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Research review paper

Challenges and solutions for biofiltration of hydrophobic volatile organic compounds

Yan Cheng^{a,b,1}, Huijun He^{a,b,1}, Chunping Yang^{a,b,c,*}, Guangming Zeng^{a,b,**,1}, Xiang Li^{a,b,1}, Hong Chen^{d,1}, Guanlong Yu^{d,1}

^a College of Environmental Science and Engineering, Hunan University, Changsha, Hunan 410082, China

^b Key Laboratory of Environmental Biology and Pollution Control (Hunan University), Ministry of Education, Changsha, Hunan 410082, China

^c Zhejiang Provincial Key Laboratory of Solid Waste Treatment and Recycling, College of Environmental Science and Engineering, Zhejiang Gongshang University, Hangzhou, Zhejiang 310018, China

^d School of Hydraulic Engineering, Changsha University of Science and Technology, Changsha, Hunan 410004, China

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ABSTRACT

Volatile organic compounds (VOCs) emitted to the environment highly probably result in ecological and health risks. Many biotechnologies for waste gases containing hydrophobic VOCs have been developed in recent years. However, these biological processes usually exhibit poor removal performances for hydrophobic VOCs due to the low bioavailability. This review presents an overview of enhanced removal of hydrophobic VOCs in biofilters. Mechanisms and problems relevant to the biological removal of hydrophobic VOCs are reviewed, and then solutions including the addition of surfactants, application of fungal biocatalysts, biofiltration with pretreatment, innovative bioreactors and utilization of hydrophilic compounds are discussed in detail. Future research needs are also proposed. This review provides new insights into hydrophobic VOC removal by biofiltration.

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* Correspondence to: C. Yang, College of Environmental Science and Engineering, Hunan University, Changsha, Hunan 410082, China.

** Correspondence to: G. Zeng, Key Laboratory of Environmental Biology and Pollution Control (Hunan University), Ministry of Education, Changsha, Hunan 410082, China.

E-mail addresses: yang@hnu.edu.cn (C. Yang), zgming@hnu.edu.cn (G. Zeng).

¹ These authors contribute equally to this paper.

1. Introduction

Atmospheric pollutant emissions have increased over the past few decades due to the development of economy, and have become one of the most important problems that governments and the general public will have to face in the present century (Delhomenie and Heitz, 2005; Malhautier et al., 2005). Volatile Organic Compounds (VOCs) such as the low-boiling hydrocarbon, halogenated hydrocarbons, alcohols, aldehydes, ketones, ethers, acids, and volatile polycyclic aromatic hydrocarbons (PAHs) have been listed as prior substances by the European Water Framework Directive because of their risks to human health and hazard to the environment (An, 2004; Farhadian et al., 2008; Rene et al., 2010b; Hassan and Sorial, 2010). Emissions of these xenobiotic compounds mentioned above constitute about 7% of all atmospheric pollutants which have continuously increased since the beginning of last century (Delhomenie and Heitz, 2005). Moreover, some VOCs such as methane are greenhouse gases with a potential to cause global warming (Boucher et al., 2009), while others such as some hydrocarbons can lead to photochemical smog with other gases (NO_x) and produce ozone near the ground (Christensen et al., 1999; West and Fiore, 2005). Though the overall emission load of VOCs remains relatively low, VOCs emitted from industry and households are very likely to become ecological and health hazards, especially to humans, animals and the environment (Guieysse et al., 2008; Mudliar et al., 2010; Rene et al., 2010b; Rene et al., 2015).

Hydrophobic VOCs are released into the atmosphere from various industrial activities. The industrial use of the commercial hydrophobic compounds contributes significantly to the overall emission of these compounds. For instance, styrene is predominantly emitted from manufacturing of plastics, polymer industries, synthetic resins, and butadiene-styrene latex (Rene et al., 2010b; Jorio et al., 2000). Ethylbenzene is typically found in petroleum products such as diesel fuel and gasoline. It is commonly used as an intermediate or solvent in organic synthesis. In European Union, benzene and toluene are emitted at 79 and 976 kt per year into the air, respectively, constituting roughly 0.02% and 3% of the total non-methane VOC emission (Rene et al., 2015). *n*-Pentane, another hydrocarbon isolated from petrol, contributes 0.4% to the total non-methane VOC emission (EURAR, 2003). Although these VOCs constitute low percentage of the total non-methane VOC emission, they have an important impact on the air quality. This is especially true for those VOCs like benzene due to their potential health hazards including possible carcinogenic effect (Christensen et al., 1999). Therefore, more and more stringent laws and regulations for emission control of VOCs have been issued in response to the adverse health risks and potential environmental problems posed by these chemicals (Delhomenie and Heitz, 2005; Hernández et al., 2010; Muñoz et al., 2007; Liu et al., 2007). For instance, the enactment of the 1990 Amendments to the Clean Air Act (CAA) facilitates the development of more efficient biotechnologies for reducing air pollutant emissions (Zehraoui et al., 2012), and the market for biotechnologies begins to thrive with these increasingly rigorous regulations.

Though there are many processes for the control of VOC emission from waste gas streams, biological processes are based on the ability of microorganisms in biofilm form immobilized or attached on packing media such as peat, composts, polyurethane foams and other types of porous solid particles (Mallakin and Ward, 1996; Znad et al., 2007; Kim et al., 2007; Yang et al., 2011). When VOCs in waste gases flow through the support medium, these pollutants are absorbed by the biofilm and converted into innocuous products such as carbon dioxide (CO₂), water, and cell mass without generating undesirable by-products (Moe and Irvine, 2001). Therefore, biological processes when designed and operated properly exhibit advantages including cost-effectiveness, reliable robust performances and eco-friendliness over conventional methods such as physicochemical adsorption, condensation, incineration, and photolysis (Delhomenie and Heitz, 2005; Kumar et al., 2011;

Malhautier et al., 2005; Mudliar et al., 2010). Recently, biological processes have become increasingly attractive and competitive, in which bioscrubbers, conventional biofilters, biotrickling filters, and novel biofilters have been used or developed (Devinny et al., 1999; Yang et al., 2003; Yang et al., 2010b; Hernández et al., 2010).

However, there still exist limitations to biological processes. One limitation involves the excess biomass accumulation, the uneven distribution of biomass and nutrient (Jorio et al., 2000; Yang et al., 2003). Many reviews on strategies of addressing this drawback are reported (Yang et al., 2010b). In addition, the low mass transfer of hydrophobic VOCs from the gas phase to the biofilm phase limits the supply of substrates to the microorganisms, resulting in a low bioavailability and a low rate of biodegradation of these compounds. Bioavailability represents the accessibility of a chemical for assimilation and possible toxicity (Alexander, 2000), and physical contact between microbes and organic compounds is an essential prerequisite for bioavailability and consequent biodegradation. To achieve contact, VOCs in gas phase usually need transfer from the gas phase to liquid phase and then to biofilm phase. Therefore, bioavailability is one of the key factors affecting VOC biodegradation in biofilters. In biofiltration system, the removal performance of hydrophobic VOCs is significantly affected not only by their physicochemical properties including the solubility in water, the Henry's law constant, the contaminant molecular structure and the gas flow, but also by microorganisms and moisture (Deshusses and Johnson, 2000; Kumar and Chandrajit, 2011; Zehraoui et al., 2012). For instance, hydrophobic VOCs such as hexane are more resilient to degradation than hydrophilic one like water soluble ketones in biological systems, as the removal efficiency of hydrophobic VOCs is limited by the low mass transfer rates from gas phase to biofilm phase (Zehraoui et al., 2012). Thus, an increase of the bioavailability of hydrophobic VOCs in the liquid or biofilm phase will be benefit for their degradation by microorganisms and improve the performance of biofilters (Arriaga et al., 2006; Laura et al., 2009; Hernández et al., 2011; Darracq et al., 2012; Ramirez et al., 2012a). However, if the mass transfer from liquid phase to biofilm phase is rate-limiting, further solubilization of VOCs may even result in an inhibition of VOC biodegradation in case of reaction limitation.

Many methods have been investigated for enhanced removal of hydrophobic VOCs in biofilters, including pretreatment, fungal biofilters, two-phase biofilters, surfactant addition, and low moisture operation, while little reviews are available in this field. This review focuses on bioavailability of hydrophobic VOCs in biofilters including factors both affecting bioavailability and biodegradation and strategies for improving bioavailability (see Fig. 1), and is supposed to help understand and design hydrophobic VOC biofiltration better.

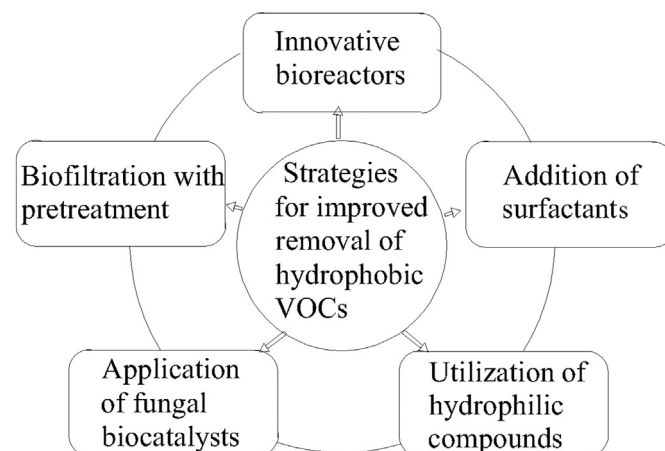


Fig. 1. Improving biodegradable approaches of hydrophobic VOCs.

2. Biofiltration mechanisms

Biofiltration for VOC removal is a complex combination of different physicochemical and biological phenomena. A typical biofilter for treatment of a waste gas stream is illustrated in Fig. 2, and Fig. 3 describes pollutant removal processes in a biofilter. Although the mechanism of VOC biodegradation is complicated, it can be grouped into the biofilm level, the medium level and the reactor level according to space scale.

Waste gas including pollutant vapors and oxygen pass through the biofilter packing media. Contaminants in the bulky gas are transferred from the gas phase to the water phase or biofilm phase by diffusion prior to biodegradation. Mass transfer rate for pollutants from the air to the water is related to the Henry's law constant. VOC pressure or concentration in the air is proportional to its concentration in the water, and the constant of proportionality is called the Henry's law constant (H_c) for aqueous samples (Anderson, 1992; Vane and Giroux, 2000; Deshusses et al., 1995):

$$H_c = \frac{C_g}{C_l} \quad (1)$$

where C_g and C_l are VOC concentrations in the gas-phase and liquid-phase, respectively. Within the biofilm, VOCs diffuse and are consumed by microorganisms simultaneously. Oxygen is also subject to diffusional resistance due to growth and replication of microorganisms. The adsorption of the pollutants is possible either after diffusion through the whole thickness of biofilms as modeled by Deshusses et al. (1995) or directly occurring on the pore of packing material (Shareefdeen and Baltzis, 1994). Metabolite will be produced as a result of VOC biodegradation occurring in the biofilm, and it undergoes the same processes of simultaneous diffusion, biodegradation and adsorption. Acidic metabolites will be neutralized by limestone powder generally mixed with the medium prior to the packing of the biofilter (Smet et al., 1996) or other pH buffer agents such as $\text{Ca}(\text{OH})_2$, NaOH , NaHPO_4 , NaHCO_3 and urea added into nutrient solution (Yang et al., 2008a; Wang et al., 2014). However, metabolites are seldom observed in biological processes, suggesting that they are degraded faster than their parent compounds by the primary VOC degraders themselves or other ancillary strains in direct contact with the primary VOC degraders. The CO_2 produced by VOC oxidation diffuses and is transferred to the gas phase (CO_2 retrodiffusion) or forms carbonate in aqueous phase.

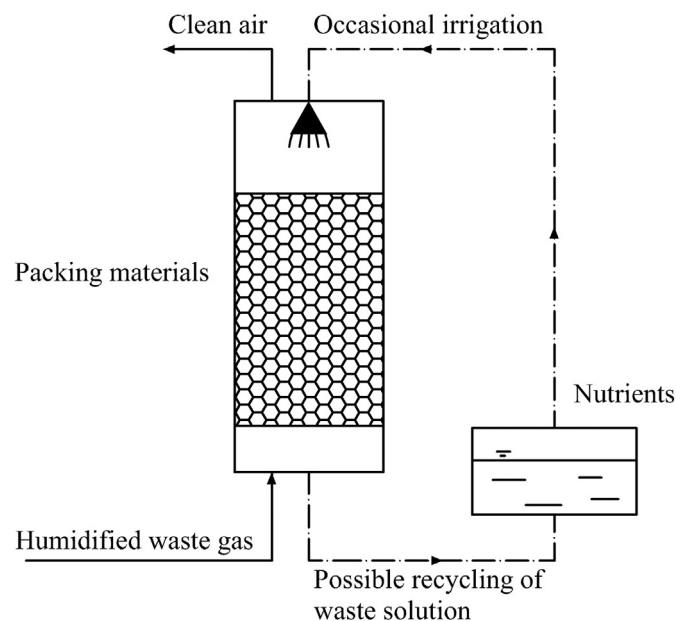


Fig. 2. Schematic view of a conventional biofilter.

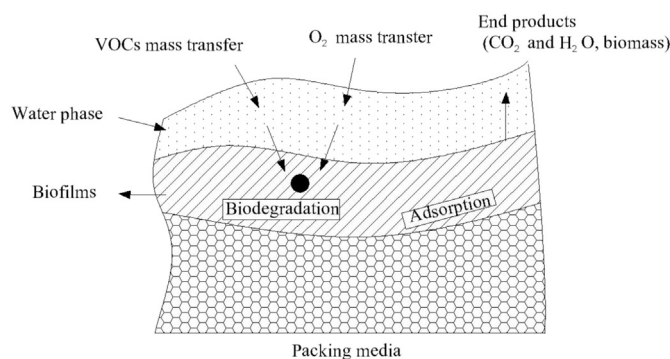


Fig. 3. Phenomena involved in the operation of bioreactors.

A main function of packing media in biofilters is to provide a surface for microorganism's attachment and growth (Anet et al., 2013; Gutiérrez-Acosta et al., 2012). Moreover, it serves as a reservoir for water, pollutants and nutrients by adsorption on its matrix and absorption in pore water. In general, the packing medium (organic medium) comprises an amount of organic residues which may be utilized as nutrients by the VOC degraders that are affected by operating conditions or their direct environment. Some biofilters packed with the inorganic medium need to add nutrients and microorganisms. In biofiltration, biofilms will gradually grow thick during a long period of operation, which is especially true when biofilters are operated at high VOC loadings (Wang et al., 2014; Yang et al., 2008a; Yang et al., 2004). The growing biofilm within biofilter media usually leads to change in porosity of biofilter bed because the pores within the packing are highly irregular in shape (Devinny and Ramesh, 2005). The porosity of the filter bed gradually decreases with increased duration of operation, increased VOC loading, or decreased gas bed residence time (EBRT) value (Yang et al., 2008b, 2009).

Pressure drop of biofilters increases gradually due to the continuous accumulation of biomass during biodegradation processes. Supply of nutrients, oxygen, and carbon sources to microorganisms within the deep portions of biofilms may be limited by diffusion at some point. Some operational problems such as clogging of media, excessive head loss, and channel formation of gas streams within biofilters beds can also occur because of excessive biomass accumulated in a biofilter bed (Wang et al., 2014).

3. Factors affecting VOC bioavailability and biodegradation in biofilters

The bioavailability and biodegradability of hydrophobic VOCs are controlled by numerous factors that can be divided into four categories: mass transfer of pollutants, microbial populations, packing media and moisture (Deshusses and Johnson, 2000; Prado et al., 2006; Gaudin et al., 2008; Ding et al., 2008; Rene et al., 2012a).

3.1. Mass transfer of pollutants

Mass transfer of VOCs is a crucial factor for affecting the fate of a VOC molecule and effective gas biofiltration among these key biofilters variables (Ralebitso-Senior et al., 2012). Mass transfer involves gas-liquid and liquid-biofilm transfer, and is frequently assumed to be balance at the interfaces of two phases (Kraakman et al., 2011; Yang et al., 2010a). The mass transfer mechanism is dependent on the mass transfer coefficient, the exchange area and the discharge concentration and the flow rate of the target gas (Shareefdeen and Singh, 2005; Kraakman et al., 2011). Temperature of the gas must also be considered because appropriate gas temperature will facilitate gas solubilization for optimum microbial catabolism. In addition, salts in aqueous phase and the presence of biomass and extracellular metabolites such as

biosurfactants (rhamnolipid) can also alter the gas-liquid phase equilibrium according to Henry's law and thus affect mass transfer of pollutants (Peng and Wan, 1998; Albino and Nambi, 2009; Yang et al., 2010a).

It is usually accepted that biofilters are only suitable for the removal of VOCs with a moderate to low Henry's law constant. For VOCs with high Henry's law constants, the elimination capacity is limited (Deshusses and Johnson, 2000; Zhu et al., 2004). Table 1 presents a VOC classification on the basis of the Henry's law constants which can be used to estimate removal performances in biofilters due to mass transfer limitation. Despite that the general tendency for compounds with high Henry's law constant has lower removal rates, biofiltration can still be effective for very hydrophobic compounds such as hexane or α -pinene (van Groenestijn and Liu, 2002; Jin et al., 2006), which can be explained by the fact that the presence of organic material in biofilms that can sorb the pollutant results in higher partitioning to a biofilm (Mohseni and Allen, 2000). However, a higher partitioning to a biofilm does not lead to higher transport rates of VOC molecule through the film (Miller and Allen, 2004). Therefore, it is needed to explore some mechanisms to explain the transport and degradation of hydrophobic pollutants in biofilms.

3.2. Microbial populations

The presence of microorganisms and the development of biofilms are critical to the effective removal of VOCs in bioreactors. Microorganisms are catalysts of pollutant degradation (Delhomenie and Heitz, 2005). Biodegradation of pollutants involves the breakdown of molecules either through biotransformation into less complex metabolite or through mineralization into nontoxic by-products (inorganic minerals, H₂O and CO₂). Pollutants are oxidized completely, which results in mineralization. In some cases, partial oxidation may also occur when the oxygen is not enough or the pollutant is in high concentration in the liquid (Christen et al., 2002). Also, some recalcitrant compounds such as trichloroethylene (TCE) can be converted by co-metabolic processes which is metabolic transformation of a substrate where a second substrate serves as primary energy or carbon source (Shareefdeen and Singh, 2005; Jung and Park, 2005).

Wastewater sludge as inoculum is usually used for the startup of biofilters in waste gas treatment (Wang et al., 2013). However, as the increasing chemical complexities of molecules, it is also necessary to use specific monocultures or microbial communities to degrade the target pollutant in waste gas. Various methods of enrichment and isolation of catabolic species and microbial communities are used to obtain appropriate cultures. These methods may be considered to depend on the target molecule. In this process, different pollutants exhibit different inhibitive concentration for different microorganisms (Vergara-Fernández et al., 2011). For the same monocultures or microbial community, microbial growth and substrate utilization rates are also different between batch experiments and continuous biofiltration, and they are affected by specific operational parameters within similar

bioreactors. In this case, the use of microbial community is common in biofilters for VOC degradation, instead of pure cultures. At this stage, kinetic analysis can be used to evaluate microbial growth and contaminant degradation and determine microbial growth rate, saturation constant and limitation of oxygen, nutrient and pH (Devinny and Ramesh, 2005).

In a biofiltration system, the attachment of microorganisms to the surface of packing media is crucial to biofilm formation (Chávez et al., 2006). Biofilms are composed by mixed cultures of bacteria, fungi, actinomycetes and algae, all constituting a complex ecosystem in bioreactors. In general, there are 10⁶–10¹⁰ cfu of bacteria and actinomycetes and 10³–10⁶ cfu of fungi per g of bed in a typical biofilter (Ottengraf, 1987). Also, the degrading microbes present in a biofilter usually account for 1–15% of the total microbial population (Pedersen et al., 1997; Delhomenie et al., 2001). In addition, communities are affected by changes of environmental conditions during biodegradation processes. Therefore, investigating and analyzing their diversity helps optimize design and operations of such biological systems. Some advanced analysis methods such as confocal laser scanning microscopy (CLSM), microautoradiography (MAR), polymerase chain reactions (PCR), quantitative reverse transcriptase real-time PCR (qRT-PCR), single strand conformation polymorphism (SSCP) (Omri et al., 2011), denaturing gradient gel electrophoresis (DGGE) (Okunishi et al., 2012) or fluorescence in situ hybridization (FISH) for assessing microbial diversity have proven to be powerful tools, and their potential applications in waste gas attenuation studies have been summarized by Ralebitso-Senior et al. (2012).

3.3. Packing media

Packing media in biofiltration systems are typically defined as a solid media on which microorganisms adhere to and develop into biofilms. A main function of packing media is to facilitate contaminants to contact with microorganisms, allowing a formation of a stable microbe aggregate (Anet et al., 2013; Gutiérrez-Acosta et al., 2012). Thus, the choice of the media is a key factor to maintain a stable biodegradable rate of VOCs in biofilters.

Specific physicochemical properties of packing media need to be considered before their utilization (Swanson and Loehr, 1997; Gabriel et al., 2007; Maestre et al., 2007; Gaudin et al., 2008; Anet et al., 2013): a) an important porosity and a high void fraction, both of which are crucial to the microbial growth, gas flow distribution and clogging prevention; b) a high surface area to promote water retention properties and improve the transfer of pollutants, nutrients, and oxygen; c) a good water retention capacity to avoid bed drying. In addition, adsorption characteristics of packing media for the target pollutant should also be carefully considered in biofiltration.

Organic or inorganic nature of packing media and the size of particles have an important effect on the mechanical properties of the packing medium and the operating costs in biofilters. Bed compaction,

Table 1
Hydrophilicity/hydrophobicity and Henry's law constant of VOCs.

| | Hydrophilic | Moderately hydrophilic | Hydrophobic |
|--|--|--|---|
| VOCs | Dimethyl sulfide Dimethyl disulfide Hydrogen sulfide Methanol Methyl ethyl ketone Formaldehyde Isobutanol Acetone | α -Pinene BTEX Dichloromethane Isopropylbenzene Styrene Chlorobenzene Trichloromethane – | Ethene Ethane Hexane Methane Pentane Acetylene Cyclohexane – |
| Henry's law constant ^a at 25 °C | 0.0001–0.099 | 0.1–0.99 | 1–70 |
| Mass transfer limitation risk | → | | |
| Toxicity risk | ← | | |

^a Henry's law constant is dimensionless.

clogging, channeling and consequent the increase of pressure drop can be caused when the porosity of packing media is too small (Woertz et al., 2002a; Yang et al., 2011). Also, if the packing medium in biofilters is organic, uneven water distribution caused by packing medium deterioration significantly affects the microbial activity of biofilters, leading to a decrease of bioavailability of VOCs and a reduced packing medium lifespan over time even if organic filter media are abundant and economically feasible (Estrada et al., 2013b). A mixture of both inorganic and organic media is utilized to overcome these problems as mentioned above. The mixed media can maintain a rigid structure with large pores to avoid compaction and minimize pressure drop (Sheridan et al., 2002; Anet et al., 2013). Inorganic inert materials are able to be used alone as the packing materials in bioreactors. However, extra nutrients and microorganism inoculation need to be added into the bed medium. In addition, the adsorption capacity of inorganic material is lower than that of organic material, because there is the larger variety of reactive groups, such as carboxyl, amino, hydroxyl and so on located on the surface of organic material (Malhautier et al., 2005).

Overall, packing media play a key role in biofiltration. Choosing or developing an appropriate packing media is a prerequisite for effective removal of VOCs in gas biofilters. Besides, for the packing with the same amount of volume, when the pore size is smaller, there is more surface area within the packing to provide more chances for microorganisms to contact with hydrophobic VOCs, which reduces the limitation of mass transfer between the gas and the biofilm, and biofilms in the packing grow slowly when treating hydrophobic VOCs. Therefore, a small pore size of the packing may be suitable for hydrophobic VOCs treatment in biofilters.

3.4. Moisture

It is well known that when treating VOCs in biofilters, maintaining enough moisture is a major concern for biofilter effectiveness (Kennes and Veiga, 2004), because microorganisms need enough water to maintain their normal metabolic activity (Krailas and Pham, 2002). Insufficient moisture concentration results in drying of medium beds and consequent channeling and short-circuiting as well as pressure drop of gas streams (Zhu et al., 1998; Krailas and Pham, 2002). Deprivation of water which is necessary for the microorganisms leads to a reduction of microbial activity and a drop of biofilter performance (Krailas and Pham, 2002). Excess water in bed media can cause a formation of anaerobic zones, compaction and clogging within bed, which becomes a barrier in the transport of oxygen and hydrophobic VOCs to biofilms and limits the reaction rate (Krailas and Pham, 2002; Armeen et al., 2008). Consequently, the bioavailability of hydrophobic VOCs is reduced. Therefore, coordinated moisture control is necessary to achieve stable and robust performance of biological system for the treatment of a wide number of gas-phase contaminants. Optimal moisture content is affected by packing media containing surface area, porosity and other factors (Kumar and Chandrajit, 2011). In general, the value of recommended moisture in biofilters is 40%–60% of the water-holding capacity of media, depending on the filtering medium used (Mcnevin and Barford, 2000).

4. Strategies for improving biofiltration of hydrophobic VOCs

Hydrophobic VOCs are more difficult to biodegrade than hydrophilic ones majorly due to the limitation of VOC mass transfer from gas phase to biofilm phase through liquid phase. To improve removal of hydrophobic VOCs in biofilters, a lot of researches are reported and most of them are related to enhancing the bioavailability of hydrophobic VOCs to biofilm phase. These methods could be grouped into the following five groups: addition of surfactants, application of fungal biocatalysts, biofiltration with pretreatment, innovative bioreactors, and utilization of hydrophilic VOCs.

4.1. Addition of surfactants

The poor gas-liquid transfer rate of hydrophobic VOCs often significantly limits the efficiency of biodegradation. A method to enhance mass transfer of hydrophobic VOCs from gas phase to liquid phase or biofilm phase is thus very important. One possibility is to use surfactants for such a purpose.

Surfactants are agents which can reduce surface and interfacial tensions by altering the molecular forces at the liquid-gas or liquid-liquid interfaces. These surfactants are amphiphilic compounds that have a structure with a hydrophilic head and a hydrophobic tail. Surfactants are classified into chemical and biological surfactants or four groups: anionic, cationic, non-ionic and dual charge. Surfactants in aqueous solution are able to increase the solubility, bioavailability of hydrophobic or insoluble organic compounds (Singh et al., 2007; Kumari et al., 2012), which have been extensively studied in contaminated soils and sediments (Mulligan et al., 2001). Also, numerous studies have indicated that surfactants have a crucial effect on gas-liquid mass transfer of VOCs (Anderson, 1992; Cheng et al., 2009; Yang et al., 2010a; Galindo et al., 2011). Furthermore, surfactants have the potential to increase the biodegradation rate of hydrophobic organic compounds in contaminated environments by increasing the total aqueous solubility of these compounds (Yu et al., 2006; Zhou and Zhu, 2007; Li et al., 2011).

In biofiltration systems, chemical surfactants have been introduced and researched as means for enhancing solubility in recent years. Some examples of surfactants used to enhance biofilter performance of VOC removal are listed in Table 2. Among these surfactants, the use of nonionic surfactants in biofilters for improving VOC removal has attracted more concern and been reported commonly (Chan and You, 2009; Chan and You, 2010). In a biotrickling filter (BTF), Tween 20, a nonionic surfactant was used to examine its effect on ethylbenzene removal, removal efficiency of ethylbenzene was enhanced from 67% to 86% at an EBRT of 30 s and an ethylbenzene concentration of 1100 mg m⁻³ when an optimal Tween 20 concentration of 12 mg L⁻¹ was added in the feeding nutrient solution (Wang et al., 2013), and ethylbenzene removal efficiency even reached 94% (Wang et al., 2014). It is worth to note that the concentration of Tween 20 is 0.10 CMC which is much lower than 1.0 CMC, and this is due to the possible accumulation of Tween 20 within the liquid and biofilm phase. The phenomena may be attributed to the fact that ethylbenzene possesses a higher aqueous solubility in the presence of the surfactant, so a lower mass transfer resistance between the gas phase and the biofilm phase and consequent more easier bioavailability were resulted. Anionic surfactants can also increase the solubility which helps overcome the rate limiting step, and has been applied in enhancing biofilter performance (Liu et al., 2007; Cheng et al., 2016). Cheng et al. (2016) found that the elimination capacity of 50.4 g m⁻³ h⁻¹ was achieved at a fixed loading rate of 72 g m⁻³ h⁻¹ when 0.1 CMC of SDS was added in BTFs for *n*-hexane removal. However, not all surfactants are effective for enhancing biodegradation of VOCs in biofilters. For example, Kim et al. (1999) found that no significantly improved removal efficiency of gaseous trichloroethylene (TCE) and tetrachloroethylene (PCE) was observed when a nonionic surfactant Alfontic R810-60 was introduced into an activated carbon biofilter at a residence time of 1.5 or 2 min. Besides, the study on cationic surfactants in biofilter is rare, therefore, more research on applications of surfactants in biofilters need to be done.

Compared with these chemical surfactants, biosurfactants such as saponins and rhamnolipids have some advantages in biodegradation of VOCs because biosurfactants are natural compounds which are more environmentally friendly, less toxic and more biodegradable (Zhou et al., 2011). Because of these advantages, biosurfactants have been frequently studied to improve solubility and bioavailability of hydrocarbon in contaminated soils (Souza et al., 2014). In gas biofiltration systems, the potential of biosurfactants is also studied. Tu et al. (2015) used saponins to enhance the removal of *n*-hexane in BTFs, and a maximum RE of 88.4% was achieved at the optimal saponin concentration of

Table 2
Examples of surfactants used in biofilters for treating VOCs.

| Bioreactor | Surfactant | Group | Target VOC | Reference |
|--|--------------------------------|---------------------|---------------|--------------------------|
| A composite bead biofilter | Brij 35 | Nonionic surfactant | Toluene | Chan and You (2009) |
| A jet loop reactor | Tween 81 | Nonionic surfactant | Toluene | Park et al. (2008) |
| Biofilters packed with inert materials | Brij 35 | Nonionic surfactant | Methane | Ramirez et al. (2012a) |
| Biofilters packed with stones | Brij 35 and Tweens | Nonionic surfactant | Methane | Ramirez et al. (2012b) |
| BTFs packed with polyurethane foam | Tween 20 | Nonionic surfactant | Ethylbenzene | Wang et al. (2013) |
| BTFs packed with polyurethane foam | Triton X-100 | Nonionic surfactant | Styrene | Song et al. (2012) |
| TBABs packed with palletized diatomaceous earth biological support media | Triton X-100 and Tomadol® 25–7 | Nonionic surfactant | Hexane | Hassan and Sorial (2008) |
| A trickling biofilter packed with raschig rings | SDS | Anionic surfactant | Chlorobenzene | Liu et al. (2007) |
| BTFs packed with polyurethane foam | SDS | Anionic surfactant | Hexane | Cheng et al. (2016) |

50.0 mg L⁻¹, a loading of 71.7 g m⁻³ h⁻¹ and gas EBRT of 30.0 s. The authors also found that saponins could decrease the biomass accumulation rate within the medium bed. Li et al. (2014) reported that rhamnolipids produced by *Pseudomonas aeruginosa* in a BTF were the main factor of enhancing siloxanes removal from biogas.

Adding surfactants also has the potential to become an alternative for efficiently removing the excessive biomass from medium beds. Song et al. (2012) found that the pressure values of a BTF with the surfactant Triton X-100 were lower than that of the BTF without the surfactant in a study of styrene removal from waste gas streams in BTFs, which meant that the surfactant could control the biofilm growth. Also, this similar phenomenon was reported by authors (Wang et al., 2014; Tu et al., 2015). A likely explanation for this is that the non-ionic surfactants have a washing effect on packing media due to its detergent principle (Ramirez et al., 2012a).

Above all, adding surfactants is effective not only for enhancing the biodegradation rate of hydrophobic VOCs, but also for controlling biofilm growth within the medium bed. However, applications of biosurfactants in biofilter systems are not widespread. To date, the effort of biological treatment in most of studies only has focused on the effect of surfactants on the biofilter performance of VOC removal. Effects of surfactants and the biodegradation intermediates of some surfactants on microorganisms and a distribution of surfactants with beds are rarely studied in bioreactors. As well, the process mechanism of surfactants for controlling biofilm growth is not quite clear. Thus, more researches are needed to better understand the mechanism of the effect of surfactants on VOC removal in bioreactors.

4.2. Application of fungal biocatalysts

Bioreactors on the basis of bacteria are reported as a robust and stable biological technology for the waste gas treatment. Unfortunately, a decrease of biofilter removal performance can occur at low moisture contents, low pH values and limited nutrient concentrations (Estrada et al., 2013a). Moreover, the low solubility of hydrophobic VOCs in the aqueous biofilm is one of the principal problems, which limits their treatment in biofilters because it restricts both mass transfer and reaction rates. It has been proposed that this obstacle may be reduced by using fungi (Kennes and Veiga, 2004; Vergara-Fernández et al., 2008). Recently, research and development of fungal bioreactor have become a research focus in the field of treating hydrophobic VOCs.

Fungi have several advantages for the treatment of hydrophobic VOCs in biofilters and there were many fungal candidates for VOC removal, such as ligninolytic fungi, *Exophiala* spp., and *Scedosporium* spp. (Kennes and Veiga, 2004). In general, fungi grow slowly. However, fungi have the ability to degrade a greater variety of VOCs, the tolerance to low pH and the resistance to low water activity favored by highly

hydrophobic proteins called hydrophobins existing in the hyphal surface. Additionally, fungi are able to colonize unoccupied space with the aerial hyphae and penetrate the solid support hence increasing the availability of nutrients (Kennes and Veiga, 2004; Arriaga and Revah, 2005a, 2005b; Vergara-Fernández et al., 2008; Zehraoui et al., 2013). These advantages demonstrate that fungal biofilters may be suitable for the treatment of waste gases containing hydrophobic VOCs such as toluene, styrene, α -pinene or hexane. In addition, extensive studies on the removal of hydrophobic VOCs in fungal biofilters have been reported. Some examples of fungi degrading hydrophobic VOCs in recent years are listed in Table 3. It is worth to note that little attention has been paid to the study on halogenated hydrocarbon and their derivatives which have a more potent effect on human. Kennes and Veiga (2004) reviewed that fungi generally grow on a narrow range of substrates compared with bacteria, limiting their application in waste gas stream with a reduced number of different pollutants. Therefore, further study should focus on finding the new fungi which can metabolize a broader range of substrates.

Higher elimination capacities for hydrophobic VOCs can be obtained in biofilter inoculated with fungi (Arriaga et al., 2006; Jin et al., 2006; Rene et al., 2010a, 2010b). In a study of toluene removal, García-Peña et al. (2001) reported that the fungal biofilter was an effective system to efficiently remove high toluene loads, and high performances were achieved under controlled conditions of moisture and nutrient availability, however, it induced homogenous growth with a pressure drop. Estrada et al. (2013a) systematically compared the performance of fungal and bacterial biofiltration when treating a VOC mixture. These authors reported that fungal biofiltration exhibited a final pressure drop of 60% which was higher than that of the bacterial biofilter due to the

Table 3
Literatures on biofilters for gas treatment with fungi.

| Target VOC | Microorganism | Reference |
|---------------------|--|---|
| BTEX | <i>Trametes versicolor</i> ; <i>Exophiala</i> sp. | Aranda et al. (2010) Rene et al. (2012a) |
| Toluene | <i>Phanerochaete chrysosporium</i> | Zamir et al. (2011) |
| Chlorobenzene | <i>Phanerochaete chrysosporium</i> | Wang et al. (2008a) |
| Styrene | <i>Sporothrix variegibatus</i> | Rene et al. (2010a) |
| α -Pinene | <i>Ophiostoma</i> | Jin et al. (2006) |
| Hexane and methanol | Fungi | Zehraoui et al. (2013) |
| Styrene and acetone | <i>Sporothrix variegibatus</i> | Rene et al. (2010b) |
| Methanol | <i>Pichia pastoris</i> | Arriaga et al. (2012) |
| Hexane | <i>Fusarium solani</i> | Hernandez-Melendez et al. (2008) |

mycelial growth. Moreover, some authors also reported that tangled erect filaments produced by fungi may obstruct the airflow and cement the particle medium together. Head loss may be increased due to heavy growth of erect forms, which eventually leads to channeling and clogging problems in biofilters (Devinny et al., 1999; Kennes and Veiga, 2004). This is the most important drawback in fungal biofiltration, particularly in the removal of high organic load of pollutants (García-Peña et al., 2001; van Groenestijn and Liu, 2002). To solve this problem, the predator-prey system has been applied in fungal biofilters, which added mites to the filter bed to graze on the fungal mycelium in order to reduce such problem (Woertz et al., 2002a, 2002b). Mendoza et al. (2004) also put forward other methods such as the utilization of chemical, air-sparging or backwashing. These methods would be useful for decreasing the pressure drop in bioreactors whose microbial culture was made up of a more complex bacterial-fungal community. Besides, photo-assisted processes such as photolysis or photocatalysis have the potential to overcome the fungal spores emitted from biofilters, which meant that the implementation of photolytic and photocatalytic post-treatment processes resulted in spore deactivation since wavelengths in the range of 254 nm denatures protein of microorganisms (Saucedo-Lucero et al., 2014). Nevertheless, further research is still needed in order to assess and optimize biological, physical and chemical alternatives to reduce head losses.

Despite the extensive research effort in the field of fungal biofiltration, the performance of fungal biofilters depends on its activity which is related to the growth condition including pH, water content, temperature and nutrient solution. Therefore, it is necessary to provide right conditions for fungal growth. Zehraouia et al. (2014) found that no fungal community was detected by the microbial analysis in trickle-bed-air-biofilters (TBABs) run at neutral pH and fungi initially acclimated to TBABs at pH 4, illustrating that the acidic pH could facilitate fungal growth in biofilters. Moreover, the fungal composition and its mycelial aerial growth can significantly increase mass transfer of hydrophobic VOCs from the gas phase to the biofilm phase (Vergara-Fernández et al., 2008). Maestre et al. (2007) reported that a reduced watering volume from 200 to 100 mg L⁻¹ depending on the watering flow rate of 0.1 and 0.2 L day⁻¹ and period resulted in an increase of the toluene removal in fungal biofilters due to a lower water accumulation in the packed bed. Systematical study on the conditions of fungi for treating a VOC mixture or a sole VOC to optimize reactor performance and maintain a high performance for long periods under stable conditions is also needed according to reported literature by García-Peña et al. (2001). Some fungal strains have the potential pathogenicity found in biofilters because fungi are a biological material constituted bioaerosols in bioprocess such as compost. Bioaerosol exposure especially containing fungi, bacteria and viruses may represent an additional health risk, in particular for risk groups such as immunosuppressed persons or persons suffering from allergies or respiratory diseases (Biermann et al., 2013). Usually, these fungi have not been paid close attention to, therefore more studies are needed.

4.3. Biofiltration with pretreatment

There is a need for innovative VOC treatments due to urbanization coupled with stringent environmental legislation, especially for hydrophobic and recalcitrant VOCs. A recent advance that is the combination of single techniques can break limitations of individual approaches and remove more VOCs (Rene et al., 2012b). Ultraviolet (UV) oxidation (photolytic oxidation and photocatalytic oxidation) and biological technologies (biofilter and biotrickling filter techniques) have been integrated into treating hydrophobic and recalcitrant VOCs.

UV photooxidation that can convert hydrophobic and recalcitrant compounds (chlorobenzene, toluene, dichloromethane) into soluble and biodegradable compounds, is generally chosen as a suitable pretreatment prior to the biofilter to improve the removal performance of recalcitrant VOCs (Wang et al., 2008b; Yu et al., 2014). Several

researchers tried to use combined UV-biofilters to treat hydrophobic and recalcitrant compounds. Results indicated that this combined system could provide much better removal capability than the single reactor (Moussavi and Mohseni, 2007; Wang et al., 2008a). However, some previous researches have showed that harmful byproducts such as O₃ were produced during the process of UV photooxidation. Toxicities of these harmful byproducts might be higher than their parent compounds (Wang et al., 2009). Koh and Thiemann (2001) also reported significantly acute toxicities for the photo-degradation products of several chlorinated paraffins. Wang et al. (2008a) showed that chlorobenzene vapor was converted to compounds with greater toxicities. The exhaust gases containing these byproducts represent a potential health risk for the public. Thus, applications of UV photooxidation may be limited in gas biofiltration.

Recently, photocatalytic oxidation (PCO) has become an attractive technique due to its low energy consumption, relatively moderate operating cost and environmental safety (Babbitt et al., 2009). PCO utilizes semiconductors like TiO₂, ZnO, WO₃, FeTiO₃, and SrTiO₃ to carry out a photo-induced redox process, and it could protect microorganisms from toxic shock and break down the target pollutants into more soluble and easily biodegradable compounds than their parent compounds and thereby increase the biological treatment efficiency (Demeestere et al., 2004; Hinojosa-Reyes et al., 2012). Thus, PCO has the potential to provide more effective elimination for hydrophobic VOCs in gaseous phase. Several research have found that many VOCs including benzene (Rene et al., 2012a; Lichtin and Sadeghi, 1998), toluene (Moe and Irvine, 2001; Sun et al., 2009) and styrene (Kim et al., 2005; Lu et al., 2009) could be removed by single biological or PCO purification technology. However, the operational cost of photocatalysts (3–10 US \$ 1000 m⁻³) is much higher than that of biological treatments (0.3–2.5 US \$ 1000 m⁻³) for a similar elimination capacity (Kennes and Thalasso, 1998). Moreover, some shortcomings such as slow biological oxidation of hydrophobic VOCs for biological treatment and photocatalysts deactivation for PCO technology still exist when using single technology to treat waste gases (He et al., 2012). Therefore, VOC removal by either single biological technology or PCO may be not high enough. Combining PCO with biological technology is considered to be another promising technology based on long-term stable biodegradation efficiency for VOCs in biofilters and broad selectivity of PCO for various VOCs (He et al., 2012). Hinojosa-Reyes et al. (2012) carried out with the objective of enhancing removal efficiency of ethylbenzene by a hybrid system consisting of a photooxidation technology using an indium-doped TiO₂ photocatalyst coupled with a biological process, and they found that the coupled system obtained a maximal EC of 275 g m⁻³ h⁻¹ which was higher than that of the control biofilter (60 g m⁻³ h⁻¹). It is attributed to the utilization of photooxidation process which enhanced the ethylbenzene degradation. Wei et al. (2010) investigated combining a photocatalytic oxidation reactor and a biofilter for the treatment of gases containing toluene and found that the integrated system could effectively oxidize toluene with high removal efficiency.

4.4. Innovative bioreactors

Although biological treatment is successfully applied to treat a wide number of hydrophobic VOCs, the removal performance is not better when treating VOCs in gas-phase bioreactors during a long period of operation. Uneven distribution of VOCs and biomass accumulation in some bioreactors are usually considered to be main reasons of a deterioration of biofilter performance. Some innovative gas phase bioreactors have therefore been developed to overcome these problems. For instance, the rotating drum biofilter (RDB) can make VOC loadings and biofilms more uniformly distributed on beds and enhance the stable and robust performance of biofilter significantly even at high organic loading rates over a long period of operation (from about one month to six months or more) (Yang et al., 2004, 2008a, 2008b; Chen et al., 2012). Vinage and

von Rohr (2003a, 2003b) developed and evaluated a modified rotating biological contactor (RBC) for toluene removal, which has maintained a stable long-term performance for toluene removal for more than one year under typical standard operating conditions. Carvalho et al. (2009) found the suspended-growth bioreactor (SGB) could effectively remove VOCs and it was shown to be robust, especially with a high performance of VOC removal after night and weekend shutdown periods. Kan and Deshusses (2003) reported a new type bioreactor that was a foamed emulsion bioreactor (FEBR) on the basis of an organic-phase emulsion and actively growing pollutant-degrading microorganisms. The FEBR is not subject to clogging due to the absence of packing media in the reactor. Also, performance of FEBR that is evaluated by mathematical modeling of the process and proof of concept using a laboratory prototype greatly surpassed the performance of existing gas-phase bioreactors. This reactor is also applied to another study of co-metabolic biodegradation of trichloroethylene (TCE) and is proved to be a very effective setup for treating such air toxics that require co-metabolism (Kan and Deshusses, 2006).

Apart from bioreactors described above, another bioreactor configuration mentioned in several studies is the two phase-partitioning bioreactors (TPPBs). The aim of this bioreactor is to overcome the low mass transfer of hydrophobic VOCs from the gas phase to biofilm phase as well as the microbial inhibition caused by the presence of high VOC or toxic metabolite concentration (Arriaga et al., 2006; Muñoz et al., 2007; Hashemi et al., 2012). TPPBs rely on the addition of a non-aqueous phase (NAP) which has a high affinity for the target pollutant. Therefore, NAP can significantly improve removal efficiencies of hydrophobic VOCs by increasing the driving force for mass transfer to the microorganisms (Nielsen et al., 2003; Hernández et al., 2010; Montes et al., 2012). Several investigations have indicated that microorganisms could grow up inside NAP, which provided a chance to directly contact with target VOCs and ingest them. Furthermore, the solubility of VOCs in NAP is higher than that of in water, enhancing opportunities for the bio-availability of hydrophobic VOCs (Hernández et al., 2012; Muñoz et al., 2013). Consequently, the VOC removal performance in TPPBs is frequently superior to that recorded in conventional bioreactors (Muñoz et al., 2007). Lebrero et al. (2014) reported that the addition of 10% of silicone oil as NAP into the biofilter for hexane removal significantly improved its removal performance by 72% compared with the control biofilter. The results have further confirmed the superior performance of TPPBs over conventional biofilters for VOC biodegradation in terms of elimination capacity and process stability. In spite of the potential benefits of operating TPPBs, some challenges still exist. The optimization of the power consumption is probably the main issue for TPPBs, which needs to be overcome prior to being considered for full-scale applications (Muñoz et al., 2012). In this regard, further researches on new reactor configurations and operation strategies should be done to reduce the energy consumption per unit volume of treated VOCs to those of well-established biological systems (biofilters and biotrickling filters) and help to lead TPPBs from an innovative technology to a mature one.

4.5. Utilization of hydrophilic compounds

The suitability of biofilters for treating gas-phase VOCs significantly depends upon the solubility of VOCs in the liquid layer of the biofilm and their Henry's law constant (Zhu et al., 2004). The low mass transfer rates of hydrophobic VOCs from the gas phase to the biofilm phase limit their biodegradability. Thus, an increase in bioavailability of hydrophobic VOCs in biofilms phase will facilitate their biodegradation and enhance removal performances of biofilters. One method is that hydrophilic contaminants are mixed with hydrophobic VOCs to enhance the bioavailability of hydrophobic VOCs and thereby improve the performance of biofilters for treating waste gases containing VOCs.

For mixing hydrophilic compounds with hydrophobic VOCs in the practical project, one operational method is that the mixtures of

hydrophobic VOCs and hydrophilic contaminants enter into the biofilter and pass through the bed so that they are degraded by microorganisms simultaneously. Moreover, hydrophobic VOCs and hydrophilic contaminants are often found in different industrial waste gases such as fire-reinforced plastics industry (Rene et al., 2010a) and pulp and paper industry (Mohseni and Allen, 2000). It is worth to note that air emissions are always mixed gases rather than a sole VOC. Additionally, biofiltration of the mixture of hydrophobic VOCs and hydrophilic contaminants has been studied by several authors (Rene et al., 2010a; Dixit et al., 2012; Zehraoui et al., 2012, 2013).

In co-treatment of mixtures of hydrophobic and hydrophilic VOCs, the removal performance of hydrophobic VOCs in biofilters depends on the amount of hydrophilic compounds loaded to the system. The high loading rate of hydrophilic compounds may be a solvent to help the water solubilization of hydrophobic VOCs, triggering more hydrophobic VOCs to be bioavailable. However, a competition between these two kinds of compounds may occur at the high concentration of hydrophilic compounds. Hydrophilic compounds at the low loading rate improve hydrophobic VOC removal by enhancing biomass growth in biofilters or may be added as co-substrate to provide additional carbon source and energy source to promote biomass growth and thereby enhance the removal performance of hydrophobic VOCs. For example, some compounds, especially chlorinated organics, cannot be employed by cells as an energy source, but they can be degraded by co-metabolic processes (Jung and Park, 2005). Unfortunately, to date, it is not clear up for the enhancement mechanisms. Therefore, further investigations should be done to understand the interaction between hydrophobic VOCs and hydrophilic compounds.

Several studies have investigated the bioavailability of hydrophobic VOCs in the presence of hydrophilic contaminants. Zehraoui et al. (2012) introduced methanol into waste gas streams containing *n*-hexane to increase the bioavailability of *n*-hexane in TBABs. The results showed that the removal efficiency of *n*-hexane was significantly improved in the presence of methanol for *n*-hexane loading rates less than $13.2 \text{ g m}^{-3} \text{ h}^{-1}$. Even though the methanol had an impact on *n*-hexane biodegradation, its removal efficiency was still higher than *n*-hexane removal alone. This result could be explained by the fact that the methanol as a co-substrate promoted the accumulation of biofilms on the surface of the media within the TBAB. Moreover, the performance of TBAB with the relatively high methanol loading rate was higher than that of TBAB with a relatively low methanol loading rate when the *n*-hexane loading rate was less than $13.2 \text{ g m}^{-3} \text{ h}^{-1}$. This result could be due to the fact that the relatively high methanol loading rate could trigger more *n*-hexane to dissolve in the liquid layer of the biofilm, making them bio-available. Dixit et al. (2012) observed that the presence of *n*-propanol at a low concentration had a favorable effect for the removal of toluene. A reason may be that a readily degradable carbon and energy source facilitate biomass growth and enhance microbial activity in the biofilter, and thus increase the biofilter performance. This explanation is supported by the discovery that microbial density increases in the biofilter when *n*-propanol is fed into the bioreactor together with toluene. Zhang et al. (2006) found that methanol addition improved dimethyl sulfide (DMS) removal in a biofilter. One possible explanation is that methanol is an easily degradable carbon source and added as a co-substrate to enhance biomass growth in the biofilter, leading to an increase of DMS removal. However, the effect of hydrophilic compounds added in the biofilter on the removal performance of hydrophobic VOCs is not always positive. For instance, Dehghanzadeh et al. (2005) used the biofilter packed with yard compost and shredded high density plastics to treat styrene and acrylonitrile which was a hydrophilic and easily biodegradable compound. They found that when acrylonitrile was depleted or there was little acrylonitrile in the air stream, styrene biodegradation rate was increased in the lower sections of the biofilter. Mohseni and Allen (2000) also reported that the higher the loading rate of methanol was, the lower the removal rate of α -pinene was. These two results may be explained by the fact

Table 4
Effect of hydrophilic compounds on hydrophobic compounds.

| Substrate treated | Microorganism | Effect | Reference |
|-----------------------|---|---|----------------------------|
| Toluene | Indigenously microbial consortium from a compost-woodchip mixture | A positive effect at low concentrations of <i>n</i> -propanol; a negative effect at high concentrations of <i>n</i> -propanol | Dixit et al. (2012) |
| <i>n</i> -Hexane | Indigenously microbial consortium from diatomaceous earth biological support media | A positive effect for <i>n</i> -hexane LR less than 13.2 g m ⁻³ h ⁻¹ ; a negative effect for <i>n</i> -hexane LR higher than 13.2 g m ⁻³ h ⁻¹ but removal efficiency of <i>n</i> -hexane higher than that of <i>n</i> -hexane alone | Zehraoui et al. (2012) |
| DMS | Microbial consortium obtained from activated sludge | A positive effect on the biofiltration of DMS by enhancing biomass concentration and viability; a competitive effect on DMS biodegradation; a need to sustain a high removal rate of DMS in inorganic biofilters | Zhang et al. (2006) |
| Styrene | Fungus <i>Sporothrix varicribatus</i> | A slight effect on styrene removal | Rene et al. (2010b) |
| Styrene | Indigenously microbial consortium obtained from yard waste compost and activated sludge | A negative effect on styrene removal | Dehghanzadeh et al. (2005) |
| α-Pinene | Indigenously microbial consortium from a mixture of compost and wood chips | A negative effect on α-pinene removal capacity of the biofilters by suppressing the growth of α-pinene degrading microbial community | Mohseni and Allen (2000) |
| Toluene | Microbial consortium obtained from activated sludge | The elimination capacity of toluene being higher than that of acetone at similar influent carbon loading | Chang and Lu (2003) |
| Toluene ethyl acetate | Indigenously microbial consortium from a mixture of wood-chip and compost | An inhibition effect on toluene removal at high ethyl acetate concentration | Deshusses et al. (1999) |
| Hydrogen sulfide | Mesophilic microorganisms | Neutral effect | Solagar et al. (2003) |
| methanol | | | |

that hydrophilic compounds suppress the growth of hydrophobic VOCs degrading community during the biodegradation of binary mixtures. The absence of hydrophilic compounds provides an opportunity for the organisms which are capable of degrading hydrophobic VOCs to grow in the system and thereby degrade hydrophobic VOCs. Therefore, an interaction exists between hydrophilic and hydrophobic compounds. In some cases, the addition of hydrophilic compounds might also have neutral (Solagar et al., 2003), positive (Dixit et al., 2012) or negative (Mohseni and Allen, 2000; Paca et al., 2012) effect (Table 4), which is related to factors of affecting biofiltration. For example, too high load rates of hydrophilic compounds can lead to excess biomass growth problems, resulting in poor VOCs removal (Dixit et al., 2012). Another study has observed that acetone removal was inhibited by the presence of styrene when evaluating mixtures of gas-phase styrene and acetone with the fungus *Sporothrix varicribatus*, whereas the biodegradation of styrene was affected only slightly in the presence of acetone (Rene et al., 2010b).

In sum, despite the important advances achieved in improving the biofilter removal performance of hydrophobic VOCs, there still are some inadequacies in every method. Thus, innovative experiments and mechanism study on enhancing removal efficiency of hydrophobic VOCs are necessary to be done.

5. Conclusions

Biological technologies for air pollution control offer advantages over physicochemical methods. One of the main drawbacks of biological technologies is the low bioavailability or slow biological oxidation of hydrophobic VOCs, making the biofilter very large and uncompetitive.

Hydrophobic VOC removal in biofilters is affected by many factors including VOC mass transfer, microbial populations, packing media and moisture.

Surfactants can increase the biodegradation rate of hydrophobic organic compounds by increasing the total aqueous solubility of these compounds. However, the biodegradation intermediates of surfactants by microorganisms and the distribution of surfactants on the packing material are often overlooked. Moreover, the application of mixed anionic-nonionic surfactants in gas biofiltration and the process mechanism of surfactants for biofilm growth control are rarely studied. Fungal-based biocatalysts have shown some potential but are limited by their growth conditions. Some innovative technologies such as physicochemical-biological methods or innovative bioreactors (TPPBs or RDB) have been developed to overcome the poorly soluble or

recalcitrant substances. Nevertheless, further research is still needed in order to eliminate potential nuisances from these new techniques. It will help to move these new techniques from innovative to mature. There is an experimental evidence that the removal efficiency of hydrophobic compounds can be improved in the presence of the hydrophilic compounds. Further investigations on the precise mechanisms are necessary as well. A model for hydrophobic and hydrophilic VOC biofiltration is imperative to predict the effect between hydrophobic and hydrophilic VOCs removal.

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