachate collection and

| Table 1  |
|--|
| Formulation and concentration of nutrient solution |

| Component                            | Concentration<br>(mg/L) | Component                            | Concentration<br>(mg/L) |  |  |
|--------------------------------------|-------------------------|--------------------------------------|-------------------------|--|--|
| K <sub>2</sub> HPO <sub>4</sub>      | 28.16                   | KH <sub>2</sub> PO <sub>4</sub>      | 9.25                    |  |  |
| MgSO <sub>4</sub>                    | 4.4                     | NaNO <sub>3</sub>                    | 490                     |  |  |
| NaHCO <sub>3</sub>                   | 24                      | FeCl <sub>3</sub>                    | 0.0926                  |  |  |
| CaCl <sub>2</sub>                    | 2.69                    | CuCl <sub>2</sub> ·4H <sub>2</sub> O | 0.062                   |  |  |
| MnCl <sub>2</sub> ·4H <sub>2</sub> O | 0.144                   | CoCl <sub>2</sub> ·6H <sub>2</sub> O | 0.866                   |  |  |
| Folic Acid                           | 0.00089                 | D-pantothenic Acid                   | 0.0035                  |  |  |
| Vitamin B2                           | 0.0023                  | Nicotinic Acid                       | 0.0023                  |  |  |
| Biotin                               | 0.0023                  | Aminobenzoic Acid                    | 0.0023                  |  |  |

sprinkling water. The nutrient solution and airflow direction in BTF were operated in co-current mode. The nutrient solution was evenly sprayed on the filler from top to bottom at a rate of 5.28 L/ d under the action of submersible pump and time controller, which acted as a nitrogen source for microorganisms to promote its growth and metabolism (Cheng et al., 2016b). The bottom effluent was collected and not cycled. The gas distribution system regulated the flow of the gas through a rotameter to split the clean gas from the air compressor into two streams. The major stream was used for humidification, and the minor stream to promote the volatilization of volatile organic compounds. The two streams entered the plexiglass column after being mixed, and the VOCs were degraded by the microorganisms attached to the filler as carbon sources.

#### 2.5.2. Experimental set-up

At the BTF start-up stage, A single pollutant of n-hexane was introduced into the BTF A with a corresponding inlet concentration of 200 mg m<sup>-3</sup>. Meanwhile, the target pollutant in BTF B was a mixture of n-hexane and 4-methyl-2-pentanone with inlet concentrations of 200 and 300 mg m<sup>3</sup>, respectively. After being successfully started up, both BTF systems were run at different gas empty bed residence times (EBRTs) (30, 60, 75, 45, 15 s) and different temperatures (10, 15, 25 °C), which was to evaluate the effect of hydrophilic 4-methyl-2-pentanone on the performance of BTFs. In order to maximize the positive effect of hydrophilic VOCs on the removal of hydrophobic n-hexane by BTFs, toluene was introduced into BTF B and the removal of n-hexane was studied under different mixing loading ratios (6:1, 1:2, 1:1, 8:1) of n-hexane and toluene. The removal performance of BTFs was evaluated in terms of the elimination capacity, EC (g  $m^{-3} \ h^{-1})$  and removal efficiency, RE (%).

## 3. Results and discussion

## 3.1. BTFs start-up

BTF A and B were operated for 177 days under different operation conditions. As illustrated in Table 2, BTF A was used as a control unit to remove the hydrophobic VOC (n-hexane), while BTF B was used as an experimental unit to eliminate the mixture of n-hexane and 4-methyl-2-pentanone/toluene.

The performance of the BTFs in start-up stage was evaluated (Fig. 2). In the first 5 d, the RE of n-hexane in BTF A was very low (<30%), and a gradual increase was observed and it reached more



**Fig. 1.** Schematic diagram of the BTF, where: ① air pump, ② flow meter, ③ n-hexane, ④ toluene/4-methyl-2-pentonone, ⑤ water, ⑥ effluent liquid, ⑦ thermometer, ⑧ gas sampling port, ⑨ mixed gases, ⑩ biofilm sampling port, ⑨ pressure gauge, ⑳ nutrient solution + time controller.

than 60% after 13 d of operation. On day 17, the RE increased to 68% which corresponded to an EC of 14.5 g n-hexane  $m^{-3} h^{-1}$ . Over the next few days, the RE maintained at around 70%, which meant the successfully start-up of BTF A. The entire process lasted 22 d. As for BTF B, the process of start-up was faster. The RE for 4-methyl-2-pentanone in BTF B remained 100% since day 2. On day 7, the RE of n-hexane m<sup>-3</sup> h<sup>-1</sup> and 29.7 g 4-methyl-2-pentanone m<sup>-3</sup> h<sup>-1</sup>. The RE of n-hexane fluctuated between 38% and 43% with a maximum EC of 10.4 g n-hexane m<sup>-3</sup> h<sup>-1</sup> and 48.5 g 4-methyl-2-pentanone m<sup>-3</sup> h<sup>-1</sup> in a week after day 14, which could be regarded as a successful start of BTF B.

# 3.2. Effect of EBCT on performance of BTFs

When the BTFs were successfully started, the airflow rates were changed to achieve the purpose of altering EBCT during 22–52 d. The effect of EBCT on the RE of hydrophilic and hydrophobic VOCs in BTFs was evaluated (Fig. 2). The RE of n-hexane in BTF A and B was slightly promoted since EBCT was increased from 30 s to 75 s. BTF A obtained the maximum RE of 82.3% for n-hexane with an EBRT of 60 s and an inlet load of 16.4 g m<sup>-3</sup> h<sup>-1</sup>. Meanwhile, the maximum RE of n-hexane in BTF B was 65.6% under the condition of 60 s and 12 g m<sup>-3</sup> h<sup>-1</sup>. Besides, the removal of n-hexane in BTFs was greatly declined when EBCT dropped to 15 s.

During this phase, the average RE of n-hexane in BTF A was higher than that in BTF B. This result could be explained by the fact that when the residence time of the contaminant in the BTF was shortened, the probability of being trapped by the microorganism was lowered, and consequently resulting in a decrease in degradation efficiency (Lebrero et al., 2012). However, the removal rate of 4-methyl-2-pentanone in BTF B was not affected by EBCT and it remained at 100%. This may be related to its strong hydrophilicity (Table S2), which was preferentially utilized as carbon source by microorganisms. Similar phenomenon had been observed by other research teams (Vergara-Fernández et al., 2018). The authors had proved that low EBCT (5 s) had little effect on the removal of toluene with a relatively high hydrophilicity. An interesting conclusion was obtained that the RE of n-hexane in BTF A was higher compared to BTF B under the EBRT of 15 s. This indicated that the presence of 4-methyl-2-pentanone might inhibit the degradation of n-hexane, yet promote the stable operation of BTFs under the condition of short EBRT.

#### Table 2

A summary of operation conditions in BTF A and BTF B.



Fig. 2. Effect of EBRT on the performance of BTFs: (a) n-hexane in BTF A; (b) n-hexane in BTF B.

### 3.3. Effect of temperature on performance of BTFs

During day 74 to day 108, since temperature was an important factor for the performance of BTFs, temperature was altered to test

| · · · · · · · · · · · · · · · · · · ·             |         |          |           |          |          |  |          |          |          |  |  |
|---|---------|----------|-----------|----------|----------|--|----------|----------|----------|--|--|
| BTF A (n-hexane)                                  |         |          |           |          |          | BTF B ( $\alpha = n\text{-hexane},\beta = 4\text{-methyl-2-pentanone},\gamma = toluene)$ |          |          |          |  |  |
| Time (d)  | 0-20    | 21-29    | 30–37     | 38-45    | Time (d) | 0–20   | 21-29    | 30-37    | 38-45    |  |  |
| Concentration (mg m <sup>-3</sup> )               | 130-234 | 261-381  | 529-682   | 381-645  | α        | 165-297  | 198-314  | 495-620  | 323-509  |  |  |
|   |         |          |           |          | β        | 149-446  | 132-280  | 290-558  | 88-251   |  |  |
| Loading rate (g m <sup>-3</sup> h <sup>-1</sup> ) | 16-28   | 15-22    | 25-33     | 30-51    | α        | 20-36  | 12-19    | 24-30    | 26-41    |  |  |
|   |         |          |           |          | β        | 18-54  | 8-17     | 14-27    | 7-20     |  |  |
| EBCT (s)  | 30      | 60       | 75        | 45       | EBCT (s) | 30   | 60       | 75       | 45       |  |  |
| Time (d)  | 46-52   | 53-64    | 65-73     | 74-108   | Time (d) | 46-52  | 53-64    | 65-73    | 74-108   |  |  |
| Concentration (mg m <sup>-3</sup> )               | 104-155 | 337-724  | 1024-1206 | 182-661  | α        | 74-136   | 264-744  | 859-1140 | 231-711  |  |  |
|   |         |          |           |          | β        | 70-140   | 83-149   | 215-810  | 33-413   |  |  |
| Loading rate (g m <sup>-3</sup> h <sup>-1</sup> ) | 25-37   | 20-44    | 62-73     | 11-40    | α        | 18-33  | 16-45    | 52-69    | 14-43    |  |  |
|   |         |          |           |          | β        | 17-34  | 5-9      | 13-49    | 2-25     |  |  |
| EBCT (s)  | 15      | 60       | 60        | 60       | EBCT (s) | 15   | 60       | 60       | 60       |  |  |
| Time (d)  | 110-131 | 132-150  | 151-167   | 168-177  | Time (d) | 110-131  | 132-150  | 151-167  | 168-177  |  |  |
| Concentration (mg m <sup>-3</sup> )               | 513-949 | 602-1745 | 320-397   | 826-1224 | α        | 530-843  | 648-1650 | 305-491  | 383-1243 |  |  |
|   |         |          |           |          | γ        | 249-928  | 305-889  | 129-748  | 23-75    |  |  |
| Loading rate (g m <sup>-3</sup> h <sup>-1</sup> ) | 31-57   | 36-106   | 19-24     | 50-74    | α        | 32-51  | 39-100   | 18-30    | 66-164   |  |  |
|   |         |          |           |          | γ        | 15-56  | 18-54    | 8-45     | 4-10     |  |  |
| EBCT (s)  | 60      | 60       | 60        | 60       | EBCT (s) | 60   | 60       | 60       | 60       |  |  |



**Fig. 3.** Effect of LRs of n-hexane and 4-methyl-2-pentanone on the performance of BTFs: (a) n-hexane in BTF A; (b) n-hexane in BTF B.

its effect on the removal of mixed contaminants. The decline of temperature played a major role in the reduction of the activity and metabolism of microorganisms in biofilms (Vergara-Fernández et al., 2018). Therefore, when the temperature of BTFs was decreased from 25 °C to 10 °C, the maximum RE of n-hexane in BTF A decreased from 65% to 38.0%. As the temperature raised to 25 °C, the removal performance of BTF A and B was greatly improved compared with that at 10 °C (Fig. 3). However, the downward trend of n-hexane removal rate in BTF B was smaller than that in BTF A. Research has been reported that the liquid mass transfer resistance of VOC decreased with the temperature which was lower than the constant temperature (Parnian et al., 2016). Therefore, this could be explained that the high mass transfer efficiency of 4-methyl-2pentanone made it less affected by temperature changes, and BTF B could also have a more stable operation performance at low temperatures. The result also indicated the high flexibility of BTFs in the treatment of a mixture of hydrophobic and hydrophilic contaminants under low temperatures.

# 3.4. Removal performance of BTF at presence of hydrophilic VOCs

3.4.1. Effect of hydrophilic 4-methyl-2-pentanone on removal of n-hexane

BTF A was operated at LRs of 26–67 g n-hexane m<sup>-3</sup> h<sup>-1</sup>. While BTF B was operated at LRs of 22–61 g n-hexane m<sup>-3</sup> h<sup>-1</sup> and 4–32 g

4-methyl-2-pentanone  $m^{-3} h^{-1}$  from day 53 to day 73 (Fig. 3). The performance of BTF A deteriorated with the increase of LR of n-hexane, which can be explained by the inhibition of the growth and metabolism of microorganisms by a single carbon source with high LR (Sun et al., 2018). The performance of BTF B was also affected by LRs, and REs of n-hexane were lower than that of BTF A. Similar investigation had found that the increasing in LR of chloroform adversely affected the RE of toluene and damaged the overall performance of BTF. It was also mentioned that the inhibitory effect may be caused by the change of dominant bacteria in the BTFs (Balasubramanian et al., 2012).

When the loading ratio of n-hexane and 4-methyl-2-pentanone was 3:1, there was little difference in EC of n-hexane between BTF A and B (Fig. S1). Once the mixing ratio dropped to 1:1 or even 1:2, the RE of n-hexane in the BTF B began to decline. The maximum EC of n-hexane in BTF A and B was 18.6 g m<sup>-3</sup> h<sup>-1</sup> and 14.4 g m<sup>-3</sup> h<sup>-1</sup> for the LR of 27.5 g m<sup>-3</sup> h<sup>-1</sup>. Similar result elaborated that high concentration of n-butanol could inhibit the removal of toluene, which might be due to the competitive inhibition between n-butanol and toluene, or the excessive accumulation of biofilm caused by n-butanol, thereby reducing the performance of the BTFs (Dixit et al., 2012). Previous study also reported that methanol inhibited the removal rate of a-pinene and hydrogen sulfide under a certain load (Jin et al., 2007).

However, the removal of n-hexane in BTF B was better than that in BTF A when the mixing ratio was increased to 6:1. It could be interpreted that the low 4-methyl-2-penranone LR in BTF B might lead to an increased bioavailability of n-hexane as compared to BTF A. For multi-component VOCs with different hydrophobicity, the removal of hydrophobic components might be inhibited by the presence of hydrophilic components (Zehraoui and Sorial, 2015). The degree of inhibition was reduced if the metabolism of the hydrophilic substrates was stimulated in BTFs. Thus its inhibitory impact on the hydrophobic component would be weakened when the LR of hydrophilic component was decreased (Ikemoto et al., 2006). Similar result was obtained when the mixture of methanol and n-hexane were degraded in BTFs (Zehraoui et al., 2013).

# 3.4.2. Effect of moderately hydrophilic toluene on removal of nhexane

The results showed that the addition of hydrophilic 4-methyl-2-pentanone inhibited the degradation of n-hexane in most cases, and only when the LR of 4-methyl-2-pentanone was quite low could it promote the removal of n-hexane in BTFs slightly. Therefore, a mixture of n-hexane and toluene was introduced into biofilters as carbon sources. During day 109 to day 177, BTF A was operated at LRs of 21–82 g n-hexane  $m^{-3} h^{-1}$ . While BTF B were operated at LRs of 25–79 g n-hexane  $m^{-3} h^{-1}$  and 5–58 g toluene  $m^{-3} h^{-1}$  (Fig. 4).

With the steady operation of BTFs, the RE of n-hexane in BTF A was stable at around 50% under the condition of 38 g m<sup>-3</sup> h<sup>-1</sup>. In contrast, toluene inhibited the removal of n-hexane, resulting in a removal rate of less than 35%. The inhibition was more pronounced with a high LR of n-hexane. This might due to the competitive inhibition between toluene and n-hexane in terms of nutrients and preferential degradation (Zhao et al., 2011). Some other studies also confirmed this, and reported that the presence of benzene greatly inhibited the biofiltration of n-hexane (Hassan and Sorial, 2010). However, when the ratio of n-hexane and toluene increased to 6:1, the inhibition disappeared and was replaced by toluene's promotion of n-hexane (Fig. S2). This boost was shown with low LRs of toluene. The REs of n-hexane were greatly improved, and the maximum RE reached 90% with a LR of 29 g m<sup>-3</sup> h<sup>-1</sup>. The result obtained was superior to other literatures that investigated nhexane as a single pollutant in bioreactors (Hu et al., 2015). In other



**Fig. 4.** Effect of LRs of n-hexane and toluene on the performance of BTFs: (a) n-hexane in BTF A; (b) n-hexane in BTF B.

words, the presence of hydrophilic substrates could promote the removal of stubborn VOCs in BTFs. The addition of hydrophilic VOCs can stimulate the growth of microbial populations in biofilms (Hu and Wang, 2015), and their demand for carbon sources.

#### 3.4.3. Mass balance of carbon

Carbon balance analysis was performed on the experimental systems. The mass balance of carbon for the treatment of n-hexane and hydrophilic VOCs in BTFs was illustrated in Table 3. Apart from sodium bicarbonate and CO<sub>2</sub> in the background, the only energy source and electron donor in the nutrient solution was VOCs. Whereas sources of effluent carbon in the liquid and gas phase included undegraded VOCs, CO<sub>2</sub> produced by metabolic processes, carbon in the leachate, and the effluent VSS (Aly Hassan and Sorial, 2011; Yang et al., 2004). The carbon equilibrium equation was expressed as

$$Carboninput = VOC_{inlet} + CO_2gas + TC_{liquid}$$
(1)

 $Carbon_{output} = VOC_{outlet} + CO_2gas + TC_{liquid} + VSS_{liquid}$ 

+ VSS<sub>biomass</sub> (2)

The average carbon recovery efficiency varied between BTF A and BTF B. It was defined as the ratio of the effluent and influent

carbon for the same phases. The values of the sources and products of carbon were normalized to the units of mg carbon  $h^{-1}$ . The recovery rates were calculated to be 89.1-97.3% for BTF B under loading rates of  $18.5-109.0 \text{ g m}^{-3} h^{-1}$ , while the recovery efficiency for BTF A was in a range values of 88.0-98.2%. It was noting that about 30.0-41.9% of the carbon in the inlet air stream was converted into inorganic carbon in BTF A. About 4.5-4.9% of the carbon was changed to biomass. However, the percent mineralization of VOCs in BTF B reached at 37.6-48.3% with a biofilm production of 10.5-14.8%. This could be interpreted that the performance of BTF A for VOCs removal was inferior to that of BTF B. As the main carbon source of BTF A, n-hexane was only partially degraded, and most of it constituted the effluent carbon in untreated form (Avalos Ramirez et al., 2008).

# 3.5. Effect of hydrophilic VOCs on biofilms in BTFs

#### 3.5.1. EPS fraction in biofilms

EPS, as an important part of biofilms, provided a wide surface area for microorganisms and were responsible for the mass transfer of substrates. In addition, the content of EPS would change some significant surface characteristics of biofilms, thus affecting the mass transfer of substrates (Sponza, 2003). EFS was mainly composed of proteins and polysaccharides. Changes of proteins and polysaccharides in BTFs during day 21 to day 170 were shown in Fig. 5. The concentrations of proteins and polysaccharides from all parking layers of BTF B were higher than that of BTF A on day 21. which indicated that the addition of 4-methyl-2-pentanone had a positive effect on the increase of EPS. It was worth noting that the addition of 4-methyl-2-pentanone promoted the growth of EPS (especially the protein) in BTF B mainly in the first + second layers. This phenomenon could be explained by the fact that the removal of 4-methyl-2-pentanone rarely occurred in the third + fourth layers of BTF B (Fig. S3), which lead to less increase in protein and polysaccharide concentrations.

For the BTF B added with toluene, it was seen that the content of both polysaccharides and proteins in all parking layers were significantly increased and obtained the maximum values with a corresponding toluene LR of 30.1 g m<sup>-3</sup> h<sup>-1</sup> (the increase from 33.3 to 94.7 mg  $g^{-1}$  MLVSS for protein, from 24.6 to 34.2 mg  $g^{-1}$  MLVSS for polysaccharide). Furthermore, the ratio of protein and polysaccharide (PN/PS) in BTF B kept an increased trend from day 130 to 170. The results showed that addition of toluene promoted the proportion of protein for the EPS in the biofilms. Previous studies indicated that the composition of EPS was strongly correlated with the hydrophobicity of biofilms. It was considered that protein possessed a good deal of non-polar groups and was regarded as the main hydrophobic component in the EPS, while polysaccharide with a large amount of polar groups mainly contributed to the hydrophilic fraction of EPS in biofilms (Li et al., 2016; Wilén et al., 2003). Therefore, the assumption could be drawn that existence of toluene, instead of 4-methyl-2-pentanone, made the EPS in the biofilms more hydrophobic.

## 3.5.2. Microbial growth in biofilms

The growth of microorganisms could be reflected by the total number of colonies in the biofilms (Malakar et al., 2018). Significant differences existed between BTF A and BTF B in the cell concentration (Fig. 6). The initial cell concentration of biofilms from A and B after the acclimation were  $1.9 \times 10^3$  and  $8.9 \times 10^5$  CPU mL<sup>-1</sup>, respectively. It showed that the introduction of 4-methyl-2-pentanone promoted the microbial growth. Futhermore, a slight increase in cell concentration of biofilms with a mixture of n-hexane and toluene in BTF B. The microbial cell numbers varied from  $2.0 \times 10^6$  to  $7.9 \times 10^6$  CPU mL<sup>-1</sup> during day 64 to 130, which

| Table 3 |      |         |     |       |     |     |    |
|---------|------|---------|-----|-------|-----|-----|----|
| Carbon  | mass | balance | for | BTF A | and | BTF | B. |

| BTF | Carbon input rate (mg $h^{-1}$ ) |              |             |       | Carbon output rate (mg $h^{-1}$ ) |              |                |                 |                  |       | Carbon Recovery<br>(%) |
|-----|----------------------------------|--------------|-------------|-------|-----------------------------------|--------------|----------------|-----------------|------------------|-------|------------------------|
|     | VOC                              | $CO_2$ (gas) | TC (liquid) | Total | CO <sub>2</sub><br>(gas)          | VOC<br>(gas) | TC<br>(liquid) | VSS<br>(liquid) | VSS<br>(biomass) | Total |                        |
| A   | 38.4                             | 46.1         | 0.3         | 84.8  | 62.2                              | 8.3          | 5.0            | 0.7             | 4.0              | 81.1  | 94.5                   |
|     | 76.9                             | 59.0         | 0.5         | 126.3 | 89.2                              | 12.0         | 6.3            | 0.8             | 6.2              | 114.5 | 90.7                   |
|     | 136.9                            | 49.0         | 0.7         | 196.6 | 100.5                             | 58.0         | 8.4            | 1.0             | 8.9              | 176.7 | 88.0                   |
|     | 205.0                            | 54.7         | 1.0         | 260.7 | 127.5                             | 101.8        | 9.2            | 1.1             | 12.4             | 252.1 | 89.9                   |
|     | 259.7                            | 53.3         | 1.1         | 314.0 | 135.1                             | 145.6        | 11.2           | 1.2             | 15.1             | 308.2 | 96.7                   |
|     | 314.4                            | 63.4         | 1.3         | 379.1 | 157.8                             | 164.5        | 13.0           | 1.3             | 18.6             | 349.2 | 98.2                   |
| В   | 57.8                             | 43.2         | 0.3         | 101.3 | 71.1                              | 6.7          | 2.7            | 1.8             | 10.6             | 92.9  | 92.1                   |
|     | 100.9                            | 51.8         | 0.5         | 153.2 | 94.4                              | 26.5         | 4.0            | 3.0             | 18.1             | 146.0 | 95.2                   |
|     | 127.8                            | 61.9         | 0.7         | 190.4 | 110.5                             | 37.3         | 5.9            | 4.1             | 24.8             | 182.6 | 95.9                   |
|     | 201.3                            | 60.5         | 1.0         | 262.6 | 136.1                             | 49.2         | 7.5            | 6.0             | 36.2             | 233.9 | 89.1                   |
|     | 249.6                            | 51.8         | 1.1         | 302.5 | 150.6                             | 82.1         | 9.4            | 7.5             | 44.9             | 294.5 | 97.3                   |
|     | 340.6                            | 60.5         | 1.3         | 402.4 | 190.1                             | 104.5        | 11.2           | 8.7             | 52.6             | 367.2 | 91.2                   |



Fig. 5. EPS (protein and polysaccharide) in biofilms of BTF A and BTF B.

indicated the enhanced growth of microorganisms in the presence of hydrophilic VOCs. It was worth noting that the total number of colonies on the 170th day of BTF A, not long after the removal of the excess biofilms, was still kept at 7.0  $\times$  10<sup>6</sup> CPU mL<sup>-1</sup>. It could be concluded that the addition of hydrophilic VOCs contributed to the stable operation of BTFs.

# 3.5.3. Pressure drop

The pressure drop reading of a U-tube pressure gauge was used to assess the biomass accumulation and operational stability of BTFs in this study (Yang et al., 2003b). The pressure drop ranged from 21 to 59 Pa for BTF B and from 53 to 304 Pa for BTF B during the whole run (Fig. 7). The pressure drop of BTF A was quite low. The main reason was that small amounts of n-hexane were biodegradable, which limits the growth and metabolism activities of microorganisms (Zehraoui and Sorial, 2015). As the addition of hydrophilic 4-methyl-2-pentanone and toluene, biofilms in the packing material form BTF B gradually thickened. It might due to the complete degradation of hydrophilic VOCs, which speed up the formation and growth of biofilms. However, a sharp increase in pressure drop on day 65 and 141 was observed. The values reached 178 and 304 Pa, respectively, which meant that excessive biomass



Fig. 6. Total microbial cell counts of BTF A and BTF B.

was finally formed. In order to prevent the accumulation of excessive biomass from damaging the performance of BTF B, the corresponding measures were taken. The amount of pollutants and nutrient solution were reduced to control the growth of biomass. The excess biomass was removed by pressing the polyester sponges in nutrient solution (Yang et al., 2010b).

# 3.6. Interaction mechanism of hydrophilic and hydrophobic VOCs

For multi-component VOC mixtures with different hydrophobicity, the removal of hydrophobic VOCs could be inhibited by hydrophilic VOCs. The inhibition might be due to the following reasons. Firstly, the hydrophobic natures of hydrophobic VOCs limited their degradation in biotrickling filters (Lebrero et al., 2013). Secondly, the presence of high-LR pollutants reduced the operational performance of BTFs. In addition, the matrix competition between hydrophobic and hydrophilic VOCs resulted in the preferential degradation of hydrophilic VOCs with strong hydrophilicity, while the degradation of hydrophobic VOCs was limited by high-LR toluene (Zamir et al., 2012).

In addition, the presence of some hydrophilic VOCs stimulated



Fig. 7. Profiles of pressure drop during the operation of BTF A and BTF B.



Fig. 8. Interaction mechanism between the hydrophobic and hydrophilic VOCs.

the removal of reluctant VOCs in BTFs. Previous studies had also found that methanol can be used as a co-metabolizing substrate to improve the RE of dimethyl sulfide when the binary mixture of dimethyl sulfide and methanol were degraded in BTFs (Zhang et al., 2010). As demonstrated in Fig. 8, the addition of hydrophilic VOCs (4-methyl-2-pentanone or toluene) could stimulate the growth of microbial populations in biofilms, and stimulating their demand for carbon sources. Once microorganisms grow rapidly, hydrophobic nhexane was mostly utilized to meet the requirements of their growth and metabolism. Hence, reducing the LR of hydrophilic 4methyl-2-pentanone or toluene could promote the consumption of hydrophobic n-hexane in a disguised way.

# 4. Conclusions

The effect of hydrophilic VOCs on removal of hydrophobic nhexane in BTFs was evaluated. Short EBRT (15 s) and low temperature (15 °C) did damage to the removal performance of hydrophobic n-hexane. The addition of hydrophilic 4-methyl-2pentanone could mitigate the negative effect to ensure the stable operation of BTFs. The elimination of n-hexane in BTFs was promoted in the presence of hydrophilic 4-methyl-2-pentanone and moderately hydrophilic toluene. The positive effect of 4-methyl-2pentanone on n-hexane was only demonstrated when the LRs of 4methyl-2-pentanone were extremely low, for 4-methyl-2pentanone LRs less than 6.2 g m<sup>-3</sup> h<sup>-1</sup>. The promoted degradation of n-hexane by toluene occurred when the loading ratio between n-hexane and toluene was greater than 4. The enhanced removal of n-hexane by hydrophilic VOCs was reflected in the rapid growth and reproduction of microorganisms in biofilms.

## **Declaration of competing interests**

The authors declare no competing financial interest.

#### **CRediT authorship contribution statement**

Yeting Cheng: Investigation, Methodology, Writing - original draft, Validation, Writing - review & editing. Xiang Li: Investigation, Methodology. Haiyang Liu: Writing - review & editing, Methodology. Chunping Yang: Conceptualization, Project administration, Funding acquisition, Writing - review & editing. Shaohua **Wu:** Methodology. **Cheng Du:** Conceptualization, Project administration, Writing - review & editing. **Lijun Nie:** Writing - review & editing. **Yuanyuan Zhong:** Writing - review & editing.

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## Appendix A. Supplementary data

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#### References

- Abhinayaa, R., Jeevitha, G., Mangalaraj, D., Ponpandian, N., Meena, P., 2019. Toxic influence of pristine and surfactant modified halloysite nanotubes on phytopathogenic bacteria. Appl. Clay Sci. 174, 57–68.
- Alberto, V.F., Sergio, H., Sergio, R., 2010. Phenomenological model of fungal biofilters for the abatement of hydrophobic VOCs. Biotechnol. Bioeng. 101, 1182–1192.
- Aly Hassan, A., Sorial, G.A., 2011. Treatment of dynamic mixture of hexane and benzene vapors in a Trickle Bed Air Biofilter integrated with cyclic adsorption/ desorption beds. Chemosphere 82, 521–528.
- APHA (American Public Health Association), 1998. Standard Methods for the Examination of Water and Wastewater, twentieth ed. AQ, Washington, DC, USA).
- Amin, M.M., Rahimi, A., Bina, B., Nourmoradi, H., Hassanvand, M.S., Mohammadi-Moghadam, F., Norouzi, S., Heidari, M., 2017. Biodegradation of n-hexane as single pollutant and in a mixture with BTEX in a socria/compost-based biofilter. Process Saf. Environ. Protect. 107, 508–517.
- Avalos Ramirez, A., Benard, S., Giroir-Fendler, A., Jones, J.P., Heitz, M., 2008. Kinetics of microbial growth and biodegradation of methanol and toluene in biofilters and an analysis of the energetic indicators. J. Biotechnol. 138, 88–95.
- Balasubramanian, P., Philip, L., Murty Bhallamudi, S., 2012. Biotrickling filtration of complex pharmaceutical VOC emissions along with chloroform. Bioresour. Technol. 114, 149–159.
- Barbusinski, K., Kalemba, K., Kasperczyk, D., Urbaniec, K., Kozik, V., 2017. Biological methods for odor treatment - a review. J. Clean. Prod. 152, 223–241.
- Bordoloi, A., Gapes, D.J., Gostomski, P.A., 2019. The impact of environmental parameters on the conversion of toluene to CO<sub>2</sub> and extracellular polymeric substances in a differential soil biofilter. Chemosphere 232, 304–314.
- Cheng, Y., He, H., Yang, C., Zeng, G., Li, X., Chen, H., Yu, G., 2016a. Challenges and solutions for biofiltration of hydrophobic volatile organic compounds. Biotechnol. Adv. 34, 1091–1102.
- Cheng, Y., He, H., Yang, C., Yan, Z., Zeng, G., Qian, H., 2016b. Effects of anionic surfactant on n-hexane removal in biofilters. Chemosphere 150, 248–253.
  Chen, Y., He, H., Liu, H., Li, H., Zeng, G., Xia, X., Yang, C., 2018. Effect of salinity on
- Chen, Y., He, H., Liu, H., Li, H., Zeng, G., Xia, X., Yang, C., 2018. Effect of salinity on removal performance and activated sludge characteristics in sequencing batch reactors. Bioresour. Technol. 249, 890–899.
- Chheda, D., Sorial, G.A., 2017. Evaluation of co-metabolic removal of trichloroethylene in a biotrickling filter under acidic conditions. J. Environ. Sci. 57, 54–61.
- Dixit, R., Deshmukh, S., Gadhe, A., Kannade, G., Lokhande, S., Pandey, R., Vaidya, A., Mudliar, S., Deshusses, M., 2012. Treatment of mixtures of toluene and npropanol vapours in a compost–woodchip-based biofilter. Environ. Technol. 33, 751–760.
- Eregowda, T., Rene, E.R., Lens, P.N.L., 2019. Bioreduction of selenate in an anaerobic biotrickling filter using methanol as electron donor. Chemosphere 225, 406–413.
- Gągol, M., Boczkaj, G., Haponiuk, J., Formela, K., 2015. Investigation of volatile low molecular weight compounds formed during continuous reclaiming of ground tire rubber. Polym. Degrad. Stabil. 119, 113–120.
- Hassan, A.A., Sorial, G.A., 2010. Biofiltration of n-hexane in the presence of benzene vapors. J. Chem. Technol. Biotechnol. 85, 371–377.
- Hinojosa-Reyes, M., Arriaga, S., 2012. Enhancing ethylbenzene vapors degradation in a hybrid system based on photocatalytic oxidation UV/TiO2-In and a biofiltration process. J. Hazard Mater. 209–210, 365–371.
- Hu, Q.Y., Wang, C., Huang, K.X., 2015. Biofiltration performance and characteristics of high-temperature gaseous benzene, hexane and toluene. Chem. Eng. J. 279, 689–695.
- Hu, Q.Y., Wang, C., 2015. Interaction of gaseous aromatic and aliphatic compounds in thermophilic biofilters. J. Hazard Mater. 300, 210–217.

- Ikemoto, S., Jennings, A.A., Skubal, K.L., 2006. Modeling hydrophobic VOC biofilter treatment in the presence of nutrient stimulation and hydrophilic VOC inhibition. Environ. Model. Software 21, 1387–1401.
- Jin, Y., Veiga, M.C., Kennes, C., 2007. Co-treatment of hydrogen sulfide and methanol in a single-stage biotrickling filter under acidic conditions. Chemosphere 68, 1186–1193.
- Kasperczyk, D., Urbaniec, K., Barbusinski, K., Rene, E.R., Colmenares-Quintero, R.F., 2019. Application of a compact trickle-bed bioreactor for the removal of odor and volatile organic compounds emitted from a wastewater treatment plant. J. Environ. Manag. 236, 413–419.
- Kim, D., Cai, Z., Sorial, G.A., Shin, H., Knaebel, K., 2007. Integrated treatment scheme of a biofilter preceded by a two-bed cyclic adsorption unit treating dynamic toluene loading. Chem. Eng. J. 130, 45–52.
- Lebrero, R., Rodríguez, E., Estrada, J.M., García-Encina, P.A., Muñoz, R., 2012. Odor abatement in biotrickling filters: effect of the EBRT on methyl mercaptan and hydrophobic VOCs removal. Bioresour. Technol. 109, 38–45.
- Lebrero, R., Volckaert, D., Pérez, R., Muñoz, R., Langenhove, H.V., 2013. A membrane bioreactor for the simultaneous treatment of acetone, toluene, limonene and hexane at trace level concentrations. Water Res. 47, 2199–2212.
  Li, X., Yang, W., He, H., Wu, S., Zhou, Q., Yang, C., Zeng, G., Luo, L., Lou, W., 2018.
- Li, X., Yang, W., He, H., Wu, S., Zhou, Q., Yang, C., Zeng, G., Luo, L., Lou, W., 2018. Responses of microalgae Coelastrella sp. to stress of cupric ions in treatment of anaerobically digested swine wastewater. Bioresour. Technol. 251, 274–279.
- Li, Y., Zheng, P., Zhang, M., Zeng, Z., Wang, Z., Ding, A., Ding, K., 2016. Hydrophilicity/ hydrophobicity of anaerobic granular sludge surface and their causes: an in situ research. Bioresour. Technol. 220, 117–123.
- Malakar, S., Saha, P.D., Baskaran, D., Rajamanickam, R., 2018. Microbial biofilter for toluene removal: performance evaluation, transient operation and theoretical prediction of elimination capacity. Sustainable Environment Research 28, 121–127.
- Parnian, P., Zamir, S.M., Shojaosadati, S.A., 2016. Effect of operating temperature on styrene mass transfer characteristics in a biotrickling filter. Environ. Technol. Lett. 38, 1324–1332.
- Qian, H., Cheng, Y., Yang, C., Wu, S., Zeng, G., Xi, J., 2018. Performance and biofilm characteristics of biotrickling filters for ethylbenzene removal in the presence of saponins. Environ. Sci. Pollut. Control Ser. 25, 30021–30030.
- Rene, E.R., Sergienko, N., Goswami, T., López, M.E., Kumar, G., Saratale, G.D., Venkatachalam, P., Pakshirajan, K., Swaminathan, T., 2018. Effects of concentration and gas flow rate on the removal of gas-phase toluene and xylene mixture in a compost biofilter. Bioresour. Technol. 248, 28–35.
- Saingam, P., Baig, Z., Xu, Y., Xi, J., 2018. Effect of ozone injection on the long-term performance and microbial community structure of a VOCs biofilter. J. Environ. Sci. 69, 133–140.
- Saucedo-Lucero, J.O., Quijano, G., Arriaga, S., Muñoz, R., 2014. Hexane abatement and spore emission control in a fungal biofilter-photoreactor hybrid unit. J. Hazard Mater. 276, 287–294.
- Song, T., Yang, C., Zeng, G., Yu, G., Xu, C., 2012. Effect of surfactant on styrene removal from waste gas streams in biotrickling filters. J. Chem. Technol. Biotechnol. 87, 785–790.
- Sponza, D.T., 2003. Investigation of extracellular polymer substances (EPS) and physicochemical properties of different activated sludge flocs under steadystate conditions. Enzym. Microb. Technol. 32, 375–385.
- Sun, Z., Yang, B., Ding, C., Li, Z., Wang, L., 2018. Enhanced removal of gaseous 1,3dichlorobenzene in biotrickling filters by rhamnolipid and Mg (II). J. Hazard Mater. 360, 571–577.
- Tu, Y., Yang, C., Cheng, Y., Zeng, G., Lv, L., Wang, L., 2015. Effect of saponins on nhexane removal in biotrickling filters. Bioresour. Technol. 175, 231–238.
- Vergara-Fernández, A., Yánez, D., Morales, P., Scott, F., Aroca, G., Diazrobles, L., Morenocasas, P., 2018. Biofiltration of benzo[α]pyrene, toluene and formaldehyde in air by a consortium of Rhodococcus erythropolis and Fusarium solani: effect of inlet loads, gas flow and temperature. Chem. Eng. J. 332, 702–710.
- Volckaert, D., Ebude, D.E.L., Van Langenhove, H., 2016. SIFT-MS analysis of the removal of dimethyl sulphide, n-hexane and toluene from waste air by a two phase partitioning bioreactor. Chem. Eng. J. 290, 346–352.
- Wang, C., Xi, J.Y., Hu, H.Y., Yao, Y., 2009. Effects of UV pretreatment on microbial community structure and metabolic characteristics in a subsequent biofilter treating gaseous chlorobenzene. Bioresour. Technol. 100, 5581–5587.
- Wang, L., Yang, C., Cheng, Y., Huang, J., He, H., Zeng, G., Lu, L., 2013. Effects of surfactant and Zn (II) at various concentrations on microbial activity and ethylbenzene removal in biotricking filter. Chemosphere 93, 2909–2913.
- Wilén, B., Jin, B., Lant, P., 2003. The influence of key chemical constituents in activated sludge on surface and flocculating properties. Water Res. 37, 2127–2139.
- Xi, J.Y., Kang, I.S., Hu, H.Y., Zhang, X., 2015. A biofilter model for simultaneous simulation of toluene removal and bed pressure drop under varied inlet loadings. Front. Environ. Sci. Eng. 9, 554–562.
- Yang, C., Qian, H., Li, X., Cheng, Y., He, H., Zeng, G., Xi, J., 2018. Simultaneous removal of multicomponent VOCs in biofilters. Trends Biotechnol. 36, 673–685.
- Yang, C., Suidan, M., Zhu, X., Kim, B., 2003a. Comparison of single-layer and multilayer rotating drum biofilters for VOC removal. Environ. Prog. 22, 87–94.
- Yang, C., Suidan, M., Zhu, X., Kim, B., 2003b. Biomass accumulation patterns for removing volatile organic compounds in rotating drum biofilters. Water Sci. Technol. 48, 89–96.
- Yang, C., Suidan, M., Zhu, X., Kim, B., 2004. Removal of a volatile organic compound in a hybrid rotating drum biofilter. J. Environ. Eng. 130, 282–291.
- Yang, C., Suidan, M., Zhu, X., Kim, B., Zeng, G., 2008. Effect of gas empty bed contact time on performances of various types of rotating drum biofilters for removal of

VOCs. Water Res. 42, 3641-3650.

- Yang, C., Chen, H., Zeng, G., Yu, G., Liu, X., Zhang, X., 2009. Modeling variations of medium porosity in rotating drum biofilter. Chemosphere 74, 245–249.
- Yang, C., Chen, F., Luo, S., Xie, G., Zeng, G., Fan, C., 2010a. Effects of surfactants and salt on Henry's constant of n-hexane. J. Hazard Mater. 175, 187–192.
- Yang, C., Chen, H., Zeng, G., Yu, G., Luo, S., 2010b. Biomass accumulation and control strategies in gas biofiltration. Biotechnol. Adv. 28, 531–540.
- Yang, C., Yu, G., Zeng, G., Yang, H., Chen, F., Jin, C., 2011. Performance of biotrickling filters packed with structured or cubic polyurethane sponges for VOC removal. J. Environ. Sci. 23, 1325–1333.
- Yao, X.-Z., Chu, Y.-X., Wang, C., Li, H.-J., Kang, Y.-R., He, R., 2019. Enhanced removal of methanethiol and its conversion products in the presence of methane in biofilters. J. Clean. Prod. 215, 75–83.
- Zamir, M., Halladj, R., Sadraei, M., Nasernejad, B., 2012. Biofiltration of gas-phase hexane and toluene mixture under intermittent loading conditions. Process

Saf. Environ. Protect. 90, 326-332.

- Zehraoui, A., Hassan, A.A., Sorial, G.A., 2012. Effect of methanol on the biofiltration of n-hexane. J. Hazard Mater. 219–220, 176–182.
- Zehraoui, A., Hassan, A.A., Sorial, G.A., 2013. Biological treatment of n-hexane and methanol in trickle bed air biofilters under acidic conditions. Biochem. Eng. J. 77, 129–135.
- Zehraoui, A., Sorial, G.A., 2015. Treatment of dynamic mixture of n-hexane, benzene, and methanol and fungi community characterization in an integrated scheme of cyclic adsorption/desorption beds and trickle bed air biofilter. Air Soil. Water Res. 2, 31–41.
- Zhang, Y., Steven, N., Allen, G., 2010. The effects of methanol on the biofiltration of dimethyl sulfide in inorganic biofilters. Biotechnol. Bioeng. 95, 734–743.
- Zhao, K., Xiu, G., Xu, L., Zhang, D., Zhang, X., Deshusses, M.A., 2011. Biological treatment of mixtures of toluene and n-hexane vapours in a hollow fibre membrane bioreactor. Environ. Technol. 32, 617–623.